CRISTINA ECHEVARRÍA BONET

SIZE INDUCED ELECTRONIC AND MAGNETIC CHANGES IN NANOMETRIC RARE EARTH ALLOYS
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CRISTINA ECHEVARRÍA BONET

Departamento de Ciencias de la Tierra y Física de la Materia Condensada
Facultad de Ciencias
Universidad de Cantabria

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**SUPERVISORS:**
Dr. Luis Fernández Barquín
Dr. Daniel Rojas Pupo

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I am among those who think that science has great beauty. A scientist in his laboratory is not only a technician but also a child placed before natural phenomena which impress him like a fairy tale.

— Marie Curie

A ti, Yayo.
En esta tesis se ha abordado el estudio de aleaciones nanoestructuradas de intermetálicos de tierras raras (TR), TbCu$_2$ e YbAl$_3$, seleccionadas por su gran interés. El TbCu$_2$ (masivo) es una aleación antiferromagnética con una temperatura de orden $T_N = 50$K (la más alta de la serie TR-Cu$_2$); mientras que el YbAl$_3$ (masivo) es una aleación de valencia intermedia no magnética, que puede ser de gran importancia en dispositivos termoelectricos, gracias a un gran coeficiente Seebeck.

Las aleaciones masivas de partida fueron fundidas en un horno de arco, en cantidades de unos 5 gramos. Posteriormente se practicó un tratamiento térmico durante 5 días a 750°C, para disponer de una buena homogeneización metalúrgica. Para obtener unos tamaños de partícula del orden de los nanómetros, las aleaciones recocidas se molieron en un molino planetario de bolas (de carburo de tungsteno, WC, o zirconia, ZrO$_2$) en atmósfera de Ar, durante unos tiempos determinados (que dependen del material a moler) y que no superaron las 70 horas. La caracterización estructural se garantizó por medio de difracción de rayos X (en el laboratorio, con $\lambda = 1.5418$Å para el tubo de Cu y $\lambda = 0.7107$Å para el de Mo) y por microscopía electrónica de transmisión (200 kV). Además, en algunas de las muestras, se confirmó el estado cristalográfico mediante difracción de rayos X ($\lambda = 0.4126$Å) en el sincrotrón ALBA (Barcelona, España) y mediante difracción de neutrones ($\lambda = 2.423$Å) en el Laboratoire Léon Brillouin (Saclay, Francia). Todos los resultados indican que se han conseguido nanopartículas de TbCu$_2$ de entre 23 y 6 nm y de YbAl$_3$ con 10 nm. Además se mantienen las estructuras cristalográficas Imma y Pm-3m del TbCu$_2$ e YbAl$_3$ masivos, respectivamente.

En lo que respecta a la serie de nano-TbCu$_2$, las medidas M(H,T) y representación de Arrott establecen la coexistencia de un estado superantiferromagnético (SAFM) con un comportamiento de vidrio de espín (spin-glass, SG) a bajas temperaturas ($T \leq 10$K), cuando en el TbCu$_2$ llega a saturarse el tamaño de partícula hasta los 6 nm. La transición SAFM (con una temperatura de orden $T_N$) se ve modifi-
cada por efectos de tamaño finito que se pueden explicar por medio de teorías de escalado habituales. Además la dinámica de espín (manifestada en el desplazamiento de la temperatura de congelamiento $T_f$) confirma ambas transiciones con unos exponentes críticos (susceptibilidad AC, $f = 10\text{Hz} - 10\text{kHz}$) para el congelamiento, cercanos a los de los sistemas SG. La estructura magnética de los nano-TbCu$_2$ es la misma que en la muestra masiva (antiferromagnética conmensurable con vectores de propagación $q_1 = (0,0,0)$ y $q_2 = (1/3,0,0)$). Se observa una correlación dentro de la partícula y además correlaciones para bajos valores del vector dispersión ($Q \lesssim 0.7\text{Å}^{-1}$) en $T < T_N$. La presión hidrostática ($P \lesssim 10\text{kbar}$) modifica la irreversibilidad, disminuyendo la $T_f(P)$, como cabría esperar. Finalmente, las medidas del calor específico $C_p$ y de la resistividad eléctrica $\rho(T)$ confirman la existencia de una $T_N$ macroscópica y muestran signos asociados al desorden por lo que respecta a las contribuciones magnéticas, fonónicas y electrónicas.

Los resultados en nano-YbAl$_3$ indican la modificación del estado electrónico ya que la magnitud de la susceptibilidad disminuye y la temperatura a la que se sitúa el máximo asociado a la interacción Kondo aumenta. En la $\rho(T)$ aparece un máximo hacia 125K que no aparece en la aleación convencional de LuAl$_3$ ni en la del valencia intermedia YbAl$_3$ masivo. Este máximo es debido a una hibridación de estados y su origen también podría tener relación con una contribución Kondo de alta temperatura. Se observa asimismo un mínimo en la resistividad eléctrica a bajas temperaturas cuyo origen es asignado a una combinación de efectos cuánticos, asociados al alto desorden estructural y a un efecto de decoherencia desde un comportamiento Kondo red a un Kondo impureza.
Some ideas and figures have appeared previously in the following publications:

ARTICLES:


CONTRIBUTIONS TO CONFERENCES:

1. (Poster) C. Echevarria-Bonet, D. P. Rojas, L. Fernández Barquín, 
   Size and disorder effects on the magnetic properties of TbCu$_2$ nanomagnets (“Joint European Magnetic Symposia (JEMS)”), Krakow (Poland) August 23$^{rd}$ - 28$^{th}$, 2010.

2. (Poster) D. P. Rojas, L. Fernández Barquín, C. Echevarria-Bonet, J. Rodríguez Fernández, Magnetic properties of TbAl$_2$ nanometric alloys (“Recent Trends in Nanomagnetism, Spintronics and their Applications (RTNSA)”), Ordizia (Spain) June 1$^{st}$ - 4$^{th}$, 2011.


4. (Poster) D. P. Rojas, L. Fernández Barquín, C. Echevarria-Bonet, J. Rodríguez Fernández, Magnetic properties of TbAl$_2$ nanometric alloys (“XXXIII Reunión Bienal de la Real Sociedad Española de Física”), Santander (Spain) September 19$^{th}$ - 23$^{rd}$, 2011.


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INTRODUCCION

El control y manejo de nanoestructuras constituye un campo de investigación fundamental de los materiales, desde una gran variedad de puntos de vista. Esto se debe, básicamente, a sus potenciales aplicaciones tecnológicas relacionadas con el uso de la reducción del tamaño en componentes inteligentes. Frecuentemente, estas nanoestructuras conllevan la presencia de varias capas de materiales con estados cristalográficos y/o composicionales diferentes que fomentan la existencia de varias propiedades macroscópicas simultáneas [1, 2, 3]. En otras palabras, es relativamente fácil crear nanomateriales que presenten una combinación de diferentes respuestas físicas. De esta manera, podríamos considerar que la Nanociencia y la Nanotecnología están íntimamente relacionadas y que no son solamente un nuevo tema a investigar, sino que se ha extendido a distintas disciplinas que tratan muy diversos conocimientos, como pueden ser la Física, Química, Biomedicina o Ingeniería, entre otros. En un sentido más simple, el control del tamaño de los materiales ha alcanzado un estado igual al que consiguió hace unos años la aplicación de alta presión o, hace unas décadas, la variación de campos magnéticos o temperatura.

En el caso de materiales magnéticos, esta importancia está muy arraigada [4]. Mucho antes del ahora repetido mantra (pronunciado brillantemente en el Laboratorio Caltech por el premio Nobel R. P. Feynman), existía ya un interés en lo que se llamó magnetismo de partículas pequeñas. Sorprendentemente, las muestras relacionadas eran óxidos de Fe, en algunos casos recogidos y estudiados por Geólogos como muestras naturales. La gran figura de Louis Néel (premio Nobel en 1970) forjó las bases en las que se ha basado el conocimiento del magnetismo, relacionado con la reducción del tamaño de los materiales y, consecuentemente, del número de dominios magnéticos en la escala nanométrica. El resultado fue la aparición de estructuras monodominio cuyas propiedades fueron inicialmente explicadas por el fallecido Prof. Néel y que se bautizaron como supermagnetismo [5, 6, 7]. Al principio era obvio que al analizar las partículas mag-
néticas, la variación de coordinación entre los átomos que formaban la capa exterior y aquéllos en el núcleo debía seguramente provocar (en este caso) un acoplamiento magnético. La mayor consecuencia es la conocida anisotropía magnética, publicada por primera vez por W. H. Meiklejohn y C. P. Bean en el General Electric Laboratory [8]. El magnetismo de partículas pequeñas estaba siendo continuamente desarrollado en las décadas de los 60s y 70s. El inestimable uso del efecto túnel al principio de los años 80 por otros científicos premios Nobel (G. Binnig and H. Rohrer) resultó en el diseño y fabricación de microscopios de efecto túnel de barrido [9], lo cual constituyó el principio de la carrera de la Nanociencia. Esta competición se mantiene hasta nuestros días, y se espera que sea un tema permanente de trabajo. Esta necesidad de nanoestructuras llevó a la existencia de diferentes rutas de fabricación con las que se pudieran cambiar las propiedades que dependían del tamaño. Muchas de las técnicas relacionadas son bastante sofisticadas y esos materiales están dedicados, mayormente, al campo de la espintronica. Afortunadamente, existen otras rutas más simples y asequibles. Entre ellas, la simple molienda de los materiales masivos (estrategia top down, en el lenguaje de la nanociencia) ha sido aplicada intensivamente. Ésta preveé un mucho mejor escalado hacia una producción industrial. Hoy en día, las nanopartículas magnéticas se vienen estudiando también en situaciones mucho más delicadas que las estudiadas por Néel, como es el análisis de la interacción Kondo en quantum dots, que forman otro campo de interés.

La situación actual que concierne a las nanopartículas magnéticas (una forma extendida de nanoestructuras) está relacionada con un tercer ingrediente (a parte de las dos mencionadas modificaciones de núcleo y superficie), constituido por la influencia de partículas cercanas en la respuesta macroscópica. éstas normalmente reciben el nombre de interacciones interpartícula y dependen del material en cuestión; es decir, si las nanopartículas están incrustadas en una matriz conductor o metálica, es obvio que las interacciones dipolar o RKKY jueguen un papel importante. Como ocurre en muchos otros aspectos del estudio de la materia condensada durante el principio del siglo XXI, la situación se convierte en más y más compleja. Donde hace años sólo unos casos límite (ejemplos) eran encontrados, como los sistemas tipo Kondo, vidrios desordenados magnéticamente o los mencionados sistemas superparamagnéticos. Sin embargo, ahora existe una amplia (cuasicontinua) variación en la interacción de las
entidades magnéticas, que todavía reclama una definición adecuada y mejorada [10, 11].

Las interacciones entre partículas tienen efectos importantes en las propiedades magnéticas de las nanopartículas. El campo que incluye el magnetismo de las nanopartículas es el llamado supermagnetismo [12]. Cuando las partículas están suficientemente separadas de manera que las interacciones entre partículas son despreciables, el conjunto recibirá el nombre de superparamagnético (SPM). A medida que la concentración de nanopartículas aumenta, llegaremos a un comportamiento de super vidrio de espín (SSG), en el que los superespines de las partículas se congelan a una temperatura determinada $T_f$. Para más altas concentraciones, encontramos los órdenes superferromagnético (SFM) o superantiferromagnético (SAFM), en los que las nanopartículas magnéticas se comportan como un conjunto de espines que se ordenan paralela o antiparalelamente, respectivamente, dentro de la partícula.

La combinación de los tres ingredientes es uno de los temas actuales más fascinantes y requiere un entendimiento más profundo. Las interfases magnéticas pueden ser parte de superficies (capas) conectadas (por ejemplo en capas delgadas) o más comúnmente, en esta década, en granos nanométricos [3]. El hecho de que, habitualmente, las estructuras cristalográficas en una nanoestructura no sean equivalentemente simétricas y que las interacciones magnéticas pudieran estar apantalladas o acentuadas dependiendo de la naturaleza o espesor, constituye un campo muy atractivo. En el pasado esto ha sido tradicionalmente estudiado en películas, pero hoy en día el conocimiento técnico de la Nanociencia ha promovido un panorama mucho más amplio en el que estudiar estas interacciones magnéticas. Las interfases contituyen un factor importante, no sólo debido a la obvia interconexión entre nanoentidades (partícula, película, etc.) con el material adyacente, sino también porque en muchos casos existe una leve distinción entre la propia interfase y la -normalmente llamada- frontera del grano. En este sentido, es posible examinar la competencia entre el núcleo y la superficie respecto al comportamiento electrónico/magnético al abordar diferentes estrategias. Un ejemplo sencillo es el papel jugado por el magnetismo de la superficie, que puede ser establecido si se selecciona un núcleo antiferromagnético. Dentro de un punto de vista más general, se puede observar asimismo el control magnetoeléctrico ejercido por la superficie al incrementar...
el número de las capas de átomos superficiales (2-3 nm), para crear de una manera eficaz una superficie más gruesa que tenga conexión con otras nanopartículas. Si esta frontera se extiende, idealmente, tendríamos una colección de nanopartículas incrustadas en una matriz. Esto podría constituir otro caso límite. Es importante remarcar aquí que nosotros somos perfectamente conscientes de estos casos límite, tanto para granos aislados magnéticamente [5] como para otros: los granos magnéticos diluidos en matrices débilmente magnéticas han sido estudiados profundamente en la literatura, con excelentes descubrimientos y aplicaciones [6, 7].

Curiosamente, una gran mayoría del trabajo ha sido enfocado a nanomateriales magnéticos con metales de transiciones 3d, mientras que el magnetismo de los iones 4f se ha dejado, parcialmente, olvidado. Es verdad que se han practicado esfuerzos para entender las propiedades de los imanes permanentes de Nd-Fe-B (y otros) para aplicaciones tecnológicas, utilizando la reducción del tamaño de partícula como una mejora. De todas maneras, según nuestro conocimiento, la investigación de aleaciones nanoestructuradas basadas en iones 4f es mínima. Esto puede entenderse por el hecho de que las propiedades macroscópicas tradicionales que aparecen en intermetálicos de tierras raras en aleaciones binarias o ternarias fueron muy bien definidas hace décadas [13]. Hoy en día, el núcleo de la investigación de los 4f está dedicado a los efectos electrónicos que estén relacionados con una definición más plausible y mejorada del llamado estado de la materia de los No Líquidos de Fermi; esto es estudiado, idealmente, en un estado monocristalino. Teniendo en cuenta lo dicho anteriormente, la falta de resultados en las nanoestructuras 4f parece que demuestra una cierta falta de perspectiva. En este sentido, nuestro punto de vista personal, nos ha llevado a abordar esta metodología con el objetivo principal de buscar nuevos fenómenos electrónicos o magnéticos en los sistemas arquetipo 4f en un estado nanométrico.

En esta tesis entraremos en los pequeños detalles de dos compuestos intermetálicos, TbCu$_2$ e YbAl$_3$, que serán caracterizados magnéticamente y electrónicamente, después de haber sido molidos mecánicamente hasta un tamaño nanométrico.

Para empezar, el TbCu$_2$ nanométrico ha sido estudiado previamente en [14], donde se observó que la transición AFM desaparecía dando lugar a un comportamiento SG cuando las muestras eran molidas durante 120 horas. Nuestro objetivo aquí es realizar un estudio com-
pleto de la evolución de estos dos comportamientos como una función del tiempo de molienda o, en otras palabras, del tamaño de partícula. Se han realizado también experimentos en Grandes Instalaciones que han revelado el comportamiento magnético microscópico de estos sistemas.

Por otro lado, el YbAl\textsubscript{3} es un compuesto de valencia intermedia en el cual la valencia de los átomos de Yb se reduce desde 2.86 (en el compuesto masivo) hasta 2.70 cuando la muestra es molida durante 120 horas [15]. Esto se relacionó con un cambio en la coordinación de los átomos de la superficie de la nanopartícula, llevando al compuesto hacia un estado menos magnético. Aquí, detallaremos el comportamiento electrónico (resistividad eléctrica). De esta manera, estaremos encargados de estudiar directamente el comportamiento de los electrones y fonones y otras contribuciones asociadas al estado nanoestructural de las aleaciones.

La estructura de la tesis se detalla a continuación: después de la introducción (actual Capítulo 1), los conceptos físicos más importantes necesarios para la comprensión de los sistemas estudiados son resumidos en el Capítulo 2. En el siguiente Capítulo 3 se presentan la fabricación de las aleaciones y la correspondiente molienda mecánica de las nanoestructuras. Se detallarán los procesos de aleación y molienda, junto con las técnicas experimentales usadas en este trabajo para obtener las propiedades estructurales, magnéticas y de transporte. Los resultados y análisis de los dos sistemas estudiados en esta tesis se presentan en el Capítulo 4 para el TbCu\textsubscript{2} y en el Capítulo 5 para el YbAl\textsubscript{3}. Finalmente, se resumirán las conclusiones finales, obtenidas en esta tesis en el Capítulo 6.
INTRODUCTION

The control and handling of nanostructures has brought in a fresh breeze in the present materials research from a variety of points of view. This is mostly due to the potential technological applications, which are inherent to the size reduction applicable in smart components. Frequently, those nanostructures involve the presence of several layers of materials in different crystallographic and/or compositional state promoting the simultaneous existence of a bunch of tailored macroscopic properties \[1, 2, 3\]. In other words, it is relatively facile to create nanomaterials exhibiting a combination of different physical responses. Hence, we could consider that Nanoscience and Nanotechnology are intimately related and are not just a new topic to investigate but rather have become worldwide spread disciplines grasping very diverse knowledge. The latter stems from Physics, Chemistry, Biomedicine or Engineering, to cite a few. In a very simple way, the size control of materials has reached a status equal to the one achieved some years ago by the regular application of high pressure, or by the variation of magnetic fields and temperature, decades ago.

In the case of magnetic materials, this importance is also well-established [4]. Much before the now repeated mantra regarding the brilliant conference delivered at Caltech by Nobel prize awarded R. P. Feynman, there was an interest in what it was called fine particle magnetism. Surprisingly the samples related to this knowledge were simple Fe-oxides, in some cases gathered and studied by Geologists as natural samples. The giant figure of Louis Néel (Nobel prize in 1970) built up the basis for the understanding of magnetism related to the reduction of size of the materials, and consequently, of the number of magnetic domains to the nanometric scale. The outcome is that single-domain structures emerged and their properties were initially explained by the late Prof. Néel and christened as superparamagnetism \[5, 6, 7\]. Just at the very beginning it was also obvious that if magnetic nanoparticles were analysed, the variation of the coordination between atoms forming the outer shell and those in the particle core was necessarily bound to provoke some (in this case) magnetic coupling. The main consequence is the well-known ex-
change anisotropy, first reported by W. H. Meiklejohn and C. P. Bean at the General Electric Laboratory [8]. Then, fine particle magnetism was developing steadily in the late sixties and earlier seventies. Suddenly, the priceless use of the tunneling effect at the beginning of the 80s by other Nobel prize scientists (G. Binnig and H. Rohrer) resulted in the design and fabrication of scanning tunneling microscopes [9] which constituted the starting blow for the nanoscience race. The competition is maintained until these days, and it is expected to become a permanent new kid on the block. This need of nanostructures spurred the existence of different fabrication routes to tune in size-dependent properties. Most of the techniques involved are quite sophisticated and the materials were mostly devoted to the field of spintronics. Fortunately, other more simple and affordable routes have become available. Among them, the simple milling of bulk materials (top down approach, in the nanoscience language) has been thoroughly applied. The latter foresees a much better up scaling for mass industrial production. Nowadays, it is not only that magnetic nanoparticles in the Néel sense are hugely studied but also other more delicate physical situations, such as for example the analysis of Kondo interaction in quantum dots, which form another corpse of interest [16].

The present situation concerning the magnetic nanoparticles (a widespread form of nanostructures) is related to a third ingredient (apart from the two mentioned core and shell modifications) constituted by the influence of nearby particles in the macroscopic response. These are generally labeled as interparticle interactions and depending on the material situation, that is to say, whether nanoparticles are embedded in an insulating or in a metallic matrix, it is obvious that either dipolar or RKKY interactions (or both) will have to play a role. As occurs in many other aspects of early XXI\textsuperscript{th} century condensed matter research, the situation becomes more and more complex. Where years ago only some limiting (case examples) situations were found, as Kondo systems, disordered magnetic glasses or the mentioned superparamagnets, there is now an ample (quasi-continuous) variation on the interaction of magnetic entities (cluster/glasses) which is still begging for an improved definition [10, 11].

The interparticle interactions have significant effects on the magnetic properties of the nanoparticles. The field that involves the overall magnetism of the nanoparticles is the so-called supermagnetism [12]. When particles are separated so far apart that interparticle inter-
actions are negligible, the ensemble will be called superparamagnetic (SPM). As nanoparticle concentration increases, we will reach the super-spin-glass (SSG) behaviour in which the superspins of the particles freeze at a certain freezing temperature $T_f$. For higher concentrations but below the physical percolation, superferromagnetic (SFM) or superantiferromagnetic (SAFM) arrangements are found, in which the magnetic nanoparticles behave as an ensemble of spins that order parallel or antiparallel, respectively, to each other inside the particle.

The combination of the three ingredients is one of the most intriguing present topics requiring deeper understanding. The magnetic interfaces can be part of the connected (shell) surfaces (for example in thin films of investigation through years) or more common in this decade of nanometric grains [3]. The fact that, commonly, the crystallographic structures in the composite (nanostructure) usually are not symmetrically equivalent and that the magnetic interactions could be screened or enhanced depending on the nature/thickness constitutes a very attractive field. In the past this was traditionally studied in films, but nowadays the nanoscience know-how has promoted a much broader landscape to scrutinise these magnetic interactions. The interfaces constitute an important factor, not only due to the obvious interconnection among the nanoentities (particle, layer, etc.) with the neighbour material, but also because in many cases there is a dull distinction between the interface itself and the -usually termed- as grain boundary. In this sense, it results possible to examine the interplay of the core and the surface layer (commonly termed as shell) respect the electronic/magnetic behaviour by seizing different strategies. A simple example, the magnetic role of the shell can be ascertained if an antiferromagnetic core is selected. Within a more general standpoint one can also observe the magnetoelectronic control ejected by the surface by increasing the number of surface layers (2-3 nm) so as to create effectively a thicker shell with connection with others. If this boundary is extended, ideally we will end up with a collection of nanoparticles in a matrix. This would constitute the limiting case. It is important to remark here that we are perfectly aware that some of those limiting cases, either (core-shell in relation with exchange anisotropy) magnetic isolated grains [5] or the other: magnetic grains in weak magnetic matrices, have been covered thoroughly in the literature, with excellent discoveries and applications [6, 7].
Curiously an overwhelming majority of the work has been carried out in 3d-transition magnetic materials whereas 4f-magnetism has been left partially behind. It is true that efforts to understand the properties of permanent magnets of Nd-Fe-B (and others) for technological application grabbed the particle size reduction as a possibility for improvement. Nevertheless, to the best of our knowledge, the research in nanostructured 4f-based alloys is marginal so far. This can be understood by the fact that the macroscopic traditional properties appearing in Rare-Earth intermetallics in binary and ternary alloys were extremely well-defined some decades ago [13]. Nowadays the core of the 4f-research is interested in electronic effects mostly related with a plausible and improved definition of the so-called Non-Fermi liquid state of matter; this is ideally studied in materials in single crystal state. Bearing in mind the above related statements, the lack of results in 4f-nanostructures honestly seems an arguably absence of a global perspective. From our personal standpoint, this has prompted us to tackle this methodology with the main objective of searching for new electronic/magnetic phenomena in archetypal 4f-systems in nanometric state.

In this thesis we will be getting down to the nitty gritty on two intermetallic compounds, TbCu$_2$ and YbAl$_3$, that will be magnetically and electrically characterised, after being mechanically milled down to a nanometric particle size.

Firstly, nanometric TbCu$_2$ has been previously studied in [14], where it was observed that the AFM transition disappeared giving rise to a SG behaviour when the samples were milled for 120h. Our aim is to perform a comprehensive study of the evolution of these two behaviours as a function of the milling time or, in other words, of the particle size. Experiments in Large Facilities will be also performed to disclose in detail the macroscopic magnetic behaviour of these systems.

On the other hand, YbAl$_3$ is an intermediate valence compound in which the valence of the Yb ions was reduced from 2.86 in bulk to 2.70 when the sample was milled for 120h [15]. This was related to the change of coordination of the atoms on the surface of the nanoparticle, driving the compound to an even less magnetic character. Here, we will pinpoint the electronic transport (electrical resistivity) behaviour. Therefore, we will be committed to the challenge to studying directly the electron and phonon behaviour and other contributions associated to the nanostructural state of the alloys.
The structure of the thesis report is as follows: after the introduction (current Chapter 1), the main physical concepts needed for the understanding of the studied systems are briefed along the Chapter 2. Next, Chapter 3 presents the fabrication of the master alloys and following mechanical milling of the nanostructures. Details of the alloying and milling procedures will be given, together with the experimental techniques used in this work in order to obtain the structural, magnetic and transport properties. The results and analysis of the two systems studied within this thesis are presented in Chapter 4 for TbCu$_2$ and Chapter 5 for YbAl$_3$. Finally, the main conclusions gathered along this thesis are summarised in Chapter 6.
2.1 RARE-EARTH INTERMETALLICS

Since decades ago, to understand the magnetism in 4f-compounds has constituted a productive field gathering an enormous research activity. Recently there are a lot of relevant reports [17, 18], focusing largely the attention on:

- Intermetallic compounds made of rare-earths (RE) and transition metals (TM) that could present interesting phenomena, like giant magnetostriction, magnetic superconductors... as a consequence of the interplay between interactions.

- Strongly correlated electron systems (SCES): systems including Ce, Yb, Sm or Eu as RE-elements. These systems present intermediate valence, heavy fermion, non-Fermi liquid (NFL) behaviours, amongst others, promoted by the competition of Ruderman - Kittel - Kasuya - Yosida (RKKY) and Kondo interactions.

The interplay of the magnetic interactions in all these compounds is responsible of their properties and particular behaviour. Consequently, we will start with a brief description of the different interactions as well as the most important associated phenomena. The behaviour of these RE-TM compounds is determined by the localised magnetism, due to the rare-earth 4f-electrons and to an eventual delocalised magnetism of the transition metal 3d-electrons. In the following section, we will describe the magnetism of RE-intermetallics, useful for the understanding of the particular research presented in this work. All of them have been thoroughly explained in seminal textbooks [19, 20].
2.1.1 Magnetic interactions in rare-earth metallic compounds

The magnetic behaviour of the rare-earths is due, basically, to their electronic state: [Xe] 4fⁿ 5d¹ 6s². In metallic compounds, the rare-earth element usually displays a +3 valence, with the 5d- and 6s-electrons in the conduction band and leaving the 4f-band incomplete. The short spatial extension of the 4f-electron wavefunctions difficults the overlapping with neighbour atoms. For this reason, there is no direct magnetic exchange among them. This internal and localised character of the 4f-electrons leads to consider the RE³⁺ ions in the metal as ‘free’ and inside a conduction electrons sea (Fermi gas model).

In absence of direct exchange, the main magnetic interaction within these compounds is of indirect character as a result of the model proposed by Ruderman - Kittel - Kasuya - Yosida (RKKY) [21, 22, 23]. The magnetic interaction is thus transmitted via polarisation of the conduction band electrons. The exchange interaction between spins is calculated by a second order perturbation theory, taking into account that electrons are free and their interaction is punctual (Ruderman - Kittel approximation [21]). This exchange is long-ranged and of oscillating character, accounted by the Friedel function (Fig. 2.1). Consequently, the effective exchange can present a ferromagnetic (FM) or antiferromagnetic (AFM) character, depending on the value of the Fermi vector $\vec{k}_F$ and the distance between magnetic ions $\vec{R}_i$ [20].

Figure 2.1: Friedel function, with $x = 2k_F \vec{R}_i$, defined in the text.
When an ion is situated in a crystalline context, the electrostatic field caused by the rest of the ions (crystalline electric field, CEF) affects the energy levels of the rare-earth. In a simplified picture, there are two energy terms playing a combined role. On the one hand, the spin-orbit interaction is large in RE-ions ($\propto Z^4$) and, secondly, the crystal field is (relatively) small due to the screening of the internal $4f$-electrons. By contrast, this situation is reversed in magnetic TM in which the CEF are more important than the spin-orbit term. The outcome of this situation is that in RE-alloys the angular momentum and spin are coupled with a total angular momentum $\vec{J}$ (good quantum number) [19]. In this situation the crystal field destroys the degeneracy, appearing $2J+1$ levels. The magnetic moment related to every rare-earth free ion will be $\mu = \mu_B g_J J$, with $g_J$ the Landé factor. Regarding the susceptibility in the paramagnetic regime, it follows a Curie-Weiss law with an effective paramagnetic moment $\mu_{eff} = \mu_B \sqrt{J(J+1)}$.

The symmetry of the crystalline field itself leads to the appearance of an anisotropy that affects the ordering of the magnetic moments. This can lead to quite complex magnetic structures as a consequence of the competition between the interaction associated with the indirect exchange and the CEF anisotropy. In addition, the presence of inhomogeneities in the crystal at microscopic level (i.e. impurities, holes, defects...) can lead to a random distribution of local anisotropies, which affects in turn to the ground magnetic state properties. Macroscopically, the overall and simplest magnetic state can be considered ferromagnetic or antiferromagnetic depending on the RKKY coupling.

The first interpretation of ferromagnetism was performed by Pierre Weiss in 1906, with his hypothesis of the existence of a molecular field [24]. Ferromagnetic (FM) materials are characterised by a long-range ordering of their atomic moments parallel to each other, even in the absence of a magnetic field. This long-range and spontaneous magnetisation vanishes above the ordering Curie temperature $T_C$. Above this Curie temperature, a ferromagnetic material becomes paramagnetic and its susceptibility follows the Curie-Weiss law, with a large and positive paramagnetic Curie temperature $\theta_P$. P. Weiss figured out the brilliant assumption that the molecular field acts in a FM material below and above the $T_C$. On the other hand, in a huge number of magnetically ordered materials, the atomic moments couple in
an antiparallel arrangement, rather than parallel as in ferromagnets, with zero net moment. These materials are so-called antiferromagnets (AFM). The theory of AFM was developed by L. Néel [25] by extending the Weiss molecular field theory in sublattices. The susceptibility $\chi(T)$ of an AFM compound varies with temperature as the following: as temperature decreases, $\chi$ increases up to a maximum at a critical temperature called the Néel temperature $T_N$ and decreases again down to lower temperatures. Antiferromagnets have limited technical application because their net magnetisation is zero in the absence of a magnetic field. Nonetheless they constitute benchmarks of magnetic research and have recently gathered technological interest in computer science because of the exchange anisotropy or the exchange bias effect [26, 27].

Occasionally, it has been found that is possible to establish the existence of magnetic disorder within a RE-alloy. This situation is theoretically handled with the aid of the random magnetic anisotropy (RMA) concept. This implies that the local CEF is varying randomly thanks to an amorphous arrangement or to the dilution of a crystalline ferromagnet with non-magnetic species. The factor controlling the RMA behaviour is the ratio between the average strength of the local axial CEF ($D_{\text{RMA}}$) and the exchange interaction ($J$). If this ratio is expected to be strong, a disordered magnet is formed. By contrast, if $D_{\text{RMA}}/J \ll 1$, the magnetic arrangement will comprise disordered clusters, for which it is expected a quasi-ferromagnetic state with a wandering magnetisation [28]. Based on experimental results in amorphous TbFe$_2$, Harris, Plischke and Zuckermann (HPZ) proposed a Hamiltonian with Heisenberg spins. In this, all spins present an equal magnitude and each spin is coupled to the local CEF. The latter varies from site to site in a random way [29]. After simplifications the total Hamiltonian is reduced to [30]:

$$H = -J \sum_{i,j} \mathbf{j}_i \cdot \mathbf{j}_j - D_{\text{RMA}} \sum_i (\mathbf{n} \cdot \mathbf{j}_i)^2 - g_J \mu_B \sum_i \mathbf{H} \cdot \mathbf{j}_i$$

where $J$ is the nearest-neighbour Heisenberg exchange coupling and $\mathbf{j}_i$ is the total angular momentum operator for the magnetic ion on site $i$. The value $D_{\text{RMA}} > 0$ provides the magnitude of the random uniaxial strength and $\mathbf{n}$ is a vector pointing along the direction of the local anisotropy. In short, the manipulation of the composition of intermetallics and eventually of the structural arrangement is a tool to promote randomness.
Unconventional behaviour in rare-earth intermetallics

So far, we have outlined the conventional behaviour of the RE-ions, but some of these ions can present several electronic configurations in the 4f-shell. This is the case of the Ce, Eu, Sm or Yb ions, which might show different electronic occupations and, hence different valence; they are called anomalous rare-earths and are characterised by the possibility of presenting the configurations $4f^{n+1}$ or $4f^{n-1}$, instead of the usual $4f^n$.

The electronic configurations are well defined when the Fermi level is far enough (in energy) from the 4f-shell. When this is not the case, there might be a chance of valence instabilities. In some alloys the energy of the Fermi level is modified, shifting it up to higher energies than that of the 4f-shell (> 2eV). This results in a definite 3+ valence in the case of Ce-ions. Here, the system presents a localised magnetism related to the ground level $J = \frac{5}{2}$ ($S = \frac{1}{2}$, $L = 3$) of the Ce$^{3+}$, ruled by the indirect exchange interactions.

On the other hand, when the 4f-shell is above enough (in energy) from the Fermi level, all the Ce unpaired electrons are located within the conduction band, so the electronic configuration is $4f^0$, Ce$^{4+}$, and the localised magnetism disappears giving rise to a non-magnetic behaviour. This situation is the same for Sm, but exactly the other way round for Yb and Eu, where the valence would tend from 3+ to 2+, the latter corresponding to a non-magnetic behaviour (filled-shell).

When none of these extremes is found, an intermediate situation is settled down, in which the Ce electrons begin to correlate with the conduction electrons (not losing completely their localised character), leading to the state hybridisation. A consequence of the hybridisation of the 4f-state with the s and d states of the conduction band is the appearance of the Abrikosov-Suhl resonance [31, 32] at $E = E_F$ [33], when the Fermi level is very close to the 4f-energy level. Then, some anomalous effects may appear, such as Intermediate Valence, Kondo Effect [34] or Heavy Fermion [35]. The characteristics of every of these behaviours are different though all of them are caused by the mentioned hybridisation. Thus, all these phenomena are encompassed in the Strong Correlated Electron Systems (SCES).

Kondo Effect The Kondo effect can be described as an antiferromagnetic coupling between the conduction and the 4f-state elec-
trons. On the one hand, it produces an increase of the resistivity due to the conduction band electron scattering rise; and, on the other, a decrease of the magnetic moment, due to the conduction electron screening. This effect has a local and an antiferromagnetic character.

Real metals may contain impurity atoms, which might have a non-negligible and detectable influence on their electronic properties [37]. The first manifestation of the effect of magnetic impurities on the electrical resistivity appeared in the 30s, when de Haas et al. [36] observed a minimum in $\rho(T)$ at low temperatures, for Au with Fe impurities (Fig. 2.2). They could not explained this phenomenon in that moment, “the cause of the minimum is entirely obscure and constitutes a most striking departure from Mathiessen’s rule, according to which the ideal and residual resistances are additive -some new physical principle seems to be involved”. Thirty years passed before Jun Kondo, in 1964, was able to give a theory in which he related this minimum to the presence of solved atoms [38].

Several years before, J. Friedel, in the late 50s, published a previous study on the impurities in metals [39]; the most important concept that emerged from this theory was the idea of *virtual bound states*; states almost localised due to resonant scattering at
the impurity site. Later on, P. W. Anderson, in 1961, figured out this idea in another way, which today is called Anderson model \[40\]. This model contains not only a narrow resonance related to the impurity states, but also a short-range interaction between the localised electrons, needed to explain the localisation of the magnetic moments.

The Kondo theory about the electrical resistivity minimum was based on a model that assumed the existence of a local magnetic moment related to a spin \( S \), connected to the conduction electrons via exchange interaction \( \mathcal{J} \), which is known as the \( s-d \) model and can be derived from the Anderson model. Kondo showed, through a third order perturbation theory in the coupling \( \mathcal{J} \), that this interaction causes a scattering of the conduction electrons nearby the Fermi level. Then, a \(-\ln T\) contribution to the electrical resistivity \( \rho(T) \), that increases at low temperatures \[38\] is predicted. The prefactor of the logarithmic dependence contains \( \mathcal{J}^3_{k,k'} N^2(E_F) \), which depends on the density of states \( N(E_F) \) and on the energy-dependent antiferromagnetic exchange interaction \( \mathcal{J}_{k,k'} \) \[41\]. This interaction can be written as:

\[
\mathcal{J}_{k,k'} = \frac{V^2_{k,k'}}{E_F - E_{4f}}
\]

where \( V_{k,k'} \) is the hybridisation matrix element between the \( f \) electrons and the conduction band. Years later, in a study about CeAl\(_2\), Buschow \[42\] showed the existence of a Kondo effect, but this time it was not due to isolated impurities (Kondo-impurity) but to magnetic atoms that formed a crystallographic lattice; in other words, a Kondo-lattice. From then, many systems with these characteristics have been found.

**Heavy Fermions** The hybridisation of states causes an increase of the effective mass of the electrons. This results in a higher Sommerfeld coefficient \( \gamma \) of the electronic contribution to the specific heat \( C_P \), with respect to that of a normal metal. An easy deduction is that these electrons are not free anymore. The increase of their effective mass gives rise to the name of Heavy Fermions. The first heavy fermion was discovered by K. Andres et al. in 1975, observing a large value of the linear specific heat capacity in CeAl\(_3\) \[43\], reaching \( \gamma = 1620 \text{ mJ mol/K}^2 \).
Intermediate and Mixed Valence When the hybridisation between the 4f-shell and the conduction band is very intense, the configuration $4f^n$ is not stable and a mixture of the configurations $4f^n$ and $4f^{n-1}$ flourishes, in which the electrons are still localised. In the case of Ce, there exists a mixture of the configurations Ce$^{3+}$ ($4f^1$) and Ce$^{4+}$ ($4f^0$), while for Yb the mixture is between Yb$^{3+}$ ($4f^{13}$) and Yb$^{2+}$ ($4f^{14}$). If the mixture is static, the system presents the so-called mixed valence. In this landscape, both configurations are present in different sites of the lattice during an infinite time. On the other hand, if the mixture is dynamic, the system is in a regime of intermediate valence, and every rare-earth site seems electronically identical in time average with a fixed number of electrons, $n$ or $n-1$, for every instant. The mixed and intermediate valence system can be considered as a time fluctuation ($10^{-13}$ s) of the electronic configurations $4f^n$ and $4f^{n-1}$.

In these systems, there exists a competition between indirect exchange interaction RKKY (which tends to order the magnetic moments) and Kondo effect (which screens those moments). From an experimental point of view, we can follow this change from a magnetically ordered state to a completely Kondo one, usually applying two strategies: either changing the concentration (chemical pressure) or applying hydrostatic pressure on the sample. In the 70s, S. Doniach [44] qualitatively explained this behaviour, stating that the temperature that characterises the Kondo interaction, $T_K$, follows an exponential law as:

$$T_K \propto e^{-\left(\frac{1}{4jN(E_F)}\right)}$$

while the magnetic ordering temperature, as deduced from RKKY model is:

$$T_{RKKY} \propto (\beta^2N(E_F))$$

The Doniach diagram (Fig. 2.3) describes qualitatively the competition between these two interactions with same origin, as a function of a control parameter $|jN(E_F)|$, currently labelled as the hybridisation parameter.

Thus, the ground state evolves from a magnetically ordered state at low temperatures (i.e. $|jN(E_F)|$ small, weak hybridisation) to a maximum delocalisation ($|jN(E_F)|$ high), when $T_K$ overcomes $T_{RKKY}$, and the system becomes non magnetic. In this limit, RKKY interactions
are very weak with respect to Kondo coupling, and then the mixed and intermediate valence are possible.

There are several situations in which, depending on the competition between RKKY indirect exchange interaction and the Kondo effect, we will have a variety of behaviours:

- When $T_{\text{RKKY}} \gg T_K$, the indirect exchange interaction is dominant, so the system orders magnetically.
- If $T_K \gg T_{\text{RKKY}}$, the ground state will be non-magnetic.
- If $T_K < T_{\text{RKKY}}$, but of the same order of magnitude, the ion magnetic moment is reduced because of the screening coming from the Kondo effect. In addition, the system can be magnetically ordered at a reduced temperature.

There is a certain value of $|J N(E_F)|$ for which the ordering temperature tends to zero, and the state hybridisation is remarkably important (when $|J N(E_F)| = |J N(E_F)|_{\text{crit}}$). At this point (Quantum Phase Transition, QPT) the magnetic order disappears. The study of QPT constitutes itself a tremendous field of investigation which attracts an enormous research effort as new physics is involved. The system properties in this possible QPT are very unusual and different from
those present in *Fermi liquids* (FL), and they are simply called *Non-Fermi liquids* (NFL) [46].

As we mentioned above, $|\mathcal{J}(E_F)|$ is very sensitive to chemical or hydrostatic pressure variations. This fact is very important as we can control this parameter experimentally. Under the application of high pressure, the valence of rare-earth ions generally increases as an electron is squeezed out of the $4f$-shell, leading to the demagnetisation of cerium: $\text{Ce}^{3+}(4f^1) \rightarrow \text{Ce}^{4+}(4f^0)$ and the magnetisation of Ytterbium: $\text{Yb}^{2+}(4f^{14}) \rightarrow \text{Yb}^{3+}(4f^{13})$ (see Fig. 2.3) [47].

The rich variety of theoretical and experimental findings connected to the unconventional behaviour of some rare-earth intermetallics is overwhelming [48, 49]. To analyse the results described in Chapter 5, it is recommendable to grab only the mainframe of the basic understanding which is provided by the Doniach diagram. In this sense, such a diagram has been verified in a great variety of Ce- or Yb-compounds. The experimental confirmation of Doniach diagram was performed in CePt when being diluted with Ni [50] or when applying hydrostatic pressure [51]. Both effects cause a decrease of the volume, that resulted in an increase of $T_K$ (i.e. the hybridisation increased and so did Doniach parameter). It is worth noticing that in some magnetic Yb compounds, such as $\text{La}_{1-x}\text{Yb}_x\text{Cu}_3\text{Al}_2$ [52], there exists an anomalous behaviour, which is not entirely accounted by the diagram. For our purposes, the Doniach standpoint seems sufficient for a qualitative interpretation.

### 2.2 Magnetic Nanoparticles

In the nanometric scale, a couple of factors are responsible of new phenomena observed in these systems: (a) the *size effect*, due to the increasing confinement of the atoms as the particle size decreases, and (b) the *surface effect*. A large number of atoms are located on the surface of the nanoparticles (NPs) and the magnetic behaviour of these atoms is different from those in the core due to the atomic coordination and defects. Thus, the spins in the core will maintain the same arrangement than in bulk, but a structural disorder will be found on the surface, giving rise to modifications of the physical properties. In particular, in magnetic nanoparticles, there exists another ingredient: the eventual *random and competing interparticle interactions*. These may
strongly modify the dynamic spin response of these systems by: on the one hand affecting the energy barrier (related to the relaxation time of each individual particle) and on the other hand producing a collective state [10, 11, 12, 53, 54, 55].

When particle size $D$ decreases, the magnetostatic energy (proportional to the volume) is also reduced. For this reason, the creation of domain walls is less and less energetically favourable. Eventually, a critical size is reached and the energy cost of forming domain walls is greater than the energy gained reducing the magnetostatic energy, giving rise to a single-domain particle. There is not a typical critical particle size, as it depends on the system of study, for example 15 nm for Fe, 35 nm for Co or even 700 nm for SmCo$_5$ [54, 56]:

$$r_C \approx 9 \frac{\sqrt{AK}}{\mu_0 M_s}$$  \hspace{1cm} (2.5)

where $A$ is the exchange energy density constant, $K$ the uniaxial magnetic anisotropy of the particle, $\mu_0$ the permeability constant and $M_s$ the saturation magnetisation.

Let us now consider a single-domain nanoparticle whose total magnetic moment $\mu$ has a direction $\theta$ with respect to the applied field $H$. We will not take into account any additional anisotropic terms in the energy expression, so:

$$E(\theta) = -\mu H \cos \theta$$  \hspace{1cm} (2.6)
In the case that we had a set of particles at a certain temperature $T$ (in which the system has reached a thermodynamic equilibrium with the magnetic field $H$), there exists a Boltzmann distribution of the $\theta$ values in the set of particles. The fraction of the magnetisation that is aligned by the magnetic field can be calculated averaging $\cos\theta$ in the Boltzmann distribution, obtaining the Langevin function:

$$L(x) = \coth x - \frac{1}{x}$$

where $x = \frac{\mu H}{k_B T}$ being $k_B$ the Boltzmann constant. For low fields, $L(x) \approx \frac{\mu H}{k_B T}$ whereas for higher fields nearby the saturation, $L(x) \approx 1 - \frac{k_B T}{\mu H}$ [57]. It is evident that this treatment of the thermal equilibrium of the magnetisation properties of a set of isotropic single-domain particles is analogous to the atomic paramagnetism proposed by Langevin [58]. The only difference resides in that the magnetic moment $\mu$, here, is the net result of the moments within the ferromagnetic nanoparticle, while in [58] it was considered uniquely for an individual atom. A particle may contain $\approx 10^4$ atoms ferromagnetically coupled by exchange interactions. Thus, the behaviour of the single-domain particles can be understood as a giant spin with all magnetic moments strongly aligned.

In a more realistic scenario, there always exist anisotropic contributions due to the particle shape or strain, crystalline structure... If we consider uniaxial single-domain particles, the anisotropy energy is defined by:

$$E_K = KV \sin^2 \theta$$

where $K$ is the anisotropy constant (or anisotropy energy by volume unit), $V$ is the volume of the particle and $\theta$ is the angle between the magnetic moment and the particle symmetry axis (easy axis). When a magnetic moment is applied, the energy of the particle will be:

$$E(\theta) = KV \sin^2 \theta - \mu H \cos \theta$$

In 1949, L. Néel pointed out that in single-domain particles of a small size, the thermal energy fluctuations would be large enough to overcome the anisotropy interactions and reverse spontaneously the magnetisation of a particle in an easy axis even when no magnetic field is applied [59]. Namely, the energy barrier $\Delta E$ to overcome for every particle to reverse its magnetisation will be $KV$. Each particle has a magnetic moment $\mu = M_s V$. Under an applied field, this will tend
to align the magnetic moments of the particles, whereas the thermal energy will try to disalign them. Then, in a system formed by widely spaced and isolated particles, i.e. non-interacting single-domain particles, the magnetic moments of each particle will fluctuate independently respect to another particle. Thereby, the nanoparticles behave as a superparamagnet (SPM, see Fig. 2.4). This is to say, every particle behaves like a paramagnetic atom with a total magnetic moment of \( \mu \approx 10^3 - 10^5 \mu_B \).

The transition between spin configurations takes a certain relaxation time. This relaxing process was predicted to follow an Arrhenius-Néel law:

\[
\tau = \tau_0 e^{- \frac{E_B}{k_B T}}
\]

(2.10)

where \( \tau \) is the system relaxation time, \( \tau_0 \) is the intrinsic relaxation time (typically \( 10^{-13} - 10^{-9} \) s for non-interacting particles \([10]\)), \( E_B \) is the energy barrier between both stable magnetic states of the super-spin, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The measuring time \( t_m \) of each technique is a crucial parameter when dealing with systems of magnetic nanoparticles and to the determination of the blocking temperature \( T_B \), defined as the temperature where \( \tau = t_m \). For a certain fixed \( t_m \), when \( T > T_B \) the system will behave like a SPM, and will be blocked at \( T < T_B \). Naturally, if \( T > T_B \) the SPM behaviour will present the same features as the PM state.

As the packing fraction concentration increases, the interparticle interaction becomes more important so that the system may behave as a low temperature collective state. The interparticle coupling is then assured typically by two interactions. On the one hand, it is bound to consider the effect of dipolar coupling. This coupling is weak (\( T < 5K \)) when involving individual magnetic atoms. The expression for this interaction is:

\[
2t_{ij}^{\text{dip}} = \frac{1}{r_{ij}} \left[ \mu_i \cdot \mu_j - 3(\mu_i \cdot \frac{r_{ij}}{r_{ij}})(\mu_j \cdot \frac{r_{ij}}{r_{ij}}) \right]
\]

(2.11)

where \( \mu_{i,j} \) is the magnetic moment of the impurities \( i \) and \( j \) and \( r_{ij} \) is the distance between the two interacting moments \([3]\). As it is straightforward, when the magnetic moments stem from a nanoparticle then \( T_0 \approx E_d/k_B \), and the interaction is important. This interaction depends on the distance and varies the sign of the coupling. In metallic systems, it is necessary to recall the RKKY interaction which was introduced elsewhere; the crucial characteristic to remind is that it is oscillatory and of long-range. Overall, there have been found a number
of systems which we can ascribe to the collective coupling \([60, 61, 62]\).

It should be reminded that \(E_d > E_{\text{RKKY}}\) in most of the metallic systems \([63]\). As a matter of fact, this collective state sometimes shares most of the macroscopic properties with a spin-glass (SG) state.

The first spin glass definition was proposed by J. A. Mydosh as a system presenting magnetic disorder due to a combination of competing magnetic interactions and randomness provided by the site/bond disorder. The most obvious macroscopic finding is the existence of a characteristic temperature \(T_f\) at which the magnetic (isolated in canonical spin glasses) moments become randomly frozen. This prevents the existence of long-range magnetic order. Frustration is another concept also inherent to SG systems related, basically, to the opposite sign of competing interactions. A traditional visualisation involves a triangular lattice with AFM coupling \([64, 65]\). This subject, developed in the 70s, is object of strenuous efforts to provide a definite response to the character of the possible phase transition at \(T_f\). This debate is not the object of this work but some basic ideas will be useful.

Initial theoretical understanding of SGs was provided by Edwards and Anderson (EA) in 1975 putting forward an Ising Hamiltonian allowing for a distribution of nearest-neighbours interactions \([66]\). These obey the fact that the total sum of the exchange values should be zero. For the exchange values distribution it is possible to apply a Gaussian probability function. It should be noted that already in the EA-model the frustration is naturally occurring in the sense explained above and the famous cusp in the susceptibility of canonical SG was reproduced. Later, Sherrington and Kirkpatrick (SK) proposed an extension to the EA concept (Ising) with an infinite-range approach within a mean-field point of view \([67]\). Some controversy on the solution was studied by Almeida and Thouless (AT) which predicted a popular experimental finding providing the field dependence of the freezing temperature according to the AT line with \(T_f \propto H^{2/3}\) \([68]\). A solution for the SK-model was found by Parisi with the aid of the replica symmetry breaking theory \([69]\). The results provided a magnetic phase diagram which combined the existence of ferromagnetic, spin glass and paramagnetic regions. An alternative point of view was derived by Gabay and Toulouse with a slightly modified diagram \([70]\). Since then, several approaches have been worked out based on the droplet model and digging in the possible existence of a finite phase
transition in Heisenberg spin glasses which is not supported by numerical simulations. These predict a $T_f = 0$ in 3D systems [71]. The discussion of this debate is turning to the use of spin chirality and anisotropy concepts which are out of the scope of this work. More interestingly, we should mention models especially conceived for frustrated rare-earth alloys. Supplementary to those within the RMA approach mentioned previously, it is worth noting the recent progress of proposals of new magnetic diagrams. Such approaches take into account the competition between disorder, ferromagnetism and Kondo effect [72] and antiferromagnetic and SG combination [73]. In addition, the SG systems have been object of intense debate due to the controversy on whether there is a true phase transition at $T_f$ or not. If this were the case, a singularity due to the collective behaviour should arise. In the case of a definite phase transition it ought to be then possible to define an order parameter playing the role of the magnetisation in a ferromagnet or the sublattice magnetisation in an antiferromagnet. It is clearly understood that the simple average magnetic moment is not adequate. In this sense, an order parameter $q_{EA}$ was equally defined by Edwards and Anderson; this was taken as the mean-square spontaneous magnetisation in a single energy minimum, averaged to all possible minima values. In other words, the average value of the spin-spin autocorrelation function:

$$q_{EA} = \lim_{t \to \infty} \langle \vec{s}_i(0) \cdot \vec{s}_j(0) \rangle$$

(2.12)

In the vicinity of the freezing temperature, the spin fluctuations will follow critical fluctuations. At temperatures around the freezing temperature, a spin-spin correlation length, shorter than the coherence length of the critical fluctuations, will be controlled precisely by the latter. Thus, the coherence length can be easily transformed into timescales in a conventional critical slowing down, giving:

$$\tau_m = \tau_0 \left( \frac{T_{f,0} - T_f}{T_f} \right)^{-z \nu}$$

(2.13)

where $\tau_m = \frac{1}{2\pi f}$, $\tau_0$ is the relaxation time of a individual particle moment at a frequency $f \to 0$, $z \nu$ is the dynamical critical exponent and $T_{f,0}$ is the static spin glass temperature.

When the concentration $x$ of magnetic moments is high enough ($x \approx 10\%$, $T_0 \propto x$), there could exist clusters of short-range magnetically correlated moments. Those clusters would act as dynamic magnetic units at high temperatures. Again, at low temperatures, they
could freeze [74] showing up a characteristic response, similar to the canonical spin glass systems. It is then more correct to denote them as cluster-glass states.

With a further increase of concentration but prior the physical percolation, the interparticle interactions become stronger. If there is a defined collection of nanoparticles, the situation can result in ensembles tipically connected by dipolar or RKKY interactions. In such a case, a super spin glass (SSG) is formed [75, 76, 77] (see Fig. 2.4). The final stage is found when a ferromagnetic or antiferromagnetic coupling is detected. In such a stage, FM- or AFM-correlations will arise between the supermoments (the moment of a nanoparticle, as commented above $10^3 - 10^5 \mu_B$) of the nanoparticles in addition to those between the atomic moments within the particles. The FM state of nanoparticle ensembles might therefore be called SFM, as first introduced by Mørup in 1983 [78]. As it can be realised, the present situation moves in muddy waters as it is not clear how to quantitatively account for the quasi-continuous evolution in the supermagnetism. In a recent review [12] it has been proposed that the combination of results from $M_{DC}$ (irreversibility), $\chi_{AC}$ (critical slowing down), Argand plots to distinguish the magnetic domains wall modes and the rejuvenation (ageing) form a body understanding to disclose precisely the disordered state. Within a theoretical approach, the situation is beginning to be addressed with the aid of simulations. These should be focused on the obtention of a SFM ground state in disordered 3D systems, not only bearing in mind the mentioned interactions but also other conjectures based on multipolar interaction terms and/or tunneling exchange [12]. Certainly, this matter is still under scrutiny and will need more future experimental evidence and robust modeling.
EXPERIMENTAL TECHNIQUES

In this section we will explain the techniques used along this work, not only those connected to the synthesis of the samples (Section 3.1) but also to the structural (Section 3.2) and magnetic (Section 3.3) characterisation. Other complementary techniques such as electrical resistivity and specific heat are described in Sections 3.4 and 3.5, respectively.

3.1 SAMPLE PREPARATION

The sample preparation involves three different steps. Initially we need to get the master alloy which is obtained in an arc furnace. Secondly, there might be an eventual annealing process to ensure the existence of only the expected crystallographic phase. Finally, the master alloys are crushed and grinded in a high-energy planetary mill.

3.1.1 Arc furnace melting and annealing of the starting master alloys

The arc furnace (Fig. 3.1) MAM-1 (Johanna Otto GmbH) consists of a chamber with an inert gas atmosphere (Ar, 99.99%) in which a copper crucible and a tungsten (tip) electrode are placed. These are electrically isolated and the refrigeration is procured by flowing water. By establishing a high voltage between the crucible and the electrode, a DC-current arc (~ 100A) is produced throughout the inert gas, and a large amount of heat is thus generated. With this technique, polycrystalline samples, with a mass up to 10 g, can be produced. Melting temperatures as high as 3000 K can be reached with this arc furnace.

The starting products are weighted according to the molar proportions. Starting ingots have been purchased from Alfa Aesar (Yb(3N), Lu(3N) and Al(5N)) and Goodfellow (Tb(3N) and Cu(5N)).
The sample chamber is purged 3 times before actual melting in order to avoid oxidation of the alloys. The pressure in the chamber is then kept around 200 mbar, during alloying. Prior to proper production of the desired alloys, a short duration melting of a Ti getter is accomplished to eliminate traces of remaining \( \text{O}_2 \) gas. The duration of the arc is typically 5 seconds for all the samples.

This technique is extremely exothermic and usually requires a first fusion of the starting materials at a high velocity minimising the quantity of material losses. In our cases, dealing with binary rare-earth alloys, these losses do not exceed a 0.5\% for \( \text{TbCu}_2 \) and 2\% for \( \text{YbAl}_3 \) (the latter due to Yb evaporation). The samples are turned upside down and melted several times (2-4) in order to ensure a good homogenisation. However, the low solidification rate and the inhomogeneous cooling that the crucible originates can lead to the formation of spurious phases. In that case the annealing of the starting alloy is highly recommended. The final product is a ellipsoidal pellet which is then stored in a glove box (see Fig. 3.2).
3.1 SAMPLE PREPARATION

3.1.2 Milling procedure

After the production and homogeneisation of the master pellets, these were first crushed in an agatha mortar (in order to reach an homogeneous size of the powder $\sim 10^{-6}$ m) and then milled inside a planetary high-energy ball system (Retsch PM 400/2) (see Fig. 3.3a). The handling of the samples was carried out in a glove box (Fig. 3.2) under an Ar atmosphere (99.99%) to prevent the oxidation of the samples.

The milling system consist of two circular platforms which rotate following a planetary movement. The main parameters for the milling are the material of the containers, the ball/sample weight ratio, the rotation speed and the grinding time. The selection of those is relatively empirical for each of the compositions. Although there are some general indications [79], the previous works on binary RE-alloys performed in TbAl$_2$ [80], TbCu$_2$ [14] and YbAl$_3$ [15] has provided more precise conditions. In some cases, special adjustments have been performed in view of the resulting magnetic properties. These adjustments refer to the variation of the milling time (see Section 4.4).

The tungsten carbide (WC) container provides an extremely high collision energy, derived from the huge hardness value (9 Mohs) (see Fig. 3.3b). For a crucial check of the influence of the container composition, we have also milled with a non-metallic ZrO$_2$ container and balls. This material also boasts of a remarkable hardness value (6.5-7 Mohs) (Fig. 3.3c). The ball/sample weight ratio was selected about 12:1 for the WC container and 20:1 for that made of ZrO$_2$. 

Figure 3.2: Glove box where samples are stored under an Ar (99.99%) controlled atmosphere. The air-tight WC and ZrO$_2$ containers are sealed inside the glove box.
The containers were closed and sealed (O-ring in the container lids) in the glove box under Ar atmosphere (99.99%), in order to avoid any oxygen content that could help to the appearance of oxides in the ground compound favoured by the temperature rising during grinding. The milling procedure was carried out following successive steps of 5 minutes of clockwise and anti-clockwise rotation with a 5 minutes break in between in order to avoid possible re-crystallisation processes due to temperature rising [81].

The rotation speed of the containers was always 200rpm to speed up the procedure. Small amounts of material were removed after specified times: 0.5, 1, 2, 3, 5, 10 and 15 hours of milling for TbCu$_2$ and 20 and 70 hours for YbAl$_3$ and LuAl$_3$, always keeping the mentioned ball/sample weight ratio. Obviously, the resulting product is a very fine-coarsed metallic powder. In the following, samples will be identified by their composition and milling time.

After the storage of the products in a glove box (Fig. 3.2), the containers must be cleaned up thoroughly. This is achieved in our case by milling a certain powder (Si powder + ethanol for WC and glass powder for ZrO$_2$ containers) for short times (30 minutes). The successive steps involve 1 minute of clockwise and anticlockwise rotations with 1 minute break in between to avoid an increase of temperature. After milling, this cleaning powder is removed.

![Figure 3.3: (a) Planetary ball mill Retsch PM 400/2. (b) Tungsten carbide container (125ml) and balls. (c) ZrO$_2$ container (250ml).](image-url)
3.1.3 Hydraulic press & Spark-erosion machine

The determination of certain physical properties requires proper sample shapes. In particular, the measurement of the electrical resistivity requires parallelepipedic bars to apply properly the electrical contacts and to define precisely the geometry. To shape the samples, we first pressed the milled powder in a press pellet die which is located in the centre of a Specac's Atlas Series hydraulic press (Fig. 3.4a). The required load reaches 4.5 ton. A disk (Fig. 3.4b) is then obtained, which has to be cut in a parallelepipedic shape to be measured using the 4-probe geometry (to be explained in Section 3.4).

Figure 3.4: (a) Specac's Atlas Series hydraulic press. It allows to load up to 15 ton. (b) Pellet, as taken from (a). (c) Spark-erosion machine, located in the laboratories of the Universidad de Cantabria. (d) Zoom of the cutting wire in (c).

To cut these compressed disks we use an Ona Compact 2 spark-erosion machine (Fig. 3.4c), located in our laboratories. The cut is obtained by the local fusion of the sample, produced by a electrical discharge between the sample and the Cu electrode (wire diameter \(\phi_{\text{Cu}} = 0.2\,\text{mm}\)) (Fig. 3.4d); everything is immersed in a dielectric oil. This Cu wire slides continously along the sample with a constant speed. The Cu wire, which actually is acting as a non-touching saw, can penetrate in the disk with different vertical speeds (from 2 to 10 mm/hour), depending on the sample composition, the applied voltage, the current along the wire, etc. The parameters for this cutting procedure are totally empirical for the kind of alloys of our interest. We have used a current along the wire of 3A and an applied voltage 200V, based in our large experience dealing with RE-alloys.
This spark cutting procedure provides the enormous advantage of avoiding strains induced within the sample that could modify the compound properties or even induce fracture in the case that the materials are fragile, like is our case. Finally, the equipment sports an excellent positioning system to align the sample, allowing high precision cuts (≈ 0.05mm) and defined geometry.

3.2 STRUCTURAL CHARACTERISATION

3.2.1 X-ray and neutron diffraction

X-ray and Neutron Diffraction (XRD and ND, respectively, onwards) are very common techniques performed, in the field of Condensed Matter and Materials Science, in order to characterise the structure of a material. Both techniques are based on the diffraction phenomena produced when a X-ray or neutron beam is scattered by a material and have been thoroughly explained in textbooks [82, 83].

Briefly, if we work with a crystalline material, there will be a coherent intensity at certain positions of the sample respect to the beam. This phenomenon follows the Bragg’s law:

\[ 2d \sin \theta = n\lambda \]  

where \( d \) is the distance between the crystallographic planes, \( n \) is the interference order (a natural number), \( \lambda \) is the incident X-ray or neutron beam wavelength and \( \theta \) is the angle between the incidental beam and the scattering planes [84].

In the case of a X-ray beam suffering a scattering with a given atom, there is only an interaction with the electrons; the intensity of the scattered beam is then proportional to the number of electrons, \( Z \), within the electronic cloud. Therefore, the structure of materials with atoms of similar \( Z \) may be difficult to evaluate (especially the atomic positions in the lattice). This intensity is not constant, depending on the form factor \( f(\theta) \) (Fig. 3.5) getting lower as \( \theta \) increases. In consequence, the XRD pattern of crystalline materials when of high symmetry, will provide very few peaks, concentrated at low angles.

On the other hand, neutrons do not have electrical charge so that the neutron monocromatic beam penetrates into the material eas-
ier and diffracts only with the nucleus. Thus, the scattering may be elastic and the result of two interactions. The first one, the nuclear interaction between neutrons and atomic nucleus. This is characterised by the diffusion amplitude or Fermi length, \( b \), which, unlike X-rays, \( b \) is independent of the scattering angle \( 2\theta \) and so there is no loss of peak intensity while increasing the scattering angle. On the other hand, neutrons have a spin \( = 1/2 \) and a magnetic moment \( \mu = -1.913\mu_\text{N} = -1.042\times10^{-3}\mu_\text{B} \), where \( \mu_\text{N} \) is the nuclear magneton, constant. This fact gives rise to the existence of magnetic interactions between the spins of the neutrons and the magnetic moments of the magnetic atoms. The electronic origin of the magnetic moment of the magnetic ions causes the variation of the magnetic form factor with the scattering angle, \( f_{\text{mag}}(\theta) \), similarly to the XRD \( f(\theta) \). In Fig. 3.5 we show a simple sketch with the comparison of the variation of \( f(\theta) \), \( b \) and \( f_{\text{mag}}(\theta) \). As a result of this, ND is traditionally used to reveal the moment structure of magnetic compounds [85].

![Figure 3.5: Magnetic and X-ray form factors and Fermi length (neutrons).](image)

The analysis of the structure of nanoparticles will need complementary results from XRD and ND. In the following we will describe the instruments and comment about the pros/cons of each technique.

### 3.2.2 Experimental devices

#### 3.2.2.1 Bruker D8 Advance diffractometer

Bruker D8 Advance X-ray (Fig. 3.6) equipment is a diffractometer working in the Bragg-Bentano geometry \( \theta - \theta \) scanning angles, lo-
located at the laboratory of Magnetismo de la Materia of the Universidad de Cantabria. The $\theta - \theta$ angle can be varied from $5^\circ$ to $140^\circ$ ($2\theta$) with a goniometer controlled by step-motors which allow steps of $\Delta(\theta) = 0.0005^\circ$. In this kind of $\theta - \theta$ diffractometers, the sample is placed horizontally (without movement), making possible an easy use of several types of sample holders. In our case, the sample holder is made of a Si single crystal oriented so that the background is extremely low, allowing the use of tiny amounts ($\lesssim 50$ mg) of sample. Moreover, this setup allows the obtention of better quality patterns, reducing the background signal; hence it facilitates the measurement of diffraction patterns with a very small amount of sample. The powder is poured onto a thin layer of vaseline on the Si disk.

Our room temperature sample holder is fitted with a spinner, reducing therefore the preferential orientations of the sample grains. Moreover, a fast changeover of the X-rays lamps is possible in this diffractometer; hence it is very easy to modify the wavelength, for example the Cu ($40kV$, $30mA$) or the Mo anode lamps ($50kV$, $30mA$), working at different voltages and intensities for every lamp.

Moreover, our Bruker D8 Advance counts with automatic slits, a Soller collimator and several slits to reduce or eliminate dispersed radiation. In the detection arm, there is a specific graphite monochromator for Mo-K\(\alpha\) and Cu-K\(\alpha\) ($\lambda = 1.5418\AA$ and $\lambda = 0.7107\AA$, respectively) in order to eliminate the K\(_B\) reflections. The monochromator is placed in front of a scintillator which allows the X-ray diffraction measurement in the wavelength range $\Delta\lambda = 0.5 - 3\AA$. This range covers the K\(_\alpha\) lines of the following elements: Ag, Mo, Cu, Ni, Co, Fe and Cr.

The calibration of the instrumental parameters ($U$, $V$, $W$) was carefully performed by the measurement of the LaB\(_6\) standard. This compound has very fine peaks so that we can determine precisely the instrumental contribution to the broadening of the peaks. Therefore, we will be able to calculate the particle size and strain by Rietveld refinements (see Appendix A).
3.2 STRUCTURAL CHARACTERISATION

3.2.2 ALBA synchrotron - Materials Science and Powder Diffraction (MSPD) beamline

Synchrotron radiation is produced by an electron beam emitted from a thermionic electron gun which is first bunched and sped up in a linear accelerator. Then, electrons are injected into a circular accelerator in which they are boosted by a high magnetic field (H=1T) up to velocities close to light speed (0.999c). Afterwards, they are injected into a storage ring where they travel at a constant speed by the help of bending magnets, wigglers and undulators. The electrons are deflected by these devices from their straight path by several degrees. This causes the synchrotron radiation emission, to the benefit of every beamline allowing the performance of a high variety of experiments (see Fig. 3.7).

ALBA synchrotron is a medium energy third generation synchrotron consisting so far of the following 7 different beamlines: MSPD (Materials Science and Powder Diffraction), MISTRAL (X-ray Microscopy),
NCD (Non-Crystalline Diffraction), XALOC (Macromolecular Crystallography), CLAESS (Core Level Absorption & Emission Spectroscopies), CIRCE (Photoemission Spectroscopy and Microscopy) and BOREAS (Resonant Absorption and Scattering). The synchrotron has been running regularly since autumn 2012.

![Synchrotron Design](image)

Figure 3.7: ALBA synchrotron design. (1) Electrons are accelerated through a linear accelerator into a circular one (2), where they achieve a 99.9% speed of light velocity by a high magnetic field. Then electrons are injected in the storage ring (3) where they travel at a constant speed and their path is deflected by bending magnets. This deflection causes synchrotron radiation, used in a certain beamline (4) for measurements.

Our synchrotron powder diffraction experiments were carried out in the high resolution MSPD instrument (Fig. 3.8a) at the ALBA facility (Barcelona, Spain) [86], with the help of the local contact (Dr. Francois Fauth). In this case, there is a multidetector for the diffracted beam. The energy range can be varied from 5 to 50 keV in this beamline and high pressure diffraction experiments may be also performed.

There were two different calibrations before the experiment took place. Firstly, the XRD of a Si sample was measured in order to obtain an accurate value of the wavelength ($\lambda = 0.4126\text{Å}$) of the incident beam ($E = 30\text{keV}$). Secondly, a NaCaIF sample was measured in or-
order to obtain the instrumental parameters (U, V and W), responsible of the instrumental broadening of the peaks.

The sample powder was located in a borosilicate glass capilar (diameter = 0.7 mm), Fig. 3.8b, that was closed by melting one of its extremes with a gas torch and then inserted in a sample holder (Fig. 3.8c). The collection time for each pattern (at a certain temperature) took around one hour and it was performed at the mentioned wavelength, covering a 2θ range between 2 and 35° in high resolution. The final pattern is calculated by overlapping different angular ranges.

![Figure 3.8: MSPD instrument at the ALBA synchrotron. (a) Hutch area where the sample is mounted. (b) Capilar in which the powder is poured (diameter = 0.7 mm). (c) Sample holder after melting one of the extremes of the capilar with a gas torch. The height of the sample holder + the capilar is around 4 cm.](image)

The temperature was varied between 80K and room temperature (RT) using a Cryostream Plus (liquid-Ni) cryostat. This enables a simple mounting, with a nozzle close to the capilar. The advantage is a very fast temperature change but there is a problem of sample holder icing in long runs.

The most important advantage of the selected setup is the extremely small sample quantity (≈ 50mg) allowing a fast change of temperature. In addition, the high brilliance and the monochromatic wavelength are helpful to analyse the data (in comparison with in-house XRD).
Two neutron diffraction measurements were carried out in the G4.1 diffractometer, at the Laboratoire Léon Brillouin (LLB, France) [87], with the help of Dr. Gilles André.

G4.1 is a two axis powder diffractometer (Fig. 3.9) equipped with a vertical focusing pyrolytic graphite monochromator and a 800-cells multidetector covering a 80° - 2θ range (step 0.1° between every two cells). The instrumental resolution of the spectrometer is maximum at low 2θ diffusion angles (2θ < 60°), so G4.1 is particularly well adapted for magnetic structure determination and for phase transition studies.

The high acquisition rate of the multidetector allows to perform diffraction studies (structural or magnetic) as a function of external parameters (temperature, pressure...) and to follow in situ kinetic reactions or phase transitions; the minimal acquisition time is of the order of one minute. With longer acquisition times (a few hours) it becomes possible to detect and quantify minority phases present in a multiphase compound, generally down to 0.1% (weight percentage).

The accessible 2θ diffusion angle covers the range 3 to 120°. In that range, it is possible to perform diagrams with 0.02° step (2θ). The temperature variation was provided by an orange cryostat mounted...
in the beam. This cryostat allows to cool down to 1.5 K in about 2 hours.

In this case, the used wavelength was $\lambda = 2.423\text{Å}$, but it can also be varied between 2.4 and 5.5 Å. The 2θ range in this experiment was from 4 to 84° and the step was 0.1°. The powder was inserted in a sample holder made of vanadium (as its scattering length is the lowest one: $b = -0.443x10^{-15}\text{m}$) so that approximately 2 grams could be measured and the experiment was carried out down to 1.8K. The acquisition time for every spectrum was around 8 hours per temperature in order to get good statistics. Only one sample (2 hours milled TbCu$_2$) was measured, due to the short duration (2 days) of the experiment.

In our alloys, the ND provides several features:

- It allows to establish the crystallographic state, with peaks appearing along the whole pattern, unaffected by a decrease of intensity.

- Neutrons penetrate the whole powder minimising the contribution of grain surfaces.

- The magnetic moment of the neutron allows to extract the magnetic structure of materials.

The main drawbacks are (i) the use of an expensive source (in this case a neutron reactor), (ii) the relatively low resolution in comparison with XRD, (iii) the patterns, even using fast and complex detectors, take (usually) longer times than conventional in-house and synchrotron diffractometers and (iv) normally a large quantity of sample is required (grams), hampering an extended use of nanometric samples.

3.2.2.4 Diffraction data analysis technique

The analysis of the ND or XRD patterns was carried out with the refinement techniques proposed by H. M. Rietveld, developed in the FullProf Suite [88, 89]. This method will be explained in detail in the Appendix A.
3.2.3 Electron Microscopy

In optical microscopes, the angular resolution is limited by the light wavelength. Shortly after the formulation of the wave-particle duality by Louis-Victor de Broglie \[90\], E. Ruska and W. Knoll grabbed the advantage of the short wavelength of highly accelerated electrons in a beam to effectively set up an electron microscope. For example, with an energy of 100 keV, the associated wavelength is of \( \lambda \sim 4 \) pm, much lower that the atomic radius. The electron beam trajectory is modified by using electromagnetic lenses, that is, a set of Cu coils inside Fe pole pieces. However, the quality of the electromagnetic lenses is really poor in comparison with the light lenses. As an example, the first electron microscope, in 1931, did not reach better angular resolution than a state-of-the-art light microscope. With time, electromagnetic lenses have improved notoriously, and now standard (transmission) electron microscopes provide a point resolution of several Å.

3.2.3.1 Transmission Electron Microscopy (TEM)

TEM is a technique of great importance as far as structural characterisation of nanometric systems is needed in many studies. In TEM measurements, electrons are accelerated and focused on the specimen (sample) by the condenser system, usually two lenses. After passing through the sample, the electrons are collected and the objective lenses form both images and diffraction patterns.

The main parts of the microscope are: electron source, sample holder, light and electron optics, electron detection and display. The TEM resolution (i.e the smallest distance that can be resolved), \( \delta \), is given by \( \delta = \frac{0.61\lambda}{\beta} \), where \( \lambda \) is the radiation wavelength (that depends on the electrons energy), and \( \beta \) is the semi-angle of collection of the magnifying lenses.

A very important point is that TEM only focus on a small part of the sample at a time. Moreover, TEM presents 2D images of 3D specimens, so the information is averaged through its thickness. Another limitation is related to the fact that samples must be electron transparent, which means that they must be thinner than 100 nm. For our powder specimen, preparation is easier than for thin films, and
involves selecting the fine powder, dispersing and suspending it in a non reactive liquid, and finally placing it on the Cu grid [91].

TEM experiments were performed on a Jeol JEM 2100 electron microscope (JEOL, Japan) (Fig. 3.10) at the TEM facility at the Universidad de Cantabria (SERMET), by Dr. Lidia Rodríguez Fernández, operating at an accelerating voltage of 200 kV, with an estimated point to point and line-to-line resolutions of 0.23 and 0.14 nm, respectively. It is equipped with a CCD detector (Gatan Orius SC 1000B) and an INCA Energy TEM200 (Oxford Instruments) energy dispersive X-ray spectrometer (EDS). DigitalMicrograph (Gatan) software was employed for the data collection and treatment.

The samples were prepared by suspending the solid powder in 2-PropOH under ultrasonic vibration. One drop of the prepared suspension was applied to carbon films on copper grids (Agar Scientific). In our case, the number of nanometric particles to be analysed, in order to calculate the particle size distribution, was about 1000, counted with the aid of several images.
3.3 Magnetic Properties

One of the most important parts in this work is related to the analysis of the magnetisation measurements. These results were obtained using both a Quantum Design PPMS multipurpose system and a SQUID magnetometer. In this section, we will cover the description of these instruments.

3.3.1 Magnetometry

A common procedure to characterise the magnetic properties of nanostructured magnetic materials is to study the static response (DC-magnetisation) of the system to several magnetic fields, varying the temperature. The typical zero field cooling (ZFC) process consists of a cooling down of the system in absence of an applied magnetic field. Then, at a certain (low) temperature, a magnetic field is applied and the magnetic response is recorded as a function of temperature, keeping this magnetic field constant. In the field cooling (FC) process, the system is cooled in the presence of a magnetic field and when the system reaches a low temperature, the magnetic response is measured as a function of temperature, with that magnetic field constant. Naturally, there is also a need for M(H) isotherms and hysteresis loops as in bulk materials.

Besides, given the spin relaxation processes of the magnetic moments within the particles, it is also mandatory to perform a dynamic study by means of AC-susceptibility (\(\chi_{AC}\)) [92]:

\[
\chi_{AC} = \frac{dM}{dH} \tag{3.2}
\]

This derivative character of the magnetisation \(M\) respect to the magnetic field \(H\) gives rise to the observation of subtle changes in the measurement. This allows the detection of minor magnetic phases or freezing and blocking processes. The experimental detection is usually carried out through pick-up coils at low frequency \(f (\leq 10^4 \text{ Hz})\). The voltage \(V\) is defined by:

\[
V = -n\alpha\mu_0h\chi_{AC} \tag{3.3}
\]
where \( n \) is the number of coil turns, \( a \) the cross section, \( h \) the oscillating AC-field and \( \mu_0 \) the vacuum permeability. Accordingly, the higher the frequency the better the recorded signal.

A spatially uniform magnetic field \( H \) oscillates with an amplitude \( h \) at a fixed frequency \( \omega \), then:

\[
H = h\cos(\omega t) \Rightarrow M = m\cos(\omega t - \gamma) \tag{3.4}
\]

as \( M \) and \( H \) directions differ in a certain angle \( \gamma \). Thus, it is possible to write:

\[
M = \chi'\cos(\omega t) + \chi''\sin(\omega t) \tag{3.5}
\]

and the susceptibility is then the addition of the real (\( \chi' \)) and complex (\( \chi'' \)) components:

\[
\chi_{AC} = \chi'(T) + i\chi''(T) \tag{3.6}
\]

\[3.3.1\] \textit{PPMS multipurpose}

DC-magnetisation (vs. temperature or vs. magnetic field), as well as AC-susceptibility measurements have been performed in a Quantum Design (QD) - Physical Property Measurement System (PPMS) 6000 (see Fig. 3.1), located at the laboratories of the Grupo de Magnetismo of the Universidad de Cantabria. This system has a measurement probe inserted in a liquid-He Dewar that allows a temperature range 1.9 - 400 K, with a stability of 0.01 K and a superconducting coil that provides magnetic fields up to \( H = 90 \) kOe.

The QD-PPMS multipurpose system is a very versatile system, as several options can be added to this basic configuration in order to measure specific heat, electrical resistivity, thermal transport . . . Our PPMS system is equipped with a He liquefier (Evercool system), that consists of a cryocooler - dewar system that recondenses and liquefies gaseous helium directly within the Dewar.

The DC-magnetisation signals \((M(T, H))\) are measured by a secondary set of coils, based on Faraday’s induction law: the sample is moved quickly up and down through the secondary coils, and the induced current is then measured. DC- (static) and AC- (dynamic) susceptibility can be measured in different conditions of temperature and magnetic field, with a sensitivity of \(2.5 \times 10^{-5}\) emu and \(2 \times 10^{-8}\)
emu, respectively. The AC-susceptibility, $\chi_{AC}$, is obtained again applying a small and oscillating (frequency $f$) magnetic field ($h$) and measuring the time dependence of the induced current with a lock-in detection. The alternating excitation field ($h$) supplied by the coils oscillates between 2 mOe and 15 Oe and the frequency can be set between 10 Hz and 10 KHz. As the signal depends on the frequency, it is expected that experimental susceptibility below 80 Hz presents a rather noisy signal.

The sample mounting is very easy: place the powder in a capsule and fix it with cotton to avoid movements. Then, the capsule is inserted in a plastic straw, and the straw is attached to a sample (very flexible) rod, thermally isolated by radiation shields. Due to the large signal of our powdered samples ($\approx 0.01$ emu at 300 K with $H=1000$ Oe) it is not necessary to correct the capsule diamagnetic contribution.

![Quantum Design PPMS multipurpose system](image)

Figure 3.11: Quantum Design PPMS multipurpose system. The most evident parts are the Dewar vessel (black) and the extraction motor at the top (light grey). There is a cold head inserted in the Dewar quasi-vertically in charge of the liquid-He recondensation.

3.3.1.2 SQUID magnetometer

The magnetometry for very low magnetic signals has been measured using SQUID (Superconducting QUantum Interference Device) mag-
netometry. Nowadays it is relatively common to use such detection devices and in our case this is provided by a QD-MPMS 5XL (see Fig. 3.12). Currently, this instrument is the most precise detector of magnetic fields (down to $10^{-7}$ emu in optimal conditions). It is composed by a superconducting coil with one or two Josephson junctions. In standard measurements, when a magnetic dipole moves perpendicular to the SQUID surface, a tunneling current through the Josephson barrier is produced. The generated current is proportional to the dipole size.

The samples are themselves put in a capsule in a straw and placed close to the SQUID sensor using a carbon fiber sample rod. This is a similar mounting to that of the PPMS, but straws are a bit longer and the capsule is in the center of the capsule. The latter is to assure an equivalent signal from either sides of the sample.

Our RE-based alloys give a rather large magnetic signal, even more taking into account that there is a large amount of available sample (few grams). In consequence, the SQUID magnetometry is not a reasonable option. However, it is necessary to use the MPMS if one intends to get the measure of magnetisation under pressure. This is not possible in the PPMS as the driving motor is not strong enough to hold and move the typical pressure (diamond-anvil or piston-cilinder) cell.

*Pressure cell: Easylab Mcell*

The use of high-pressure techniques is a convenient procedure to handle another variable (pressure) in order to modify the structural and magnetic states. Nowadays, this is becoming more and more important in the condensed matter field. Indeed, the pressure measurement allows the study of new phenomena of different scientific areas, such as condensed matter, chemistry, geology, biology, amongst others.

The pressure is a physical magnitude defined by the ratio between the applied force and the corresponding surface. The range of pressure to be achieved depends on the systems but it is easy to understand that the smaller the sample the higher the pressure. This, however, difficults the sample handling when the dimensions are tiny.
Figure 3.12: SQUID magnetometer. The Dewar is here enclosed within a wooden cabinet. The most salient apparatus is the arm (top of the image) guiding the sample in the SQUID and allowing the up/down movement for the extraction measurement.

To obtain the magnetisation, two pressure cells have gained great popularity: the diamond anvil and the piston-cylinder cells. Here, we have used the latter which has been acquired from the Easylab company (see Fig. 3.13).

The pressure cell is made of Cu-Be and is basically a cylinder with two ends which can be screwed inside. The idea is simple and just by tightening the nuts and consequently rotating the screws there is a force transmitted to the hydrostatic liquid through some ceramic bits. This is shown in Fig. 3.13 (left).

The steps to operate the cell start by first introducing the sample in a teflon capsule together with the liquid (with a needle, avoiding the formation of air bubbles). Simultaneously a small piece of Sn is added to determine the pressure $P$ from the superconducting transition ($T_{SC} = 3.7K$). The capsule is then closed and inserted in the Cu-Be cell (12, in Fig. 3.13) with the aid of the copper disks (5 and 8), the ceramic plugs (3 and 10) and the pistons (4 and 9). A check of the external dimensions of the cell is performed to monitor the starting dimensions. To apply the pressure, there exists an external
3.3 Magnetic Properties

![Figure 3.13: Left: EasyLab Mcell 10 cell. Right: Hydraulic system and supporting cylinder where the Cu-Be cell is placed. (1) External piston to apply the force, (2) and (11) Upper and lower screws, (3) and (10) Ceramic plugs, (4) and (9) Ceramic pistons, (5) and (8) Anti-extrusion copper disks (avoiding the deformation of the ceramic pistons), (6) Teflon capsule that contains the sample, the pressure medium (oil) and the tin detector, (7) Capsule plug, (12) Cell body, (13) Supporting cylinder, (14) Hydraulic system.]

A hydraulic system (14) with a manometer. Anyway, it is recommended to count the turns of the top nut as an indication of the applied pressure. If $P$ is large then there is some modification of the diameter of the cell. Given that these parameters (pressure in the manometer, nut turns-height of the top nut and increase of diameter) are relatively undefined, it is compulsory to perform magnetic measurements at low temperatures to detect exactly the superconducting transition of Sn (Meissner effect [93]). The empirical equation giving the pressure $P_{\text{real}}$ from the $T_{SC}$ variation is:

$$P_{\text{real}} = 5.041489 \cdot (T_{SC,0} - T_{SC})^2 + 17.81287 \cdot (T_{SC,0} - T_{SC})$$

where $T_{SC,0}$ is the Sn superconducting transition temperature at $P = 0$.

In short, the EasyLab Mcell 10 cell allows hydrostatic pressures up to around 10 kbar to be applied. It can be used not only at room temperature but also down to 1.8K and, as mentioned above, the cell can be mounted in the QD-MPMS, located in our laboratories.
Table 3.1: Relation between real pressure, $T_{SC}$ and physical parameters of the cell for the 0.5h TbCu$_2$ sample. The first column corresponds to the value of the pressure observed in the gauge; $Z$ is the distance between the screw head and the cell body, $\phi$ is the diameter of the cell in the medium point, $T_{SC}$ is the superconducting transition of the Sn probe and $P_{real}$ is the real pressure inside the capsule.

<table>
<thead>
<tr>
<th>P(psi)</th>
<th>Z (mm)</th>
<th>$\phi$ (mm)</th>
<th>$T_{SC}$ (K)</th>
<th>$P_{real}$ (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.15</td>
<td>8.537</td>
<td>3.61</td>
<td>0</td>
</tr>
<tr>
<td>460</td>
<td>5.25</td>
<td>8.544</td>
<td>3.48</td>
<td>2.37</td>
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<td>750</td>
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<td>4.76</td>
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<tr>
<td>1000</td>
<td>3.56</td>
<td>8.554</td>
<td>3.20</td>
<td>8.25</td>
</tr>
</tbody>
</table>

For the case of the nano-TbCu$_2$ alloys it is bound to give briefly details about the proper variation of the pressure in the samples. Thus, the applied pressure in the capsule is related to the values displayed in the gauge of the hydraulic press. However, the real pressure ($P_{real}$) is not, obviously, the same and has to be determined by Eqn. 3.7. Through this procedure, we can determine the real pressures for the 0.5 and 2h TbCu$_2$ milled alloys, as inserted in Tables 3.1 and 3.2, respectively. Although the most interesting data are the $P_{real}$ values, it can be evidenced how the cell diameter slowly increases while $Z$ comes down with increasing pressure. Both effects are expected considering cell response to an inside hydrostatic pressure, but it is not easy to anticipate the value of the highest pressure in the cell. In this sense, there is certainly an overwhelming lack of experimental results.

3.4 ELECTRICAL RESISTIVITY

The electrical resistivity $\rho$ has been measured at the Technische Universität Wien (TU Wien) and at the Universidad de Cantabria (UC). Although the measurement of $\rho$ follows basically the same procedure in both Universities, the employed equipment differs greatly. Thus, a detailed independent description is deserved.

At the Technische Universität Wien, measurements were carried out in a liquid $^4$He cryostat on bar-shaped samples. The geometry
Table 3.2: Relation between real pressure, $T_{SC}$ and physical parameters of the cell for the 2h TbCu$_2$ sample. The first column corresponds to the value of the pressure observed in the gauge; $Z$ is the distance between the screw head and the cell body, $\phi$ is the diameter of the cell in the medium point, $T_{SC}$ is the superconducting transition of the Sn probe and $P_{real}$ is the real pressure inside the capsule.

<table>
<thead>
<tr>
<th>$P$(psi)</th>
<th>$Z$ (mm)</th>
<th>$\phi$ (mm)</th>
<th>$T_{SC}$ (K)</th>
<th>$P_{real}$ (kbar)</th>
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<tr>
<td>0</td>
<td>8.10</td>
<td>8.537</td>
<td>3.63</td>
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<td>8.543</td>
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<tr>
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<td>8.560</td>
<td>3.19</td>
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</tr>
<tr>
<td>1200</td>
<td>2.95</td>
<td>8.560</td>
<td>3.10</td>
<td>11.0</td>
</tr>
</tbody>
</table>

follows the four probe technique (Fig. 3.14); the current is applied along the bar and the voltage is picked up by contacts in the middle. This geometry gets rid of external wiring resistivity. The geometry is standard and has also been used at the Universidad de Cantabria. Some of the bars where measured in a sample holder (Fig. 3.15 right), where four gold needles had to be stuck to the sample with a silver epoxy (Polytec PT Epo-Tek H20E), serving as electrical contacts. A setup employing an AC-resistance bridge (LakeShore 370) with an additional low resistance scanner (Model 3716L) was used.

Figure 3.14: Four-probe technique scheme showing the arrangement of the intensity ($I$) and voltage ($V$) contacts located on the sample. The $V$-contacts are separated a certain distance ($L$). The resistance measurement depends on the area ($A$) and $L$ of the sample bar.

The other samples measured in the Technische Universität Wien were placed into a sample holder (Fig. 3.15 left) where gold needles were useless. The homemade sample holder applied in this case had
already four tips to use the four probe method. The tips were adjusted with a screw to contact properly the sample surface.

Figure 3.15: TU Wien homemade sample holders for the measurement of the electrical resistivity. Left: The sample is mounted horizontally at the bottom and fixed by the four needles. Right: Here the contacts are assured with silver epoxy.

The variation of the temperature was provided by a very simple cryostat which was filled with liquid-He from an external Dewar. There was no control of temperature and the increase of temperature (from 4.2K) was dependent on the boil off rate of the small amount of liquid-He at the bottom of the cryostat.

In the Universidad de Cantabria, the PPMS multipurpose device was used to measure the resistivity of the majority of the samples presented in this thesis. The system allows a temperature controlled measurement of $\rho(T, H)$.

The measurement procedure was carried out in a dedicated sample holder (Fig. 3.16) made for this purpose, with four spring-loaded short stroke probes, in order to measure electrical resistivity by the 4-probe method (Fig. 3.14), in the same way than the one available at the Technische Universität Wien (Fig. 3.15, left). This special sample holder has been designed to be fitted onto a standard PPMS sample platform. Our holder consist of 4 spring-loaded pins (Ingun) made of Cu-Be. This (non magnetic) material was selected to avoid any interference with an eventual applied field from the PPMS superconducting coil. If the needles were magnetic, the AC-current would also induce an extra signal for the resistivity apart from a mechanical oscillation, hazardous for the quality of the electrical contacts. The needles
are attached to the Cu rig with Araldite and the distance between adjacent voltage pins is 1 mm. The contact between the PPMS platform and the tips is achieved by coated Cu wires (diameter $\phi = 0.1\text{mm}$) soldered at the top of the pins. The pin holder was screwed on top of the sample until a certain deformation was observed in the spring of the pins. The sample is isolated from the Cu platform (L-shaped) with kapton tape. This system enables an excellent contact at all temperatures, a point-like detection of the voltage and no modification of the sample structure by applying welding or silver paste techniques. The spring-loaded pins are rounded at the end not to provoke cracks in the samples. We should remind the reader that, as commented in Section 3.1.3, the milled samples had to be compacted.

As can be seen in Fig. 3.16, the sample bar (typical length: 10 mm; typical area: $2 \times 2.5 \text{mm}^2$) can sit finally vertically, parallel to the direction of an eventual magnetic field. The sample puck, including our special resistivity sample holder, is attached to the bottom of the sample enabling the contact with the PPMS AC-bridge. The typical current is around 10 mA and the PPMS instrument allows a very precise variation and control of the temperature (see Section 3.3.1.1).

In some specific cases, longitudinal magnetoresistance measurements have been carried out simply varying the magnetic field provided by the $H = 9\text{T}$ superconducting coil of the PPMS.

![Figure 3.16: Universidad de Cantabria homemade sample holder (2cm long) for the measurement of the electrical resistivity. The sample bar is mounted on a L-shaped platform covered by kapton tape. The contacts are assured by four spring loaded pins (note the golden capping). The applied magnetic field by the PPMS superconducting coil is parallel to the sample bar.](image-url)
3.5 SPECIFIC HEAT

Specific heat $C_P$ measurements were performed using the relaxation method [94] in the Quantum Design PPMS (option P6500). The sample holder or puck (Fig. 3.17) consists of a stage (platform), of an approximate area $3\times3\text{mm}^2$, in which the sample (area $\approx 2\times2\text{mm}^2$, $m \approx 8 - 15\text{mg}$) is attached by a standard cryogenic grease such as Apiezon $N$ to ensure good thermal contact. This stage is suspended in the centre of the puck by eight thin wires that serve as electrical leads for an embedded heater and a Cernox thermometer. These wires also provide well defined thermal connection between the stage and the puck. The puck is then inserted within the PPMS and the specific heat can be measured with magnetic fields up to $90\text{kOe}$ and in a range of temperatures from 1.8 to 400K.

![Image of experimental arrangement](image)

Figure 3.17: An image of the experimental arrangements of the sample puck for heat capacity measurements using the relaxation method. The sample is located at the centre on a stage, connected with 8 thin wires to the puck.

To minimise the heat loss via the exchange gas, the sample chamber is maintained at a constant very low pressure ($\approx 0.01\mu\text{bar}$). First, the temperature of both sample platform and puck are stabilised at an initial temperature $T_0$. Then, power is supplied to the platform heater for a certain time in order to increase the temperature of the platform in a $\approx 1\%$, to $T_1$. Once the heater is switched off, the temperature of the sample platform will decrease down to $T_0$. Fig. 3.18 shows this temperature exponential relaxation as a function of time, with a time constant that depends on the sample heat capacity and the wires thermal conductance through which the heat flow is trans-
mitted. The heat capacity at a certain temperature is obtained by fitting the temperature relaxation curve (calculated automatically by the PPMS software).

![Figure 3.18](image)

Figure 3.18: The black line is the plot of the heat injection to the sample and the relaxation over time.

An addenda heat capacity of the sample stage and the heat capacity of the grease are also subtracted from the measured signal to give the intrinsic sample heat capacity.

Our samples were measured in several temperature ranges; for TbCu$_2$ (i) 2-24K (1 K/min), (ii) 24-40K (2 K/min), (iii) 40-60K (1 K/min), (iv) 60-200K (5 K/min) and (v) 200-300K (5 K/min). For all these ranges, the heat injection was a temperature rise of the 2%.
Since the 90s, a great variety of intermetallic systems that present SG-like features have been studied. Effectively, this has been thoroughly reported in binary bulk $REX_2$ ($X$≡metals); in which comparisons with the main existing models based on a general random magnetic anisotropy approach (see Chapter 2) have been performed. A route to give rise to disorder, is to perform the mechanical milling of the starting compound, in which the production of nanoparticles can be achieved. This milling favours an atomic disorder in the material (but not necessarily an amorphisation) that provokes random magnetic interactions and, consequently, the SG-like behaviour [95]. This procedure is the road map for the work presented in the following.

The study of the size effects on the magnetic properties has mainly been evidenced on alloys of transition metals ($3d$) but a scarce attention has been paid to RE-based alloys ($4f$). The most outstanding works on $REX_2$ have been focused on the characterisation of, amongst others, the GdAl$_2$ and TbAl$_2$ ferromagnets. In this sense, several groups have studied the size-effect on the magnetic properties of GdAl$_2$ [96, 97, 98]; the mechanical milling process leads to nanoparticles that preserve the bulk structure. When DC- and AC-susceptibility measurements were performed, it was realised that the ferromagnetic transition ($T_C \approx 170$ K) weakened [97]. This led to the appearance of a SG transition at a lower, so-called, freezing temperature ($T_f \approx 65$ K) and the system was not longer ferromagnetic.

The same consequence due to the mechanical milling was found for TbAl$_2$ [80]; the ferromagnetic transition at $T_C = 105$ K tends to be wiped out with milling time, favouring a SG behaviour, with $T_f \approx 40$ K. Moreover, the dynamics of the magnetic relaxation, the field
and the size dependence of $T_f$ suggest the presence of an intrinsic disordered magnetic state inside the particles which conducts to a collective freezing, as occurs in super spin glasses.

A more recent study on milled TbAl$_2$ [99] showed the crossover of the size-dependent coercive field $H_C$ from the multi- to the single-domain region. The calculation of the critical size for the appearance of single-domain particles (85 nm, estimated from the magnetostatic and domain wall energy expressions) was very close to the obtained crossover value. A random anisotropy model, developed to understand ultrasoft nanocrystals of FeNbCuSiB and FeZrCuB, would explain the decrease of $H_C$ below a certain particle size, by the averaging of the nanoparticle anisotropy [100].

Figure 4.1: Real and imaginary components ($\chi'$ and $\chi''$) of the AC-susceptibility at several frequencies for a 120 h TbCu$_2$ milled sample. The inset presents the AC-susceptibility result for the antiferromagnetic unmilled TbCu$_2$ (figure taken from [80]).

On the other hand, the RECu$_2$ alloys show a great variety of behaviours depending on the rare-earth, i.e. Kondo behaviour in CeCu$_2$ [101] or metamagnetic transitions and antiferromagnetic behaviour [102] in TbCu$_2$. In several analyses of the magnetic properties of TbCu$_2$, an antiferromagnetic ordering with a transition temperature of around $T_N = 48 – 55$K (the highest Néel temperature among the RCu$_2$ alloys [13]) was observed [103, 104, 105]. However, very scarce research has been performed on milled TbCu$_2$. Previous works on
this compound accounted for the change from an antiferromagnetic transition at 50K to a spin-glass behaviour around 15K with long time millings (120h) (Fig. 4.1) [14].

We want to scrutinize in the present work the evolution from the behaviour of the bulk material to that of the milled one in archetypal TbCu$_2$. For this, a deep study has been performed in which samples have been milled from 30 minutes up to 15 hours. Later, these samples were studied initially from the magnetic point of view performing DC- ($M(T), M(H)$) and AC-susceptibility measurements. In addition, electrical resistivity and specific heat were measured in some of these samples to establish the metallic behaviour. To complete the picture, a complementary structural characterisation was performed through x-ray and neutron diffraction as well as TEM.

An intensive focus of the experimental work presented here is devoted to the full understanding of the magnetic behaviour of antiferromagnetic TbCu$_2$ nanoparticles. To ease the description we consider helpful to first concentrate on a key alloy (TbCu$_2$ milled for 2 hours), in Section 4.3 and, later, to extend the interpretation to the rest of milled alloys ($t = 0.5 - 15h$), in Section 4.4. Naturally, and in spite of the novelty of dealing with antiferromagnetic metallic nanoparticles, we discuss the results in relation to similar alloys. The comparison will be handy for the disclosure of the magnetic static and dynamic arrangements of the nanometric TbCu$_2$.

4.2 SAMPLE PREPARATION

Polycrystalline samples of the milled TbCu$_2$ series were alloyed in the Johanna Otto arc furnace, under an Ar atmosphere, from stoichiometric amounts of Tb(3N) and Cu(5N) metals obtaining large masses of alloy (~ 5g). Resulting metals were annealed for 5 days at 750°C, in vacuum ($\approx 10^{-3}$ mbar), in order to improve the crystallinity and ensure a good homogeneisation of the samples.

Later on, the samples were crushed and milled in a high-energy planetary mill, at a rotation of 200 rpm, within tungsten carbide (WC) containers with balls made also of WC in a ball/sample weight ratio 12:1. These containers were hermetically closed in the glove box in an Ar (99.99%) atmosphere to minimise the oxidation of powder. Previ-
ously, samples had been hand-milled in an agatha mortar to ensure the powder size homogeneity before ball-milling. The milling procedure was carried out following successive steps of 5 minutes of clockwise and anti-clockwise rotation with a 5 minutes break. Amounts of material were removed after certain milling times (0.5, 1, 2, 3, 5, 10 and 15 hours) to gather experimental data, as it will be explained in the following sections.

4.3 SIZE EFFECT ON THE MAGNETIC PROPERTIES OF TBCU$_2$

The present section of this chapter will deal with a case example which has been milled for 2 hours. We will start the description with a structural characterisation of the sample by XRD. This study was improved with a ND experiment in the G4.1 instrument located in the Laboratoire Leon Brillouin in Saclay, France, and complemented by TEM analysis. Afterwards, the magnetic characterisation with a PPMS; DC- $M(T)$ and $M(H)$ with several magnetic fields and temperatures, respectively) and AC-susceptibility (with several frequencies) measurements will be presented.

4.3.1 Structural characterisation

X-ray diffraction (XRD) was performed at room temperature (RT), using Cu-K$_\alpha$ ($\lambda = 1.5418\text{Å}$) radiation, as shown in Fig. 4.2. The pattern has been refined by the Rietveld method (FULLPROF suite [88, 89]) and the resolution function with a LaB$_6$ calibration. The fit was carried out using a Thomson-Cox-Hastings function, allowing the calculation of particle size ($D$) and strain ($\eta$) [106] (see Appendix A).

The Rietveld refinement indicates that the Imma symmetry of the bulk alloy is kept after milling and that the obtained orthorhombic lattice parameters $a = 4.322(1)\text{Å}$, $b = 6.833(2)\text{Å}$ and $c = 7.327(2)\text{Å}$ are very similar to those of the bulk ($a = 4.310(5)\text{Å}$, $b = 6.825(5)\text{Å}$ and $c = 7.320(5)\text{Å}$) [107]. The Bragg error ($R_B$) is only 14.6%, low for a nanometric sample so a good fit of the diffraction pattern has been achieved.
Figure 4.2: Rietveld refinement of the XRD pattern, performed at RT, for the 2h milled alloy using Cu-Kα radiation. The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns.

The strain of the particles is \( \eta = 0.2(1)\% \) and the size \( D_{\text{XRD}} = 8.6(5)\,\text{nm} \), as calculated through the refinement. This small value of the strain is due to the short grinding time, compared to other milled RE-intermetallic compounds, such as TbAl\(_2\) [80], GdAl\(_2\) [95] or YbAl\(_3\) [15]. For these, the grinding times ranged between 20 and 1200 hours. Regarding \( D \), a very small value of the particle size was also achieved in TbCu\(_2\), considering that a much lower time was dedicated.

Structural characterisation was completed via Transmission Electron Microscopy (TEM). Fig. 4.3a shows some bright field images of TbCu\(_2\) nanoparticles with sharp surfaces and absence of amorphous environments. A high resolution detail is shown in Fig. 4.3b, in which lattice planes are visible, confirming the crystallinity of the samples. A histogram analysis (inset Fig. 4.3a) results in a log-normal mean distribution \( D_{\text{TEM}} = 6.6(9)\,\text{nm} \), confirming particle sizes obtained by Rietveld refinement from XRD data. There is a slight change in particle size obtained by XRD and TEM. This is due to the fact that TEM is a very localised technique, in which 1000 particles have been sampled. By contrast a large amount of particles is employed in XRD, as
the powder mass is around 50 mg, equivalent approximately to \(3 \times 10^{16}\) particles.

Figure 4.3: TEM images of the milled sample with \(D_{XRD} = 8.6(5)\) nm (scale bars correspond to (a) 50 nm and (b) 5 nm) (a) Properly dispersed nanoparticles. (b) Zoom of a nanoparticle of TbCu\(_2\). Inset: log-normal particle size distribution of several pictures, giving \(D_{TEM} = 6.6(9)\) nm.
4.3.2 Magnetic characterisation

In the following, the static (DC) and dynamic (AC) magnetometry data for this particular milled alloy are described in detail. These are presented in two sections, providing the results interpretation for each technique ($M_{DC}(H,T)$ and $\chi_{AC}$).

4.3.2.1 Static magnetisation

$M_{DC}(T)$ (ZFC) for a magnetic field of $H = 1000$ Oe is plotted in Fig. 4.4 (in red) and compared to the $M_{DC}(T)$ (for the same magnetic field) of the bulk alloy (in black). The high temperature peak, marked with $T_N$, corresponds to the Néel temperature of the TbCu$_2$ alloy, that shifts to lower temperatures, from $T_N = 50.0(5)$ K in bulk to $T_N = 46.8(5)$ K (for 2h). A new peak, not present in bulk, appears at a freezing temperature, $T_f = 9.2(2)$ K. This peak could be related either to a SG behaviour or to a SPM blocking, in which nanoparticles would be independent. As we will confirm through the AC-susceptibility, it corresponds to a SG behaviour, in which the spins of the nanoparticles get frozen at that $T_f$ and these are not completely independent. These two transitions disclose the magnetic reentrance.

From a Curie-Weiss fit of the high temperature range of the DC-susceptibility (inset Fig. 4.4), we obtain the paramagnetic Curie temperature $\theta_P = 18.6(2)$ K and the effective magnetic moment $\mu_{eff} = 9.83(5)\mu_B$. Here, $\theta_P > 0$, so it is not longer AFM (at least not only AFM), in contrast to the bulk alloy ($\theta_P = -7(1)$ K [108]). The magnetic moment is in good agreement to that predicted for Tb$^{3+}$ effective moment ($9.72\mu_B$) by the Hund’s rules and to the experimental value of the bulk alloy [109].

$M_{DC}(T)$ ZFC curves for different magnetic fields are plotted in Fig. 4.5. The freezing temperature $T_f$, taken at the $M_{ZFC}$ low temperature maxima, follows the de Almeida-Thouless (AT) irreversibility line dependence, as shown in inset of Fig. 4.5. Both authors [68] predicted a sharp transition AT line that could scale the freezing temperature $T_f$ with $H^{2/3}$, within the framework of the mean-field theory of Sherrington and Kirkpatrick [67] (usually a first order approximation to a second order transition). This finding, associated to $T_f(H)$, is common in SG and RSG (FM-SG) and has been reported in other systems,
such as bulk multiferroic Pb(Fe$_{0.5}$Nb$_{0.5}$)O$_3$, where the coexistence of AFM and SG has also been observed [110].

The isothermal magnetisation data were initially analysed using the Arrott plots. The idea behind the Arrott plots is to define the ordering temperature and distinguish between the FM or AFM behaviour. Seizing the expansion of the magnetic field in terms of the odd powers of magnetisation [111, 112, 113]:

\[
\frac{H}{M} = a_0 + a_1 M^2 + a_2 (M^2)^2 + \ldots
\]

it is possible to represent $M^2$ vs. $H/M$ in what is called Arrott plots. For the 2h TbCu$_2$ milled alloy, these are presented in the Fig. 4.6. It is notable that they are showing the usual AFM behaviour [114], confirming the $M(T)$ data interpretation. At the AFM transition temperature at $T_N \approx 46K$, the curves start to bend, instead of being parallel to each other as for higher temperatures, changing the slope of the curve of the $M^2$ vs. $H/M$ function. If the dominant contribution is FM, the straight line corresponding to $T_C$ would pass through the origin [113].

We turn now to interprete the hysteresis loops. In Fig. 4.7, the $M_{DC}(H)$ of TbCu$_2$ nanoparticles is examined, for two different tem-
4.3 Size effect on the magnetic properties of TBCu₂

The data have been recorded up to \( H = 90 \) kOe. At \( T = 150 \) K, we obtain a PM signal, with no coercivity, and thus the response is linear. By contrast, below \( T_f \), at \( T = 5 \) K, a large signal is detected, as \( M_{DC}(H = 90 \text{kOe}) = 5.35 \mu_B \). Magnetisation does not reach saturation even at \( H = 90 \) kOe, as in other nanometric RE-intermetallic systems, such as 15 nm TbAl₂ [80], presumably due to the spin canting of the surface [115, 116]. The lack of saturation magnetisation in the \( M(H) \) is also observed in the bulk alloy (see bottom inset of Fig. 4.7). In this case, for the bulk alloy, the accepted explanation is the high value of the anisotropy [117]. In any case, it is very usual to find a lack of saturation magnetisation in nanogranular and magnetically disordered alloys [64, 80, 116, 118, 119, 120, 121, 122].

Another significant point is the existence of a kink around \( H = 20 \) kOe, not only in the milled alloy but also in bulk (marked with arrows in the figure), though in the latter the kink is much more pronounced and corresponds to the metamagnetic transition (spin-flip) of antiferromagnetic materials at a certain magnetic field as already has been observed in bulk TBCu₂ [102]. The definite outcome is that AFM is still present within the SG region \( (T < T_f) \). Moreover, there is also coercivity in the SG region \( (H_C = 260 \text{ Oe}, \text{see inset of Fig. 4.7}) \), a fact
Figure 4.6: Arrott plots for the 2h TbCu$_2$ milled sample. The Arrott plots display the typical feature of AFM systems: a bending of the lines starting at $T_N$.

which is observed in other SG systems [64, 65], such as in the reentrant antiferromagnet CO$_2$(OH)(PO$_4$), that shows $H_C \sim 50$ Oe [123].

A complementary study of the $M_{DC}(H)$ has been performed for $T < T_N$, as shown in Fig. 4.8, with magnetic fields up to 80 kOe. The aim of these measurements is to observe the coercivity dependence with temperature, as shown in the upper inset. It is important to take into account that in an ideal AFM system should not display any coercivity due to the nominal absence of conventional domains, as it is observed in our bulk TbCu$_2$ (see right inset of Fig. 4.7). The existence of AFM domain walls was predicted by Néel [124] in order to explain the magnetisation increase in several AFM compounds as a function of the applied field. In FM materials, the appearance of magnetic domains is favourable as magnetostatic energy is minimised; however, this does not happen with AFM domains. In fact, it is exactly the other way round; its appearance increases the energy system. These facts lead to the idea that there are not AFM domains in the sense of FM ones. Several authors tried to explain the existence of these AFM domains by: (i) considering an increase of the system entropy that could compensate the energy increase leading to a decrease of the Gibbs free energy (thermodynamic potential to be considered) [125] or (ii) considering that the system could be in a free
Figure 4.7: Magnetisation curves of TbCu$_2$ nanoparticles at $T = 5\, \text{K}$ (SG region) and $T = 150\, \text{K}$ (paramagnetic region) up to 90 kOe. Inset (left): Low field coercivity in the SG state. Inset (right): $M_{\text{DC}}(H)$ curve, at $T = 5\, \text{K}$, showing the metamagnetic transition of the bulk alloy. Both bulk and 2h alloys show the AF metamagnetic transition, marked with arrows.

The thermal variation of the coercivity $H_C(T)$ is very useful to evaluate the magnetic anisotropy. The latter is connected with the coupling of magnetic domains (in bulk alloys) and in the particular case of nanogranular materials, it gives magnificent information of the interparticle magnetic interplay [130]. It is well-known that two-phase magnetic nanomaterials can present peaks/dips in the $H_C(T)$ [131]. This is basically explained with the aid of the random anisotropy nanocrystalline model proposed by Herzer in 1991 [132].

In Fig. 4.8, the shape of the hysteresis loops is similar to those discussed in Fig. 4.7, and hence no further comments are required. However in the inset of Fig. 4.8, it is clearly appreciated the existence of a relatively small coercivity below $T_N$ which increases towards low temperatures ($H_C \approx 300\, \text{Oe}$ at $T = 5\, \text{K}$, as an indication). The $H_C(T)$ variation is then presented in the inset of Fig. 4.9. Although the ma-
Material is in an AFM state and should not present coercivity, it was reported that in some cases as in Tb$_{0.5}$Y$_{0.5}$Ni, due to a high anisotropy, narrow walls propagate resulting in some hysteresis [133]. However, here in our bulk TbCu$_2$ this is not found and what it is observed is that the size reduction triggers the onset of $H_C$. In essence, when the particle size is reduced there is a gradual increase of the coercivity [134]. However there is a critical size where there exists a crossover between multidomain to single-domain particles [84]. Our particle size is in the expected region in which our particles are single-domain [99], hence a minimal value for $H_C$. The presence of nearby particles can alter that simplified picture and the uncompensated spins (weakly ferromagnetic) of the AFM particles can act as a connection path for the magnetic interparticle interaction. This could modify the coercivity just taking into account the mentioned random anisotropy between two magnetic phases [132]; obviously it is highly dependent of the interparticle interfacial magnetic state: degree of crystallinity, shell thickness, sphericity, as main factors [27].

In nanogranular systems, it is a common feature to encounter a different atomic/magnetic arrangement in what it is worldwide known as core-shell structure. These two regions lead to some modification in the $H_C$ and in the hysteresis loop position. Fine particles were the
first type of systems where this shift was discovered [8]. The physical origin is the exchange anisotropy between (typically) adjacent FM and AFM layers. In fact, the phenomenon is usually studied in thin films. The most apparent macroscopic evidence is the mentioned loop shift and concommitant exchange bias (EB) [5, 26, 135]. Given that AFM particles are of nanometric size, it is expected a slight difference of the magnetic behaviour of the spins in the core and those at the surface. The surface shell may comprise a few magnetic layers of uncompensated spins. In spherical particles the shell thickness may vary around 0.6-1 nm [116, 136]. Very briefly, in a FC sequence there might appear a preferred orientation imposed by the anisotropy of the AFM. When the field is removed, the FM core suffers the field associated to the AFM resulting in the EB effect [26]. The actual measurement involves to apply the maximum possible $H$ above the $T_N$ of the AFM. Then, the sample is cooled down to the lowest temperature and the loop is recorded.

In order to elucidate the possible core-shell structure in our particles, we performed FC hysteresis loops. In Fig. 4.9 we show the hysteresis loops, at different temperatures ($T < T_N$) of the milled alloy with magnetic fields up to $H = 75$ kOe, after the field cooling
procedure. Then, to better understand the overall complementary behaviour of the coercive field $H_C(T)$ and the exchange bias (EB) $H_E(T)$ we show both of them together in the upper inset of Fig. 4.9. For this:

$$H_C = \frac{|H_{\text{left}}| + |H_{\text{right}}|}{2} \quad (4.2)$$

$$H_E = -(H_{\text{left}} + H_{\text{right}}) \quad (4.3)$$

The results depicted in Fig. 4.9 indicate the existence of a negative loop shift (see lower inset). The magnitude in 2h TbCu$_2$ is small as $H_C(T = 5K) \approx 300\text{Oe}$ and $H_E(T = 5K) \approx 30\text{Oe}$. For example, nanoparticles of Co-CoO display $H_E \approx 9500\text{Oe}$ [137, 27] and of Ni-NiO, $H_E \approx 9500\text{Oe}$ [138]. These are examples of FM metallic particles (core) with an AFM or ferrimagnetic (FiM) oxide (shell). Another archetypal example has been provided by $\gamma$-Fe$_2$O$_3$ ferromagnetic particles ($D \approx 10\text{nm}$) surrounded by a SG surface layer ($D \approx 0.6\text{nm}$) [116]. In that case, $H_C(T = 5K) \approx 2000\text{Oe}$ and $H_E(T = 5K) \approx 1500\text{Oe}$, much larger values than the ones reported for the present alloy. However, there also exist systems like Fe-Fe$_3$O$_4$ (FM-FiM) which present a small value of EB ($H_E = 120\text{Oe}$) [139]; in any case, one order of magnitude larger.

If one considers the existence of $H_E > 0$ and an increase of coercivity in AFM core particles (as in our case), this has been found in NiO [140, 141] nanoparticles, with an outstanding $H_E \approx 10\text{kOe}$. It was shown there that the exchange anisotropy could stem from a SG (shell) - AFM (core) coupling, behaving essentially as a two phase magnetic system. Precisely, the coexistence of those two very different magnetic arrangements also explains the $H_C \neq 0$ discussed above. It is worth to remind that both $T_N(\text{NiO}) = 523\text{K}$ and $T_B = 300\text{K}$ [135] are much larger than our characteristic temperatures ($T_N = 46.8\text{K}$ and $T_f \approx 10\text{K}$) supporting the large difference in $H_E$ values between their NiO and our TbCu$_2$.

Regarding pure metallic alloys, it is also feasible to bring in handy evidence for the data discussion. Effectively, it should be noted that it has been widely reported the existence of EB in SG of polycrystalline Ag$_{1-x}$Mn$_x$, with models which explain reasonably well the mechanism of anisotropy [142]. In amorphous SG it is also possible
to observe the effect; this was shown in reentrant (ferromagnetic) spin glasses of FeZr [64, 121, 143]. Moreover, it has also been published the case in which layer (bilayers) of FM-SG (Fe/NiMn) [144] or FiM-SG (NiFe₂O₄/amorphous NiFe₂O₄) [145] also give rise to the loop shift. In the latter cases the origin relies on the small amount of AFM rich regions coupled to the FM or FiM. The quantitative interpretation is again troublesome due to the low magnitude and the fact that not only the SG state gives rise to EB by itself but also in the bilayer combination. The small magnitude in our case is surely due to the relatively disordered interface provoking a minor number of uncompensated layers, reducing the overall output for the anisotropy and in consequence, reducing \( H_E \).

To end up the core/shell coupling debate, a final comment should be devoted to the increase of \( H_E(T) \) towards low temperature. In \( \gamma \)-Fe₂O₃ where there is an EB effect caused by surface spins, it was noted the existence of a two linear regime for \( H_E(T) \) [116]. In their case, there was an abrupt increase at (there labelled) \( T_{\text{crit}} \geq 30 \text{K} \). In \( 2h \) TbCu₂ the effect is still present with a much higher slope for \( T_{\text{crit}} \leq 15 \text{K} \) (see upper inset Fig. 4.9). This is due to the fact that \( H_E \) only exists while the spins on the surface of the particles are still frozen. The correlation between \( H_E \) and \( H_C \) was also underlined for the maghemite nanoparticles. Effectively, in the present work, there is an uprise in the \( H_C(T) \) below \( T_f \approx 10 \text{K} \) (see upper inset Fig. 4.9). This increase of \( H_C \) is due to the energy that is required to switch the spins, pinned by the frozen-in spin glass layers [108]. Care should be though taken into account as there are two factors altering the overall picture. The first one is that the \( H_E \) increase is observed slightly above the \( T_f \); such a finding is a result of the breadth of the particle size distribution (affecting the magnetic strength of the shell too). On the other hand, the lack of a clear kink at \( T_{\text{crit}} \) and possibly the low magnitude of \( H_E \) are a combined outcome of the existence of some interparticle magnetic coupling through the SG interface. The possible existence of this coupling is disclosed by the dynamics of the magnetic relaxation which is presented in the next section.

In consequence, the static magnetisation reflects the existence of an AFM order which becomes frozen in a reentrance process at low temperatures. This change of magnetic state is due to the presence of uncompensated and disordered spins at the particle shell.
AC-susceptibility

Figure 4.10: Real $\chi'(T)$ (top) and complex $\chi''(T)$ (bottom) components of the AC-susceptibility at several $f = \omega/2\pi$ ($h = 10^4$ Oe).

To investigate in detail the spin glass behaviour, we have measured the temperature dependence of AC-susceptibility, $\chi_{AC}(T)$, at different frequencies. The spin dynamics were studied using an oscillating field $h = 10^4$ Oe and the frequency was varied from $f = \omega/2\pi = 66$ Hz to 10 KHz (8 frequencies). In Fig. 4.10 the real $\chi'(T)$ and the complex $\chi''(T)$ components of the AC-susceptibility are plotted for several frequencies, as a function of the temperature. The shape of the real component $\chi'(T)$, related to the dispersion, is similar to the ZFC $M_{DC}(T)$. There is a main peak in 46.0(5) K marking $T_N$, practically frequency independent. As reported in [64], very high values of the frequency (from mega to gigaHz) are needed to observe a temperature shift in $T_N$. Another contribution is present at low temperatures, with a broad rounded peak which shifts to higher temperatures as fre-
4.3 Size Effect on the Magnetic Properties of Tbcu₂

Frequency is increased; its magnitude decreases with higher frequencies, corresponding to $T_f(\omega)$. This shift is commonly quantified as

$$
\delta = \frac{\Delta T_f}{T_f \Delta \log \omega}
$$

where $\delta$ is the relative shift per frequency decade. In this case, $\delta = 0.057(3)$, a larger value than that of individual spins in reentrant AFM CO₂(OH)(PO₄) where $\delta = 0.0024$ [123], but when particles are independent, i.e. an ideal superparamagnet, $\delta = 0.1 - 0.2$ is expected [146, 147]; clearly this is not our case. In ideal canonical SG, this value is much lower as the relaxation rate is much faster; for ferromagnets with reentrant state, $\delta = 0.01$ for crystalline Fe₁ₓAuₓ [148] and $\delta = 0.013(2)$ for amorphous (Fe₀.₂Ni₀.₈)₇₅P₁₆B₆Al₃ [149]. However, in some cases, the order of magnitude of $\delta$ in SGs is similar to that observed here, such as (EuSr)S ($\delta = 0.06$) [150].

In the case of $\chi^{\prime\prime}(T)$, the Néel transition is nearly absent as it is found in reentrant AFM systems [123]. This can be understood by the lack of energy absorption due to the absence of conventional domains and domain walls, if they were ferromagnets. However, the $T_f$ peak is clearly observable and, as in the real $\chi'(T)$ component, is frequency dependent. The existence of an imaginary component means that the relaxation processes are decoupling the spins from the lattice giving rise to the energy absorption.

It is mandatory to look for a critical slowing down behaviour, as it is widely reported in spin glasses or super spin glasses [151, 152] (see Eq. 2.13, in Fundamentals). The expression 2.13 is used to fit the low temperature peak of the AC-susceptibility as a function of $\tau_m$ (inverse of the frequency). Our analysis is summarised in the plot shown in Fig. 4.11 for the obtention of the most plausible $\tau_0$, $T_{f,0}$ and $z\nu$ dataset. Firstly we will concentrate on the behaviour of the relaxation times. In the inset of Fig. 4.11, the divergence of the relaxation time $\tau$ at the freezing temperature $T_f$ is included, with an increase starting up around $T_f = 14K$, slightly above $T_{f,0}$. Respect to $\tau_0$, the resulting value reveals a large $\tau_0 = 1.3(5)x10^{-5}$ s. For conventional SGs, $\tau_0 \sim 10^{-8} - 10^{-13}$ s [153], but the 2h TbCu₂ value is within the order of magnitude of other similar systems as interacting Fe-C nanoparticles ($D = 4.7$ nm) in which $\tau_0 = 10^{-6}$ s [61]. It is close to other (very different) reentrant FM-SG systems such as Heusler-based Ni₂Mn₁.₃₆Sm₀.₆₄ shape-memory alloys [154], cobaltite LaCo₀.₅Ni₀.₅O₃ [155] and pyrochlore molybdates $RE_2Mo_2O_7$ [156],
to cite a few. The fact that the present $\tau_0$ values are higher implies that the relaxation is slower and that the SG phase is constituted by randomly magnetised clusters, instead of atomic level randomness.

Figure 4.11: Critical slowing down for the TbCu$_2$ milled alloy. The inset is a plot showing the divergence of the relaxation time at the freezing temperature.

The result of the dynamic exponent $z\nu = 5.7(1.1)$ gives a low value in comparison to SG systems, but nonetheless can be included inside the SG regime, which spans $4 < z\nu < 11$ [157]. In fact, the upper limit of this range is even further away, as exposed in Ref. [158], with $z\nu < 13$. Let us discuss this issue in more detail: canonical SG Ag$_{99.5}$Mn$_{0.5}$, in metallic and crystalline state, behaves with $z\nu = 6.9(1.0)$ [157], whereas in a RSG (reentrant cluster glass) of amorphous Fe$_9$Zr$_9$, $z\nu = 7.2$ [159], considered two archetypal magnetically disordered alloys. It is evident that the $z\nu$ exponent is only partially indicative of the freezing as there is some scattered reported values. We remind here the nanoparticle state of our milled alloy, hence an extra comparison with similar nanostructures is convenient and immediately brings in the SSG state existence reviewed in the Fundamentals (see Chapter 2). Unfortunately, the literature data is very scarce for nanostructures; for instance, $z\nu = 8$ in $D = 9$ nm La$_{0.7}$Ca$_{0.3}$MnO$_3$ oxide [160], whereas $z\nu = 10.2(9)$ in Fe$_{30}$Ag$_{40}$W$_{30}$ metallic $D \lesssim 1$ nm particles. In interacting Fe-C ferrofluids $z\nu = 11.0(3)$ [61] which was interpreted as an example of collective magnetic dynamic with critical slowing down. To evaluate more efficiently the exponent values,
it is much more pertinent to observe trends in well-characterised systems. A revealing example has been reported recently for thin films of metallic Fe$_x$Ag$_{1-x}$. These comprise a collection of spherical nanoparticles embedded in a Ag matrix; in the very dilute limit ($x < 10$ at. %) there is a SSG state, which also includes dissolved Fe spins in the matrix [76]. Increasing $x$ there exists a disappearance of the matrix spins and the particles ($D \approx 3\text{nm}$) become more or less separated (interacting anyway) depending on the $x$-value. Precisely at $x = 35$ a manifest crossover between SSG and SFM behaviours is found [11, 77]. For $x = 24$, $z\nu = 8.3(6)$ (SSG); for $x = 35$, $z\nu = 4.7(4)$; and for $x = 39$, $z\nu = 4.3(3)$ (SFM). Such an exponent variation is confirming that the supermagnetic metal films are experiencing a progressive modification from disordered coupling to ferromagnetic exchange assured by inter-particle coupling. Effectively, $z\nu = 2$ in the mean field model, which is a value close to $x = 39$ (SFM). The above comparison concedes then that 2h TbCu$_2$ freezing transition is affected by the overall (within the particle) antiferromagnetic nature.

Another complementary test proof to ascertain whether the magnetic alloy is suffering a SG transition is to analyse the $\chi''(T, f)$ at several frequencies and extract another extra dynamic exponent $\beta$. It was reviewed and proposed that if there is a SG transition, a dynamic scaling would be found behaving as:

$$\chi''(\nu, T) = \epsilon^{\beta F(\nu \epsilon)^z\nu}$$

(4.5)

taking: $\epsilon = \frac{T_{\text{f}} - T_f}{T_f}$, $\beta$ is the critical exponent which establishes the variation of the order parameter $q$ (see Chapter 2), associated to the spin-spin autocorrelation function. In consequence, $\beta \rightarrow 0$ at $T_f$. Subsequently, we have performed a non-linear scaling analysis of the complete ensemble of $\chi''(T, f)$ data.

In Fig. 4.12 we are showing the result of the procedure. Its observation reveals that it is feasible to derive a good collapse (not excellent) onto a universal curve for $\beta = 0.70(5)$. This value is similar to other few examples of magnetically disordered compounds. One the one hand, if we take into account perfect crystalline alloys, some key examples in the literature include the crystalline (metallic) CeNi$_{1-x}$Cu$_x$, with $\beta = 0.70(5)$ [120]. The latter has been a paramount example of percolating clusters in a Cu-containing RE-alloy. Also, in shape memory polycrystals of Cu-Al-Mn, $\beta = 1.2$ [161] which is large in comparison to our result. On the other hand, the other structural arrangement is that constituted by amorphous reentrant CSG alloys. In this sense,
an archetypal example is the Fe-Zr based alloys for which $\beta = 0.7$ [159]. Finally, an intermediate structural case is that represented by Fe$_{30}$Ag$_{40}$W$_{30}$. These alloys were also milled and a similar analysis derived $\beta = 0.8(1)$ [162]. All these three previous examples have been interpreted in terms of interacting clusters becoming frozen below $T_f$ and following a critical slowing down. This is then irrespective of the structural (atomic) state. Our nanoparticles of TbCu$_2$, with a much more defined size than those clusters, follow the same process as above described. Computational simulation performed by a massive Monte Carlo method using $d=3$ Ising model, including positive and negative exchange coupling, results in $\beta = 0.5$ [163]. This value is slightly below our results. Calculations with a Heisenberg model in the disordered (ordered) cases give $\beta = 0.5$ [164] ($\beta = 0.36$ [165]), respectively. So, it turns out that the increase of disorder tends to become reflected in a larger $\beta$-exponent. In any case, in Section 4.4, where several TbCu$_2$ milled alloys are presented, it might be possible to find a trend for both $z\nu$ and $\beta$ dynamic exponents.

Figure 4.12: Dynamic scaling for the TbCu$_2$ milled alloy. All the frequency $f$-dependent AC-susceptibility curves collapse onto a master one for $\beta = 0.7$. 
4.3 Size effect on the magnetic properties of TbCu$_2$

4.3.3 Neutron diffraction

A microscopic magnetic structure analysis was performed at the Laboratoire Léon Brillouin (G4.1 instrument) in Saclay, Paris (France), using a wavelength $\lambda = 2.423$ Å. As it will be realised latter, the results are prominent for the final appraisal of the magnetic behaviour of nanometric TbCu$_2$.

Neutron diffraction (ND) spectra were taken at different temperatures: 1.8K and 10K ($T < T_f$), 25K and 36K ($T_f < T < T_N$) and 60K and 140K ($T > T_N$). The spectra were taken during 8 hours/temperature to get good stats, with a remarkable amount of nanometric sample of around 2 g.

The Rietveld refinement, from the nuclear contribution to ND (at $T = 140$K $> T_N, T_f$) is shown in Fig. 4.13. The lattice parameters are smaller than those for XRD at 300 K: $a = 4.3176(1)$Å, $b = 6.7842(9)$Å and $c = 7.2990(7)$Å. The size calculation yields similar particle size, $D_{\text{nuclear}} = 9(1)$nm, confirming the validity of our previous analyses, with $R_B = 10.2\%$. These refinements are performed simultaneously for the nuclear and magnetic contributions when $T < T_N$. In this sense, the calculation of the ND pattern at 1.8K was also performed and we obtained a $D_{\text{mag}} = 10(1)$nm, a very close value to $D_{\text{nuclear}}$, establishing that the magnetic structure is practically single-domain within the particle.

The magnetic structure (Fig. 4.15) corresponds to a commensurate AFM with two propagation vectors $\overrightarrow{q}_1 = (0,0,0)$ and $\overrightarrow{q}_2 = (1/3,0,0)$. Thus, the magnetic structure is not modified respect to that of the bulk alloy [103, 166]. The resulting ordered Tb$^{3+}$ magnetic moment, at 1.8K, is $\mu = 7.76(2)\mu_B$, with $R_{\text{mag}} = 4.2\%$ and $R_B = 1.1\%$. It is remarkable the very low errors in spite of dealing with a nanometric alloy. The fact can be considered relevant for a general use of ND to analyse magnetic nanoparticles. This highlight could only be achieved by the use of a large quantity of material thanks to the milling technique.

The thermal variation of the magnetic moment is presented in Fig. 4.16. There is a reduction ($\sim 78\%$) of the neutron magnetic intensity, at $T = 1.8$K, with respect to the (neutron) bulk, $\mu = 8.8\mu_B$ [103], what points to a disordered environment (spin canting), affected by
the decrease of surface coordination respect to the atoms within the particles. A rough estimation of the ratio of the surface atoms \( N_S \) respect to those in the total volume \( N_V \),

\[
N_S/N_V = (6a/D) \approx 40\%
\]  

indicating again the role of the surface spins and hence supporting the surface moment reduction. At this stage, it had not been realistic to study in detail the Brillouin curve for the thermal moment reduction due to the scarce number of (temperature) data points. In short, the AFM coupling is retained in single-domain particles, whose moment becomes reduced approaching the Néel transition.

Another matter for a productive discussion is the presence of a low angle tail for \( 2\theta < 15^\circ \). Effectively, the low-angle scattering increases with decreasing temperatures, as shown in Fig. 4.17, evidencing magnetic correlations with an interparticle length scale. The Q-range is reduced (\( 0.1\AA^{-1} < Q < 0.7\AA^{-1} \)) as it is only a part of the wide angle ND data. However, there are facts which determine the magnetic correlations among particles. Thus, there exists an increase of such low-angle contributions with decreasing temperature. Inset of
Figure 4.14: Magnetic and nuclear contributions for the milled TbCu$_2$ alloy (at $T = 1.8$K). Vertical marks correspond to the position of the allowed Bragg reflections for TbCu$_2$. Blue line corresponds to the difference between the observed (red dots) and the calculated (black line) intensity, by Rietveld refinement.

Fig. 4.17 shows beautifully that the integrated intensity grows below 20K. Such a result indicates that there is a magnetic connection among the particles, that should be taken into account for the overall interpretation of all the previously presented data. This global evaluation will be put forward over the next section.
Figure 4.15: The magnetic structure is antiferromagnetic (collinear) with large Tb atoms (blue) holding the magnetic moment (arrows) coinciding with that reported in bulk TbCu$_2$.

Figure 4.16: Thermal variation of the magnetic moment of Tb atoms. The line is just a guide for the eyes, resembling a Brillouin-like curve.
Figure 4.17: Low-angle magnetic contribution corresponding to the $0.1\text{Å}^{-1} < Q < 0.7\text{Å}^{-1}$ range. There is a marked increase of curvature pointing to the existence of interparticle magnetic correlations. Inset: Thermal variation of the integrated intensity for $Q < 0.7\text{Å}^{-1}$. 
Important remarks on the magnetic behaviour of nanocrystalline TbCu$_2$

Let us first summarise the main structural and magnetic findings described in former sections. Accordingly, we have produced a collection of TbCu$_2$ nanoparticles in which the CeCu$_2$-type crystal structure of the bulk alloy is maintained. In addition, the orthorhombic lattice parameters do not vary ($< 0.3\%$) respect to those of the unmilled alloy.

Rietveld refinements of the XRD for the milled sample provided a particle size $D_{\text{XRD}} = 9(1)\,\text{nm}$ and strain $\eta = 0.2(1)\%$. This particle size was further confirmed by TEM, where $D_{\text{TEM}} = 7(1)\,\text{nm}$. The electron microscopy revealed a random arrangement of the particle positions.

If we now interpret the magnetic evidence, it is necessary to start by stating that the milling of TbCu$_2$ produces an overall reentrant spin-glass state from an AFM coupling which is not present whatsoever in the bulk alloy (AFM with $T_N = 50\,\text{K}$ [13]). By contrast, the Néel temperature of the milled sample ($T_N = 46.0(5)\,\text{K}$) is slightly lower than that in bulk, as observed in the DC-susceptibility and there is a freezing temperature at $T_f = 9.2(2)\,\text{K}$. Throughout the critical slowing down fit of the AC-susceptibility curves, a freezing temperature $T_{f,0} = 9.65(11)\,\text{K}$ is obtained. The dynamic analysis of the freezing process reveals that a critical slowing down of the spin-spin correlation is taking place. The dynamic exponents lie in values close to disordered metals.

Our magnetisation data in the field cooled process was precise enough to disclose the existence of an exchange anisotropy coupling. This fact should be interpreted due to the interplay of the core AFM moments with disordered spins at the shell. The low values for $H_E$ and $H_C$ discussed in Section 4.3 point to the very likely interparticle coupling which decreases the exchange bias itself. Their variation with temperature, especially below $T_f$, confirms the importance of the particle shell.

We can now pinpoint the above magnetic macroscopic evidence with the ND results. The most clarifying facts acting in the single-domain AFM coupling decreasing towards $T_N$ can solely be interpreted by proposing that the 9 nm TbCu$_2$ alloy is constituted by a
set of AFM spherical nanoparticles with an intra AFM coupling surrounded by disordered spins on the surface. In other words, we have established a SAFM state coexisting with SG disorder. A simplified sketch is depicted in Fig. 4.18.

![Simplified sketch visualising the proposed overall spin nanostructure with the AFM core and the SG shell.](image)

As a result of this, this PM ↔ AFM ↔ SG phase constitutes a very attractive system to be studied as the majority of the reentrant SG transitions come from FM compounds (though there are a few AFM-SG examples, [110, 123] amongst others). As a matter of fact, the TbCu$_2$ constitutes a first example of this behaviour in metallic systems. In the following sections, we will undertake the task of searching for a sensible size variation of the alloys according to the milling time during the production of TbCu$_2$ nanoparticles.
4.4 Coexistence of SAFM and SG: Evolution with Particle Size

Here we are presenting an extended study of the evolution and dependence of, essentially, the magnetic properties on the particle size ($D$) of the milled TbCu$_2$ alloys.

As performed in the previous section, a structural characterisation via XRD is described and discussed initially. This includes synchrotron XRD data which have been obtained very recently in ALBA (Barcelona) for two alloys (milled for 2 and 5 hours). The latter patterns were recorded between 80K and RT, providing first results for the thermal expansion. The magnetic properties (static and dynamic) were carefully measured in a QD-PPMS multipurpose system and constitute the core of the discussion. Interestingly a study of the effect of the pressure on the DC-susceptibility of our milled alloys was performed in the SQUID as well. Finally, temperature dependent electrical resistivity $\rho(T)$ and specific heat $c_P(T)$ measurements are shown to confirm the metallic character and the AFM transition, respectively.

4.4.1 X-ray diffraction

The x-ray diffractograms (using either a Cu- ($\lambda = 1.5418$Å) or Mo-K$_{\alpha}$ ($\lambda = 0.7107$Å) radiations) of the unmilled and the seven milled samples ($0.5h \leqslant$ milling time ($t$) $\leqslant 15h$) are presented in Figs. 4.19 and 4.20, respectively.

A broadening of the peaks is observed as milling time increases; a sign witnessing that $D$ decreases with longer grindings [79, 167, 168]. Also, Fig. 4.19 shows that it is necessary very low milling times ($t < 1h$) to ensure nanometric particle sizes, in contrast to other very similar RE-intermetallic compounds, such as TbAl$_2$, where 300 hours were needed to reach $D = 14$ nm [80]. Here, for 0.5h particles sizes of $D = 23$nm are obtained (Rietveld analysis, see in the following text) due, probably, to the fragile nature of TbCu$_2$ [167]. A complete crystallographic summary is given in Table 4.1.

The visualisation of the XRD patterns of Fig. 4.19 indicates that it is only reasonable to determine the particle size for $t \leqslant 5h$, as for
The coexistence of SAFM and SG: evolution with particle size

Figure 4.19: X-ray diffraction (XRD) patterns (Cu-Kα) for bulk and milled TbCu₂ alloys. Peaks get broadened and display an intensity reduction as milling time increases. For 10 and 15 hours, an amorphous arrangement is evident around 2θ ≈ 30°. Spectra have been shifted up for clarity.

t > 5h the patterns show very broad peaks and a halo due to the amorphisation of TbCu₂ appears between 30° and 50°. To improve our experimental results, we decided to perform XRD with the Mo-Kα for those alloys milled for t ≥ 5h. However, as it can be observed in Table 4.1, for the 15h milled alloy, we obtain a higher value of the particle size than for 10h. This could be due to the fact that the particle size decrease has reached saturation, what is in good agreement with the tendency observed in Fig. 4.23.

A quantitative Rietveld refinement of the peaks was performed by using the FullProf Suite [88, 89] for every milled TbCu₂ alloy (Figs. 4.21 and 4.22), allowing to establish trends not only for the evolution of the mean size, $D_{XRD}$, and the maximum induced strain $\eta$ (Fig. 4.23), but also for the change of lattice parameters (see Table 4.1) with milling time at room temperature. Any amount of terbium oxide (Tb₂O₃, Tb₃O₇ [169, 170]) is below the detection limits (≲ 5%), without noticeable peaks in the patterns, especially under t ≤ 3h.

The Rietveld analysis of the diffractogram of the bulk alloy (Fig. 4.21(a)) is consistent with an orthorhombic CeCu₂-structure with unit
Figure 4.20: X-ray diffraction (XRD) patterns (Mo-K$_\alpha$) for 5, 10 and 15h milled TbCu$_2$ alloys. Clearer data is obtained with the Mo tube as Cu fluorescence is reduced although the resolution is decreased. Patterns have been shifted up for clarity.

cell parameters: $a = 4.3165(1)$Å, $b = 6.8323(3)$Å and $c = 7.3202(3)$Å. These cell parameters are in very good agreement with those found in other experimental works on bulk TbCu$_2$ [14, 98, 171]. The Rietveld refinements of the milled alloys are shown in Figs. 4.21(b)-(f) and 4.22. The evolution of the lattice parameters (Table 4.1) is not straightforward but there are indications that the volume increases around 1% for the 0.5h milled alloy. Subsequently there appears a progressive decrease towards the bulk values as it were occurring a lattice metallurgical relaxation. Although the change of the cell parameters with grinding time (Table 4.1) is less than 0.5% at a local range, it is true that the polycrystalline state is affected by the grinding. This is deduced by considering the increasing values for $\eta$, saturating around 0.7%. Such an increase is a typical result in milled alloys [15, 80, 168, 172] and is a basis to demonstrate that the atoms sitting at the particle shell become crystallographically disordered. In metallic nanoparticles, the obtained $\eta$ values range between 0.1 and 1%. For example, for hcp SmCo$_5$, $\eta = 0.1\%$ [173]; YbAl$_3$, $\eta = 0.4\%$ [15]; and TbAl$_2$, $\eta = 0.9\%$ [80]. With 3d-milled alloys, as FeCuAg, $\eta = 1\%$ [174]. Other results in spinel ZnFe$_2$O$_4$ oxides show a low (0.3%) $\eta$-value. In consequence the range is rather wide. The use of different atomic elements forming the alluded alloys/compounds makes diffic-
cult to provide a metallurgical/chemical support for each particular value; the ductility and fragility of the initial powders should be in the origin of the final strain value.

Regarding the size variation, the milling process results in nanometric particles, as discussed in Section 4.3 for TbCu$_2$ 2h and in previous works [14, 98]. The $D(t)$ and $\eta(t)$ behaviours are similar to that observed in other 4f- [80, 95] and 3d-Cu [175] based planetary-milled alloys, and the only most noticeable difference is, as it has been commented above, the reduced time required to achieve nanometric particle sizes. For example, 300 hours for 14 nm TbAl$_2$ [80], 120 hours for 21 nm GdAl$_2$ [95, 96, 97] and 20 hours for 18 nm YbAl$_3$ [15], while for TbCu$_2$ only 0.5h were necessary to reduce particle size down to 23nm.

It is clear to observe, in Fig. 4.23, that the $D(t)$ curve is saturated with grinding time ($t \gtrsim 5h$). This means that lower particle sizes can not be achieved even if we grind our samples for longer times. Moreover, in the case of the 15h milled alloy, a slightly higher value of the particle size was obtained, in comparison to the 10h milled one. This does not mean necessarily that particle size has increased, as the error in this calculation is around 0.5 nm. In short, TbCu$_2$ particles with $D \lesssim 6$ nm can not be obtained by planetary milling. In addition, it is clear that the XRD patterns become less defined for $t \gtrsim 5h$, hampering the interpretation of results. Indeed, this drawback has been taken into account for the description and evaluation of the magnetic and electronic properties avoiding an overinterpretation of the experimental evidences. Thus, in the next section, we will pay much more attention and focus our discussion on the $t \leq 5h$ alloys as they will provide an unambiguous picture for the size dependent properties.

Some final words should be expressed about the particle size definition. Thus, given the excellent agreement obtained for TbCu$_2$ 2h between the $D_{XRD}$ and $D_{TEM}$ (see Section 4.3), we have restricted ourselves to perform a simplified test just by using the TEM as a confirmation technique (with much lower statistics) for other milled alloys. In this sense, Fig. 4.24 gives a representative result for the size and morphology of the 10 and 15h samples. The particle size, as derived from those TEM images provide $\langle D_{TEM} \rangle = 6.1(7)$ nm for the 10h and $\langle D_{TEM} \rangle = 4.7(6)$ nm for the 15h. These values lie around the Rietveld particle size data.
<table>
<thead>
<tr>
<th>η (h)</th>
<th>ζ (D)</th>
<th>ν</th>
<th>c</th>
<th>d (nm)</th>
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Table 4. Orthorhombic cell parameters, a, b, and c, and strain in the particles at different milling times (η) obtained by Rietveld refinement with different XRD radiation (Cu- or Mo-Kα).
Summarising, we have found that the milling technique enables to produce a large mass of nanoparticle ensembles in which the size is fully controlled down to 6 nm, with a concomitant enlargement of the structural disorder reflected by the increased strain values. Additionally, there seems to exist a subtle crossover from these ensembles to other more disordered powders which include an incipient amorphous environment when $t \gtrsim 5h$. 
Figure 4.21: Rietveld refinement of the Cu-K$_{\alpha}$ XRD patterns of the bulk and milled TbCu$_2$ alloys (at $T = 300$ K). The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns. All the spectra were obtained after 18 hours. The long milled alloys are affected by a poorer efficiency of the Cu-radiation.
Figure 4.22: Rietveld refinement of the Mo-K\(\alpha\) XRD patterns of the milled TbCu\(_2\) alloys (at T = 300 K). The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns.
Figure 4.23: Size and strain particle for different milling times. Lines are just a guide for the eyes.

Figure 4.24: TEM images of the (a) 10 and the (b) 15 hours TbCu$_2$ milled alloys. The scale bar of both images correspond to 20 nm. In (a) nanoparticles are aggregated and display different shapes and sizes, c to (b), in which almost every nanoparticle seems to be spherical and to have very similar sizes, near to the 6nm calculated by XRD Rietveld refinement (see Table 4.1).
Synchrotron XRD was finally performed at ALBA Synchrotron Large Facility in Barcelona (Spain) for the 2 and the 5h milled alloys, using the MSPD (Materials Science and Powder Diffraction) instrument. The aim for this is to discard any noticeable contribution from other TbCu intermetallics [176]. As the data recording is relatively fast and temperature can be varied down to 80K, it enables the evaluation of eventual modifications of the metallurgical state of the nanometric TbCu2.

Figure 4.25: Rietveld refinement of the synchrotron XRD pattern of the 2h milled TbCu2 alloy (at T = 80 K). The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns. Bragg positions of the possible compositions (TbCu2, Tb2O3, TbCu6 and Tb) are marked in green.

An energy of 30 keV (i.e. a wavelength \( \lambda = 0.4126 \, \text{Å} \)) was employed in the experiment. An example of the high-quality patterns is shown in Fig. 4.25 for TbCu2 2h at T = 80K. The patterns were collected during 1h using approximately 50 mg of sample inside a borosilicate capillar. More than 98% of the integrated intensity is due to the presence of TbCu2. The minor peaks at 7.6\(^{\circ} \), 7.9\(^{\circ} \) and 8.35\(^{\circ} \) correspond to minute phases of Tb2O3, TbCu6 and pure Tb. Moreover, the particle size is in excellent good agreement with those (conventional XRD) reported in Table 4.1. Results of the Rietveld refinement of every pattern are displayed in Tables 4.2 and 4.3.
Table 4.2: Orthorhombic cell parameters $a$, $b$ and $c$ of the 2h milled alloy at different temperatures, obtained by Rietveld refinement, from results of XRD performed at MSPD instrument in ALBA synchrotron. Standard Bragg errors are denoted by $R_B$. The calculated particle size is $D = 8.8(5) \text{nm}$, in good agreement to that obtained by conventional XRD.

<table>
<thead>
<tr>
<th>T(K)</th>
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<th>$c$ (Å)</th>
<th>$R_B$ (%)</th>
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Table 4.3: Orthorhombic cell parameters $a$, $b$ and $c$ of the 5h milled alloy at different temperatures, obtained by Rietveld refinement, from results of XRD performed at MSPD instrument in ALBA synchrotron. Standard Bragg errors are denoted by $R_B$. The calculated particle size is $D = 6.4(5) \text{nm}$, in good agreement to that obtained by conventional XRD.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$R_B$ (%)</th>
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<td>7.3194(3)</td>
<td>3.5</td>
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</table>
In both Tables 4.2 and 4.3 we can observe a significant variation of the lattice parameters with temperature. This variation is plotted in Fig. 4.26, in which a linear dependence is observed, in agreement with a general result found in metallic systems close to room temperature. From the volume variation we can obtain the thermal expansion coefficient as:

\[
\alpha = \left( \frac{1}{V} \right)_{T=80\text{K}} \frac{\partial V}{\partial T} \tag{4.7}
\]

As volume dependence with temperature is linear, we can derive last equation in:

\[
\alpha = \left( \frac{1}{V} \right)_{T=80\text{K}} \frac{\Delta V}{\Delta T} \tag{4.8}
\]

From Eq. 4.8, we obtain thermal coefficients of \(\alpha = 5.1 \times 10^{-5} \text{K}^{-1}\) and \(\alpha = 3.78 \times 10^{-5} \text{K}^{-1}\) for the 2 and the 5 hours milled alloys, respectively. Values around \(10^{-5} \text{K}^{-1}\) are typical for either pure elements or alloys \[177\]. If we compare with those of other intermetallic compounds, such as orthorhombic TmCu₂ (\(\alpha \approx 8 \times 10^{-6} \text{K}^{-1}\) at \(T = 100\text{K}\) \[178\], binary DyAg (\(\alpha \approx 1.3 \times 10^{-5} \text{K}^{-1}\)) and HoAg (\(\alpha \approx 1.1 \times 10^{-5} \text{K}^{-1}\)) \[179\], amongst others, our data are slightly higher. Moreover, there is a previous report on the thermal expansion of TbCu₂ \[180\] in which they obtained a value \(\alpha \approx -5 \times 10^{-6} \text{K}^{-1}\) at \(T = 80\text{K}\), measured with the capacitance method (from 4.2 to 77K). No higher temperatures were studied in that work, but no linear behaviour was found for low temperatures. Our thermal expansion coefficient is positive in our 80-300K range while is negative at \(T = 80\text{K}\), according to Ref. \[180\]. It would be very interesting to study the thermal expansion of these nanometric alloys for temperatures down to 1.8K to ascertain if the change of sign is an intrinsic thermal expansion effect due to the nanoparticle size.

As a matter of fact, there should be expected three main contributions to the thermal expansion in a metallic and magnetic material: (i) the lattice (phonons), (ii) the conduction electrons and (iii) the magnetic ordering. At \(T > 80\text{K}\), it is obvious that (ii) and (iii) are negligible respect to atomic vibrations. In fact, the Grüneisen relation connects directly the specific heat to the thermal expansion by:

\[
\gamma = \frac{\beta V}{\chi S C_p} \tag{4.9}
\]
where $\gamma$ is the Grüneisen constant, $\beta = 3\alpha$, $\chi_S$ the adiabatically compressibility and $C_P$ the specific heat (at constant pressure). It has been shown that in nanocrystalline metals, a phonon softening of the specific heat is perceived (in Fe, Cu, Ni and LaAl$_2$ metals) \cite{181} as an excess of the $C_P$ contribution. The excess $C_P$ ($\Delta C$) appears as a peak around 50K and a slope increase above 150K. The latter slope increase has been theoretically interpreted appealing to the existence of an interface (several particle shells) forming the grain boundary \cite{182, 183}. This should be then considered for our higher value of the thermal expansion coefficient.

Figure 4.26: Linear cell volume variation with temperature for the 2 and 5 hours milled alloys, from data of Tables 4.2 and 4.3. Lines correspond to linear fits to extract the thermal expansion coefficients.
4.4.2 Magnetic characterisation

The magnetic characterisation of the 2h TbCu$_2$ provided an initial understanding of the SAFM state promoted by the size reduction. We will follow below the same methodology for the analysis of the rest of the TbCu$_2$-nano series.

4.4.2.1 DC-susceptibility

The zero field cooled (ZFC) curves of the DC-susceptibility ($M/H$) at a magnetic field of $H = 1000\text{Oe}$ shows the AFM transition around 50K which has been observed previously in Fig. 4.4 for the 2h TbCu$_2$. The magnitude of this peak becomes reduced in the alloys subjected to longer milling times. In particular, for $t = 15\text{h}$, the peak is nearly absent. By contrast, the decrease of particle size gives rise to an enhanced SG transition around 15K. Its magnitude follows the opposite tendency to that just described for the $T_N$ peak. In consequence, both transitions are clearly correlated between each other and the particle size.

Let us now focus on the surroundings of the SAFM peak transition. Above the transition temperature $T_N$, the samples are in a paramagnetic state, where they obey a Curie-Weiss behaviour (inset Fig. 4.27). The bulk sample has an effective moment of $10.04(1)\mu_B$ at 300K and a Curie-Weiss temperature $\theta_p=-7.22(15)$K (therefore, antiferromagnetic). However, when we grind our sample for up to 15 hours, the Curie-Weiss temperature increases up to $\theta_p=11.1(2)$K (hence, no longer only antiferromagnetic) and the effective moment remains more or less the same ($\mu = 9.92(1)\mu_B$, at 300K) (see inset of Fig. 4.27), close to the calculated effective moment ($9.72\mu_B$)$[82]$. This is pointing out a tendency to favour slowly a positive exchange coupling which effectively will be competing with $J_{AFM} < 0$.

The observation of Fig. 4.27 unveils the marked decrease of $T_N$ with decreasing particle size. This is better realised in Fig. 4.28; for $D \sim 7\text{nm}$, $\Delta T_N/T_N \approx -0.2$, which is an extremely large variation for the critical temperature. Effectively, in ferromagnetic TbAl$_2$ nanometric alloys, $\Delta T_C/T_C \approx -0.06$ (reaching there $D \approx 14\text{nm}$) which is an order of magnitude smaller, given in a very recent report $[99]$. The variation of the ordering temperature with size is still relatively controver-
Figure 4.27: ZFC curves (DC-susceptibility) for the bulk and the milled samples, at a magnetic field of 1000 Oe. The evolution from AFM to spin glass can be observed; for $t \geq 5$ h milled alloys, almost no AFM signal is found. Inset: Curie-Weiss fit of the high temperature range of the inverse of the DC-susceptibility of the 5 and 15 h TbCu$_2$ alloys.

In MnFe$_2$O$_4$ ferrimagnetic nanoscale particles, $\Delta T_C/T_C \approx 0.02$, thus the $T_C$ increased with decreasing size due to the interactions with the particle coating [184]. Later it was reported that manganese ferrite fine particle between 5 and 15 nm do display a $T_C(D)$ reduction relative to the bulk as size was decreased [185]. In particular, there are not many previous experimental reports as the ordering temperatures are frequently above room temperature and hence it is experimentally more demanding to obtain appropriate data. A very recent report in SiO$_2$-coated ultrafine magnetite Fe$_3$O$_4$ nanoparticles shows $\Delta T_C/T_C \approx -0.23$. Hence, it now seems clear that finite-size effects reduce the ordering temperature and the effect is drastic when $D \lesssim 10$ nm.

The drastic decrease of the ordering temperature is modelled by finite-size scaling theory predicting the following scaling law for $T_C(D)$ [186]:

$$\frac{T_C(D) - T_C(\infty)}{T_C(\infty)} = - \left( \frac{D}{D_0} \right)^{-1/\nu} \quad (4.10)$$
where $T_C(D)$ is the ordering temperature, $T_C(\infty)$ is the bulk alloy critical temperature, $\nu$ is the critical exponent and $D_0$ is a microscopic length scale connected to the lattice spacing. The fits to this expression have provided values in the literature, which are significant (especially) for the $\nu$ exponent. For the MnFe$_2$O$_4$ case, $\nu = 0.71(7)$ [184], somewhat influenced by interfacial effects, as mentioned earlier. Smaller manganese ferrite nanoparticles consistently give $\nu = 0.5(2)$ [185]. Monte Carlo simulations in ferrimagnetic $\gamma$-Fe$_2$O$_3$ (maghemite) with the spinel structure and allowing an AFM exchange of the nearest-neighbours of both sublattices have provided $\nu = 0.49(3)$ for particles with diameters from 2.5 to 8.3 nm [187, 188]. Another more recent value for the exponent in Fe$_3$O$_4$/SiO$_2$ nanoparticles procures a combination of experimental data and Monte Carlo calculations, giving $\nu = 0.82(2)$ [189]. We should remark that the three dimensional Heisenberg model predicts $\nu = 0.7048$ [190, 191]. For the metallic ferromagnetic nanoparticles of TbAl$_2$, $\nu = 0.70(4)$ [99], falling in the just mentioned theoretical value. A slightly larger $\nu = 0.77$ is found in Ni-nanowires which might be affected by the geometrical shape anisotropy [192].

Our results can also be analysed following the former procedure and are shown in the inset of Fig. 4.28. A non linear fit according to Eq. 4.10.
4.10 results in $T_N(\infty) = 49.8(4) K$, $D_0 = 2.15(6) \text{nm}$ and $\nu = 0.53(2)$. This corroborates that our nanometric TbCu$_2$ system follows a finite-size scaling law with reasonable parameters. The $\nu$-exponent is very near to the $\nu = 0.49$ predicted by Monte Carlo calculations with the mean field behaviour.

Turning our attention to the low temperature freezing temperature, Fig. 4.29 depicts the size evolution of $T_f$. There is a marked jump for $D \lesssim 7\text{nm}$ and $\Delta T_f/T_f \approx 0.28$, which is a remarkable variation. To investigate the possible size dependence, one can think of a power-law variation. For this, a log $T_f$ vs. log $D$ plot is presented in inset of Fig. 4.29. The slope of this variation provides the exponent for the law; here corresponds to $-1.27$. A pure $T_f \propto D^{-1}$ law would reflect a surface/volume direct correlation, as for example it is claimed for the anisotropy of an ideal superparamagnetic collection of nanoparticles [193]. Our value would indicate the need for another factor acting in the freezing process. A sensible ingredient explaining this is the increase of interfacial effects among the nanoparticles, provoking an enhancement of the magnetic spin disorder at the surface of the nearby particles. This reminds ourselves to the reduced $H_{EB}$ (exchange bias) shift discussed in Section 4.3.2, also supporting the former statement.

![Figure 4.29](image)

Figure 4.29: Spin-glass freezing temperature $T_f$ (blue) as function of particle size. Line is just a guide for the eye. Inset: scaling of the logarithm of the spin-glass freezing temperature respect to the logarithm of the particle size.
An evolution of the irreversibility region in ZFC-FC curves can be observed with increasing magnetic fields, as shown in Fig. 4.30 for the 0.5h milled TbCu$_2$ alloy exemplifying the general trend. The slope of every curve, below the freezing temperature, $T_f$, decreases, in absolute value, for higher magnetic fields (see inset(a) of Fig. 4.30). The range of fit (ROF) employed for the linear fits has been ROF = 5–10K. In addition, the variation of $\chi_{irr}(T)$ has been analysed in site-disordered Ni$_{75}$Al$_{25}$ to understand pinning processes in the irreversibility region. It was found the presence of a strong and weak irreversibility ranges giving rise to field-influenced $\chi_{irr}(T)$ peaks [194]. By contrast, in our case, there is a monotonic increase of $\chi_{irr}(T)$ towards the lowest temperature without any traces of irreversibility ranges, as just exposed.

Another evaluation of the irreversibility strength can be brought by using some results in the PbFe$_{0.5}$Nb$_{0.5}$O$_3$ ceramics. These are a recent paradigm of AFM and SG coexistence with $T_N = 143$K and a SG state at 27.6K [195]. In spite of the larger $T_N$, $T_f$ values compared to the ones in the nano-TbCu$_2$ in this work, the $\chi_{irr} \approx 10^{-5}$emu/gOe for PbFeNbO is two orders of magnitude smaller that the one for 3h TbCu$_2$, as typical examples, in which $\chi_{irr}(H = 10000Oe, T = 2K) \approx 10^{-3}$emu/gOe. This is indicating a very robust disordered spin state in our nanoparticles. The last piece of information is the field dependence of the irreversibility area. We define this as a simple integral, following: $A_{irr} = \int \chi_{irr}(T) dT$. Fig. 4.30 (inset b) shows a $\log A_{irr}$ vs. $\log H$ plot from which $A_{irr} \propto H^{-0.29}$ is deduced. This tendency has been far from being well-documented quantitatively and, unfortunately cannot be interpreted in detail. Nevertheless, it is an indication of the significant effect of the field to destroy the magnetic disorder of the interfacial spins of the nanoparticles.

The irreversibility is not only affected by the strength of the magnetic field but also by the application of external hydrostatic pressure ($P$). With the aim of disclosing the effect of $P$ in the characteristic temperatures and absolute values of $M(T)$, we have carried an study using a pressure cell mounted in the SQUID magnetometer (see Section 3).

The pressure dependence on the magnetisation for the 0.5h milled alloy can be observed in Fig. 4.31. Here, practically no changes are seen in the Néel transition temperature not only in the peak position but also in the proper magnitude of the static susceptibility
Figure 4.30: Irreversibility of ZFC-FC $M_{\text{DC}}$ curves for the 0.5h milled TbCu$_2$.
Inset (a): Variation of the slope of the curves in the range of fit ROF = 5 – 10K, for different magnetic fields. Inset (b): Logarithmic scale of the area $A_{\text{irr}}$ below the irreversibility curves (for different magnetic fields) with the logarithm of the magnetic field.

$M(H,T)$. For this milling time, there is only a slight sign of the SG behaviour, hampering a precise determination of $T_f$, as it was explained above. Hence, the pressure influence is negligible. By contrast, in the case of the 2 hours milled alloy (whose magnetic properties were explained in the Section 4.3), there are slight differences between the unpressed and the pressed samples, as shown in Fig. 4.32, for a magnetic field $H = 1000\text{Oe}$. The Néel temperature suffers a minor increase ($\frac{\delta T_N}{\delta P} \approx 0.01\text{K kbar}^{-1}$) which is much smaller than that reported for high pressure measurements in bulk TbCu$_2$ [180]. In this, it was found $\frac{\delta T_N}{\delta P} = -0.1 \pm 0.1\text{K kbar}^{-1}$ which is not very precise. Unfortunately, here there is no further information on $\frac{\delta T_N}{\delta P}$ for nanometric rare-earth alloys. Regarding the freezing process, it is much more clear the shift of $T_f(P)$ to lower temperatures. Fig. 4.33 shows the peaks displacement which, assuming a linear behaviour, yields $\frac{\delta T_f}{\delta P} = -0.07\text{K kbar}^{-1}$, which represents $\Delta T_f = -5.4 \pm 1.7\%$. This variation supports our interpretation as the pressure helps to hold the ordered antiferromagnetic state respect to the SG state, as occurs with increasing magnetic fields.
The variation of the Néel temperature is shown in the inset.

The response of the magnetisation to an applied field at different temperatures is discussed in the following. The Arrott plots of the isothermal magnetisation are shown in the lower inset of Fig. 4.34 for
the 1h TbCu$_2$ alloy in order to compare with the 2h TbCu$_2$ presented earlier. Again, it is easy to convey that the response follows an AFM behaviour with the special low $H/M$ bending although, naturally in this case, the line marking the $T_N$ sits around 48K, confirming the $M_{DC}(T)$ data.

In Fig. 4.34, the general $M_{DC}(H)$ behaviour of the TbCu$_2$ nanoparticles is examined. The data have been recorded up to 80 kOe. On the one hand, the metamagnetic transition present in the bulk alloy [117] is progressively reduced with the milling, being wiped out for $t \geq 3h$. Secondly, the magnetisation value follows two tendencies: for $t < 3h$, the $M(H = 80kOe)$ becomes reduced, but then for the longer milling time alloys, the magnetisation tends to recover a larger value reaching somewhat a saturation around $M = 5\mu_B/Tb$. The lack of saturation deserves the same comments posed in the previous section, which are: firstly there is an intrinsic high anisotropy in the bulk alloy and, secondly, it is a common finding in magnetically disordered materials (including magnetic nanoparticles) as a consequence of a surface spin canting [64, 80, 116, 118, 119, 120, 121, 122].

To end up with the overall analysis of the static magnetisation, an appraisal of the $H_{C}(D)$ should be commented. It was mentioned that
conventional AFM compounds should not display coercivity. Hence, in disordered systems, the competing AFM/FM interactions when passing across the freezing transition result in an intrinsic increase of the anisotropy and consequently of $H_C$ [64]. In the upper inset of Fig. 4.34, the $H_C(D)$ is represented thanks to our handful number of samples. The tendency is pristine with an increase of $H_C$ when reducing the particle size, reinforcing the fact that the coercivity found here is only due to a size reduction effect, independently of the intrinsic high anisotropy of the bulk TbCu$_2$ [117]. This fact can be understood by the relative higher contribution from a disordered shell which is randomised respect to the particle core and hence promoting a higher value of the anisotropy $K$. In superparamagnetic ideal systems, the value of $K$ is always found to be size dependent. For example, in weak ferromagnetic nanoparticles of hematite ($\alpha$-Fe$_2$O$_3$) with sizes between 6 and 27 nm, it has been reported an order of magnitude increase of the anisotropy reaching $K \approx 2.4 \times 10^4$ J/m$^3$ ($D \approx 6$ nm) [196]. A similar tendency has been revealed in metallic nanoparticles of Co sequentially sputtered in Al$_2$O$_3$. In such a case, the $K$ increase when $D$ diminishes is also quantified but an additional ingredient is included stemming from the interactions between moments in adjacent layers [193]. In short, there is an increase of the effective anisotropy (including the bulk and the surface contributions). This effect is reinforced in purely metallic nanoparticle systems (FeCuAg) in which Fe(Cu)-nanoparticles are embedded in a diamagnetic matrix of Ag. There, it was possible to establish the contribution to the anisotropy by the magnetic dipolar interaction with $K_{int} \approx 3 \times 10^5$ J/m$^3$. This system can be considered as a weak SSG in the sense that nanoparticles presented a correlated blocking temperature [62].

In AFM nanoparticles the interparticle interaction, due to dipolar coupling, is minimised and there appears a very weak ferromagnetic component due to sublattice mismatch. The interparticle interaction can be estimated as an effective temperature shifting up of the blocking temperature. In this context, the dipolar temperature $T_{dip}$ can be calculated with [115]:

$$T_{dip} \approx \frac{\mu_0}{4\pi k_B} \frac{\mu^2}{d^3}$$  (4.11)

in which $\mu$ is the average magnetic moment and $d$ is the average distance between the particles. In well-studied ferritine, the estimations for $T_{dip}$ give a tiny contribution, below 1 K. It is straightforward to consider a minor correction the dipolar interactions. Thus, as a result,
the increase of the magnetic disordered layer should be the major responsible for the increase of \( H_C \) with decreasing \( D \), observed here. Precisely, that disordered layer was causing the exchange bias effect (and the \( H_C \) increase due to this anisotropy) commented previously (see Section 4.3.2.1).

Figure 4.34: Field dependence of the isothermal magnetisation of TbCu\(_2\) milled alloys at \( T=5K \). Upper inset: coercive field dependence on the particle size for milling times \( t \leq 10h \). Lower inset: Arrott plots for the 1h milled alloy.

The static magnetisation discussion above performed lends to a physical situation in which the size reduction of the particles is a very strong driving force for the apparition of a magnetically disordered interface. Let us analyse comprehensively the dynamics of the shell and core spin of the particles presented in the following section.

4.4.2.2 AC-susceptibility

The spin dynamics are studied in a QD-PPMS magnetometer using a oscillating field \( h = 1 \) Oe, thanks to the considerable signal of the TbCu\(_2\) (\( \approx 40mg \)) samples. The frequency \( f \) was varied between 66 Hz and 10 KHz. In Figs. 4.35 - 4.39, the real- (\( \chi'(T) \)) and complex- (\( \chi''(T) \)) components of the AC-susceptibility for the 1, 3, 5, 10 and 15 hours milled TbCu\(_2\) alloys are plotted for several frequencies, as a function of the temperature. Whenever necessary, previously commented data
of 2h TbCu$_2$ alloy will be inserted in Tables and/or Figures in order to complete the series.

![Graph](image)

Figure 4.35: In-phase ($\chi'$) and out-phase ($\chi''$) components of the AC-susceptibility for different frequencies, for the 1h TbCu$_2$ milled alloy ($D = 13.5\text{nm}$).

The shape of the $\chi'(T)$ curves is similar to that observed in DC-susceptibility (ZFC curves): an AFM transition that disappears with milling, leading to a SG behaviour at low temperatures, reinforced as particle size is lowered (Fig. 4.40). Moreover, these two transition temperatures shift (i) to lower temperatures in the case of $T_N$ (with an almost negligible change) and (ii) to higher temperatures in the case of $T_f$, with increasing frequencies. Moreover, the latter peak in $\chi'(T)$ at $T_f$ decreases in magnitude with higher frequencies. In the case of $\chi''(T)$, for $t \geq 3h$, the Néel transition is nearly absent, marking that AFM is disappearing favouring an overall spin-glass state within the alloy, while the low $T_f$ peak is clearly observable showing, as for $\chi'(T)$, a positive $f$-shift.

The AC-susceptibility measurements (see Fig. 4.40) confirm the displacement of $T_N$ to lower temperatures and $T_f$ to higher temperatures with increasing milling times, which was observed and thoroughly discussed using the $M_{DC}(H, T)$. Besides, a seminal report in GdAl$_2$ [95] also finds a similar displacement in a member of the RX$_2$ family.

It has also been reported that when the TbCu$_2$ is subjected to extremely long milling times (120h), there exists a major disordered state [14]. However, the crystallographic structure is so glassy (diffi-
cult to reveal in comparison to well-crystallised nanoparticles) that it cast doubts for a quantitative assessment as the one intended here. In our nano-TbCu$_2$, as milling time increases, a hump appears, only visible in the $\chi''(T)$ (Fig. 4.40), for $t \geq 5h$ at around $T \approx 25K$. This weak contribution is not visible either in DC-susceptibility, as it can be observed in Fig. 4.27. Despite the commented structural fact that for the $t = 5, 10, 15h$ samples the XRD data become less and less undefined (see Section 4.4.1 and Fig. 4.19), it is attractive to propose a cautious interpretation for the observed shoulder; the Néel temperature is practically absent, meaning that the AFM-coupled particles are being, somehow, solved in the metallic (magnetically disordered) environment. In this situation, it is plausible that the now clustered, rather than nanoparticle, state triggers the uprise of FM-coupled moments. This would give rise to an energy absorption and thus the mentioned shoulder. Precisely, we remind the reader that $\theta_P > 0$ for $t = 15h$ in the Curie-Weiss analysis, commented in Section 4.4.2.1, which also is backing up the plausible FM-coupling. It is worth noting that when the structural arrangement is very disordered, the evaluation of the magnetic arrangements become very often qualitative, as found in milled TbFe$_{1.5}$Al$_{0.5}$ [197]. This is also similar to the case of nanometric GdAl$_2$ [198], where the structural analysis required the use of atomic pair (radial) distribution functions (XRD data), typically applied in glassy metals [199, 200].
In the following we are proceeding to explain a quantitative analysis of the spin dynamics with the aid of the AC-susceptibility data at hand. A fast (and simple) evaluation is to calculate the freezing temperature shift with frequency. This is commonly carried out by using the $\delta$-shift parameter, as:

$$\delta = \frac{\Delta T_f}{T_f \Delta \log \omega} \Rightarrow \log \omega = \frac{1}{\delta} \ln T_f + \text{constant} \quad (4.12)$$

where $\omega = 2\pi f$. If the magnetic interparticle interactions are absent (or negligible), the spin particle rotation under the uniaxial anisotropy is understood by a thermal activation process, following the well-known Arrhenius-Néel law. From Eq. 4.12 it follows:

$$\delta = \frac{1}{\ln(\omega \tau_0)} \frac{\partial \ln(\omega \tau_0)}{\partial \log \nu} = -\frac{\ln 10}{\ln(\omega \tau_0)} \quad (4.13)$$

and for a typical $\chi_{AC}$ measurement ($f = 10$-10000 Hz) in a non-interacting system ($\tau_0 \approx 10^{-9}$s), $\delta = 0.13 - 0.24$, as commonly accepted [146]. Whenever a reduction of such $\delta$-values is found, the nanoparticles become magnetically correlated and, in the limit, a cluster glass behaviour should control the spin divergence at the “critical” temperature. Finally, the $\delta$-shift is practically inexistent in canonical SG involving the freezing of individual spins ($\delta = 0.0045$ for AuMn or $\delta = 0.006$ for AgMn) [64, 147, 201] and negligible in phase transitions ($T_C$, $T_N$).
Figure 4.38: In-phase ($\chi'$) and out-phase ($\chi''$) components of the AC-susceptibility for different frequencies, for the 10h TbCu$_2$ milled alloy ($D = 5.6$ nm).

The $\delta$-values obtained from the fit to Eq. 4.12 for every milled alloy are displayed in Table 4.4. In our particular case, $\delta = 0.02 - 0.06$ for the different milled alloys, higher than spin glasses ($\delta = 0.01$ for the archetypal FeAu spin glass [148]) but lower than cluster glasses (Fe$_9$Zr$_9$, $\delta = 0.066$ [159]) and in the order of magnitude of CMR manganite La$_{1-x}$Sr$_x$MnO$_3$ ($\delta = 0.04$) [202]. As the nano-TbCu$_2$ $\delta$-values are higher than those for ideal SGs, the magnetic spin relaxation is expected to take place at a slower rate. The comparison with AFM-SG Co$_2$(OH)(PO$_4$) is productive; for the latter $\delta = 0.0024$ [123], radically smaller than our values. The phosphate compounds constitute a case example where individual spins adopt a glassy disposition below $T_f$.

The supporting physics is based on crucial (and precise) angular values for the exchange pathways between Co and O atoms.

Whenever a $\delta$-value satisfying the CSG-SG regime is found, the present scientific consensus leads to a mandatory critical slowing down analysis. With this, values for the critical exponents, usually $\nu$ and $\beta$, are extracted according to Eqs. 2.13 and 4.5, respectively. The methodology will follow that adopted in the previous section with a single sample, logically expanded now with the just described alloy series. Firstly we start checking out the divergent spin correlation at $T_f$ by fitting data to Eq. 2.13.
The parameters obtained from the fit of the data (Fig. 4.41) for every milled alloy are shown in Table 4.4, together with the 2h milled alloy result. The value of $\tau_0$ for lower milling times ($t < 5$h) is higher than expected for SGs, whereas for milling times $t \geq 5$h typical values of $\tau_0$ for SGs are achieved, with $\tau_0 \sim 10^{-8} - 10^{-13}$s [64]. The $t < 5$h large values of $\tau_0$ are related to the fact that our systems follow a relaxation rate of the nanoparticles slightly slower than in conventional SGs, as already explained in the former description. Indeed, the high $\tau_0$ for $t = 2, 3, 5$h has already been observed in FeC interacting nanoparticle ferrofluids ($\tau_0 \sim 10^{-6}$s) [203]. Moreover, as it was mentioned in the Fundamentals (Chapter 2), those interacting (collective) relaxations are very close to CSG systems which in turn also relax with an augmented $\tau_0$, such as in Heusler alloys [154], LaCo$_{0.5}$Ni$_{0.5}$O$_3$ [155] and pyrochlore molybdates [156], to cite a few.

The eventual modification of $\tau_0$ with the magnetic interactions among nanoparticles is unfortunately not considered commonly. It was proposed that $\tau_0$ is slightly temperature influenced and also dependent on the reduced damping constant $\eta_r$ associated to the flipping rate [204]. A recommendable analysis to study was reported by Dormann et al. in 1996 [60] using wonderful maghemite $\gamma$-Fe$_2$O$_3$ particles with different interparticle distances (and hence interaction strengths). It was observed that the $\eta_r$ increased when the particles were situated close by; the main outcome is a huge (6-fold orders
Figure 4.40: In-phase ($\chi'$) and out-phase ($\chi''$) components of the AC-susceptibility for different milling times, for a frequency of 1000 Hz ($h = 1$ Oe). As milling time increases, AFM disappears favouring a SG arrangement; but when $t \sim 10$ h a new phase at around $T = 25K$ begin to appear.

of magnitude) enlargement of the timescale value. A further analysis within the former report also grasped the analytical expression of another model, which taking into account the existence of interactions, provides a modified expression for the SPM energy barrier [147]. In short, there was a tendency of $\tau_0$ to increase with interactions. In this sense, the very recent published results for archetypal SSG, with stronger interactions, beautifully fit in that $\tau_0$ tendency; in [Co$_{80}$Fe$_{20}$/Al$_2$O$_3$]$_{10}$ multilayers, $\tau_0 \approx 10^{-6}$ s [152]. The value also lies close to our finding for $t \leq 3$ h. The $\tau_0$s for the $t \geq 5$ h alloys are, by contrast, close to those for the relaxation of conventional SG, for which it is universally accepted a $\tau_0 \approx 10^{-13}$ s [205]. Moving on towards the announced discussion of combined $z\nu$ and $\beta$ exponents, the results in Table 4.4 indicate that the $z\nu$ values are within the range of conventional SGs, $z\nu = 4 - 13$ [12, 77, 149, 158]. In addition to this fact, Fig. 4.42 depicts the collapsing curves of the $\beta$-dynamic scaling of the complex component following Eq. 4.5. The observation of such figures show that the scaling is improved for the $t = 5$ h sample ($\beta = 0.85$). We are now in an ideal situation to promote a general picture which governs the criticality at the freezing transition. In Fig. 4.43, we have plotted a wide and comprehen-
Figure 4.41: Critical slowing down for several milled TbCu$_2$ alloys. Key parameters for the fit are explicitly shown in the plots.

Stereoscopic selection of magnetically disordered materials which display a freezing behaviour at low temperatures. The choice of the materials looks for a representative character: they vary from the structural point of view, including amorphous alloys (i.e. Fe$_{91}$Zr$_9$ [159]) and insulators ((MnF$_2$)$_{0.65}$(BaF$_2$)$_{0.15}$(NaPO$_3$)$_{0.20}$ [206]), quasi-amorphous (Fe$_{30}$Ag$_{40}$W$_{30}$) [162], well defined nanoparticles (Fe-C [61]), multilayers (Co$_{80}$Fe$_{20}$/Al$_2$O$_3$ [207]) and finally perfectly crystalline oxides (LaPb(Mn,Fe)O$_3$ [208], LaCaMnO$_3$ [160]) and metals (CeNi$_{0.5}$Cu$_{0.5}$ [120], U$_{1-x}$Y$_x$Pd$_3$ [209], Ag-Mn [210], Fe$_{70}$Al$_{30}$ [211], Cu-Mn [212], Al$_{24}$Cu$_{70}$Mn$_6$ [161]). All these materials present a distinct irreversibility. Bearing in mind the definition of the nature of the SG transition proposed in the referenced works, we are putting forward some boundaries which will be helpful to understand the global behaviour. These are the (green) lines marking the regions for SG, CSG and SSG states. The reader can be tempted to consider these as perfectly defined regions; we dare not to fall in this idea. It is crystal clear that the disordered magnetism is a continuous change of the magnetic spin correlation coupling, preventing the existence of defined limits. This aspect is not new and it has also been thoroughly discussed in atomic disordered materials (glasses) for decades from the structural standpoint. In these, it is always underlying the continuity aspect which
allowed to progressively alter the amorphous arrangement with the inclusion, for example in glassy metals, of different proportions of metalloids and polymers [200, 213]. In summary, as a matter of fact, both magnetic and structural disorders lie in an attractive structural or magnetic universality [213].

Once the general $\beta$, $\nu$ landscape is realised, it is possible to evaluate the tendency found in nano-TbCu$_2$. In this sense, by reducing $D$, both $\beta$ and $\nu$ gradually increase and approach a range close to CSG. This fact can be understood by simply seizing the evidences exposed for the $M$DC static analysis. Effectively, the size reduction results in an expected increase of the influence of surface spins, thereby tending to relax at rates close to CSG due to the fact that they became part of an interfacial boundary of the relatively close particles. Hence, there is a coherent evidence from both the static and dynamic analyses.

Table 4.4: Parameter values of $\delta$, $\tau_0$, $\nu$ and $T_0$ for different milling times $t(h)$, calculated using Eqs. 4.12 and 2.13.

<table>
<thead>
<tr>
<th>$t$(h)</th>
<th>D (nm)</th>
<th>$\delta$</th>
<th>$\tau_0$ (s)</th>
<th>$\nu$</th>
<th>$T_{f,0}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>8.3</td>
<td>0.056(3)</td>
<td>1.3(5)x10$^{-5}$</td>
<td>5.7(3)</td>
<td>9.65(11)</td>
</tr>
<tr>
<td>3</td>
<td>7.3</td>
<td>0.044(2)</td>
<td>2.1(5)x10$^{-6}$</td>
<td>6.0(7)</td>
<td>10.4(3)</td>
</tr>
<tr>
<td>5</td>
<td>6.3</td>
<td>0.025(1)</td>
<td>2.5(5)x10$^{-8}$</td>
<td>6.6(9)</td>
<td>14.4(5)</td>
</tr>
<tr>
<td>10</td>
<td>5.6</td>
<td>0.056(2)</td>
<td>1.13(6)x10$^{-10}$</td>
<td>6.8(1)</td>
<td>15.1(1)</td>
</tr>
<tr>
<td>15</td>
<td>6.2</td>
<td>0.055(3)</td>
<td>9.4(7)x10$^{-13}$</td>
<td>7.4(1)</td>
<td>15.3(1)</td>
</tr>
</tbody>
</table>

Another dynamic aspect that may render valuable information are the Argand diagrams ($\chi''$ vs. $\chi'$ at a certain temperature), which are related to the energy barrier distribution. If single-relaxation processes are followed by the flipping spins, the complex susceptibility is described by the Casimir-du Pré equation:

$$\chi_{C-duP} = \chi(\infty) + \frac{\chi(0) - \chi(\infty)}{1 - i\omega\tau}$$

This is an analogous expression to the ones shown for dielectrics where $\epsilon'(\omega)$, $\epsilon''(\omega)$ are the parallel parameters. The expression for the case of dielectrics stems from considering the relaxation under the Debye model which, in its more facile interpretation, considers dipolar solids with configurational transitions and an oscillating electric field.
Figure 4.42: Critical slowing down analysis of the imaginary part of the AC-susceptibility $\chi''_{AC}$ data at $T < T_f$ for the 3 and 5h milled TbCu$_2$ alloys. These collapse on a master curve with $\beta = 0.75$ and 0.85, for the 3 and 5h alloys, respectively.
In the case of a SPM system, a half-circle is usually found when plotting $\chi''$ vs. $\chi'$ for the different frequencies [12]. If Argand diagrams for different temperatures collapse all into a single curve, it means that the energy barrier is independent of the temperature. Deviations from the half-circle would serve as an estimation for the energy distribution caused by the size distribution or by the dipole-dipole interaction [214], although the required range of frequencies is demanded experimentally (covering several decades).

However, for the supermagnetic systems, it has been proposed that the semicircle should appear modified as a consequence of the inter-particle couplings. In that situation, Argand representation, including a distribution of relaxation times (Cole-Cole approach), can exhibit the fingerprints of several dynamic modes [12] of domain walls: relaxation (R), creep (C), slide (SL) and switching (SW) (see Fig. 4.44). The supporting assumption for this is the necessary coupling among the nanoparticles which are then resembling the conventional domains in a ferromagnet. Very recently, the Argand plots for superferromagnetic (SFM) [CoFe(1.4 nm)/Al$_2$O$_3$(3 nm)]$_{10}$ [215] provided an experi-

Figure 4.43: General overview of several compounds depending on their critical exponents $z\nu$ and $\beta$. Data have been taken from: (Fe$_{91}$Zr$_{9}$) [159], ((MnF$_2$)$_{0.65}$(BaF$_2$)$_{0.15}$(NaPO$_3$)$_{0.2}$) [206], (Fe$_{30}$Ag$_{40}$W$_{30}$) [162], (Fe-C) [61], (Co$_{80}$Fe$_{20}$/Al$_2$O$_3$) [207], (LaPb(Mn,Fe)O$_3$) [208], (LaCaMnO$_3$) [160], (CeNi$_{0.3}$Cu$_{0.5}$) [120], (UYp$_3$) [209], (Ag-Mn) [210], (Fe$_{70}$Al$_{30}$) [211], (Cu-Mn) [212] and (Al$_{24}$Cu$_{70}$Mn$_{6}$) [161].
Figure 4.44: The four dynamical domain walls modes present, relaxation (R), creep (C), slide (SL) and switching (SW), taken from [12].

In Fig. 4.44 we show the $\chi''$ vs. $\chi'$ plot of the milled alloys. The Argand diagrams of the milled alloys ($t < 5h$) do not show a perfect half-circle (as in a SPM), as already seen in another nanoparticle systems [214]; these have only been reported in bottom-up $\text{Mn}_{12}$ and $\text{Fe}_8$ molecular single crystals [217, 218, 219]. In our case, although it has not been possible to obtain the complete half-circle, we do observe that there exists a maximum of every Cole-Cole plot. In SG systems it has also been claimed that a broad distribution of relaxation times causes a flattening of the curves [64]. This seems to be the case in our nano-$\text{TbCu}_2$ but a deep quantitative analysis is at risk due to the lack of precisely defined very high frequency data (left peak branch). In any case, by inspection of the low-frequencies (right branch) range, the width of the distribution taken from the $\chi''$ maximum value is slightly larger ($\approx 0.2 \times 10^{-3}\text{emu/gOe}$) for $t = 3h$ than for $t = 2h$ ($\approx 0.15 \times 10^{-3}\text{emu/gOe}$). This is indicating the enhancement of the SG region in that alloy. Thereby, again the fine traces of SG freezing are evident in our data.

Summarising the dynamics of the nano-$\text{TbCu}_2$ alloys, we have encountered a Néel transition without energy absorption and independent of the applied frequencies. At lower temperatures there exists a freezing transition whose dynamics are governed by a critical slowing down. The $z\nu$ and $\beta$ exponents evolve from a SG character to
values close to CSG systems with decreasing particle size as the surface shell becomes more and more important, favouring the interfacial influence. The distribution of relaxing times as deduced from the Argand plots also points to the same conclusion.
4.4.3 Specific heat

The specific heat is a common tool to evaluate the electronic, phononic and, eventually, magnetic contributions in a compound. In rare-earth alloys it has been proven to provide valuable information about the origin of the magnetic transitions [220, 221]. In Fig. 4.46 the specific heat of the 2h TbCu$_2$ is shown in the low temperature region, up to 100K, covering the main interval of interest, as a representative example of the general behaviour. The $C_p(T)$ displays an increase with increasing temperature due to electronic (band conduction) and phonon contributions. On top of both of them, the magnetic part is revealed visually by a smooth peak at around $\sim 50$K. This marks the cooperative Néel transition, revealed in the magnetisation results. In the inset of Fig. 4.46, there is an enlarged scale plot around $T_N$ for different magnetic fields. The application of $H = 9$T broadens markedly the $T_N$ peak; this fact is expected for a magnetic transition. The field-evolution is thus affected by the metamagnetic transition (spin-flip) in ordinary AFM.

$$C_p = C_{p,\text{ele}} + C_{p,\text{ph}} + C_{p,\text{mag}}$$ (4.15)

Figure 4.46: Specific heat of the 2h TbCu$_2$ milled alloy. Inset: magnetic field dependence of the specific heat, in the region corresponding to the antiferromagnetic transition.
where $C_{p,\text{ele}}$ is the conduction band electronic contribution, $C_{p,\text{ph}}$ the phononic contribution to the lattice and $C_{p,\text{mag}}$ the contribution from the magnetically coupled spins \([220, 221]\). Although a profound analysis of $C_p$ is beyond the possibilities of the present data, a simplified approach, commonly digested in the literature, will be described below. For this, it is possible to extract information on the electronic character and Debye temperature, by choosing a low temperature regime far below from the Néel temperature.

The phononic contribution can be calculated with the aid of the Debye model \([222]\), by:

$$C_{p,\text{ph}} = nf_D\left( \frac{\theta_D}{T} \right) = 9nR\left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} x^4e^x \frac{dx}{(e^x - 1)^2}$$  \hspace{1cm} (4.16)

where $f_D\left( \frac{\theta_D}{T} \right)$ is the Debye function, $n$ is the number of formula units of the empirical formula (4 in this case), $R$ the molar constant of ideal gases and $\theta_D$ is the Debye temperature. This integral may be approximated at low temperatures ($T \ll \theta_D$) as:

$$C_{p,\text{ph}} = \frac{12\pi^4Nk_B}{5} \left( \frac{T}{\theta_D} \right)^3 = 1944 \left( \frac{T}{\theta_D} \right)^3 \left[ \frac{\text{joules}}{\text{mol} \cdot \text{kelvin}} \right]^3$$  \hspace{1cm} (4.17)

The dependency of $C_p(T)$ is then $\propto T^3$. If we consider the electronic term, this behaves linearly at low temperatures, as:

$$C_{p,\text{ele}} = \gamma T$$  \hspace{1cm} (4.18)

where $\gamma$ is the electronic coefficient of the specific heat, proportional to the conduction band density of states \([222]\).

The common $\theta_D$ values for $RECu_2$ alloys range around 200K (YC\(_2\) $\theta_D = 236K$, TmCu\(_2\) $\theta_D = 194K$ and GdCu\(_2\) $\theta_D = 198K$) \([13]\), therefore our upper limit for the analysis is selected $\leq 20K$, assuming the range of fit $T \leq \theta_D/10$ put forward in textbooks \([223]\). In addition, for $T < 20K$ the $C_{p,\text{mag}}$ can be neglected as a first approximation (note that the $\lambda$-peak is absent for $T \leq 40K$). Moreover, the contribution to the $C_p$ of the SG transition is, in canonical systems, tiny and consequently, far from detectable in our $C_p(T)$ curves. In consequence, the specific heat in our case will follow:

$$C_p = \gamma T + \beta T^3$$  \hspace{1cm} (4.19)

where $\gamma$ and $\beta$ are constants associated to the electronic and phononic contributions, respectively. An easy way to analyse data is to divide Eq. 4.19 between $T$:

$$\frac{C_p}{T} = \gamma + \beta T^2$$  \hspace{1cm} (4.20)
so we will fit $C_p/T$ vs. $T^2$ to a straight line and obtain $\gamma$ and $\theta_D$. These values are presented in Table 4.5 and plotted in Fig. 4.47, as an example.

Table 4.5: The Debye temperature and the electronic coefficient to the specific heat for the milled TbCu$_2$ alloys, as a result of the fit of the specific heat curves to Eq. 4.20.

<table>
<thead>
<tr>
<th>t (h)</th>
<th>$\theta_D$ (K)</th>
<th>$\gamma$ (mJmol$^{-1}$K$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>117(5)</td>
<td>40(2)</td>
</tr>
<tr>
<td>2</td>
<td>123(5)</td>
<td>128(3)</td>
</tr>
<tr>
<td>5</td>
<td>116(5)</td>
<td>145(7)</td>
</tr>
</tbody>
</table>

The most salient feature is the low value of $\theta_D$, without a marked tendency. It was commented that bulk $\theta_D$ values in similar alloys are close to the $T \approx 200$K region. However, the study of nanometals has revealed modifications in the phonon dispersion curves at the grain boundaries. Such variations provoke an excess contribution to the specific heat $[182, 224]$. A recent report studying the $C_p(T)$ of several metals confirmed experimentally the presence of the mentioned excess $C_p(T) [181]$. In the latter, calculations of the $\theta_D$ in those metals (Fe, Cu, Ni and LaAl$_2$) resulted in reduced values, thereby explaining the above presented nano-TbCu$_2$ $\theta_D$ values, lower than in bulk state.

Regarding the $\gamma$-coefficient, our values are clearly larger than expected as for intermetallics NdCu$_2$ $\gamma = 8$mJmol$^{-1}$K$^{-2}$, TmCu$_2$ $\gamma = 9$mJmol$^{-1}$K$^{-2}$, GdCu$_2$ $\gamma = 6.7$mJmol$^{-1}$K$^{-2}$, all with $\gamma \leq 10$mJmol$^{-1}$K$^{-2}$ [13]. These are all well crystallised alloys and then a comparison with amorphous alloys should also be discussed. Indeed, for amorphous Er$_{33}$Ni$_{67}$ $\gamma = 290$mJmol$^{-1}$K$^{-2}$ and Er$_{50}$Ni$_{50}$ $\gamma = 350$mJmol$^{-1}$K$^{-2}$ [225]. It has been commented that from the structural point of view, the nanocrystalline state is in between the ordered (crystalline) and disordered (amorphous) arrangements and hence it is not surprising to find these values. Here the tendency is clear to increase while reducing the particle size. It should also be reminded that for some CSG amorphous FeZr alloys, a 4-fold $\gamma$-increase has been reported, which also reinforces our high values [226].

The measurements of $C_p(T)$ in nano-TbCu$_2$ have provided the evidence for a cooperative Néel transition and, following a simplified approach, for an excess of specific heat which turns out to decrease
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the θ_D values; a consequence of the grain boundaries. Finally, the electronic contribution is enhanced as occurs in amorphous rare-earth binary alloys. The values of θ_D will become handy and carried forward for the analysis of the electrical resistivity which is discussed in the following section.

4.4.4 Electrical resistivity

These measurements were carried out in the TU Wien in January-April 2011. Electrical resistivity data were measured at H = 0 T. The temperature dependence of the electrical resistivity ρ(T) of several TbCu₂ milled alloys is presented in Fig. 4.48, from 4K up to room temperature.
The shape of the $\rho(T)$ is completely similar to the typical found in TbCu$_2$ bulk alloys [117]. It is characterised by a sudden increase at low temperatures followed by a change of slope around 50K and finally a tender but steady increase towards RT. Evidently, the first conclusion is that the $\rho(T)$ of compacted nano-TbCu$_2$ powders is metallic. Besides, the most salient feature is the mentioned change of slope marking the Néel temperature; the electronic scattering with the sublattice AFM moments increases up to $T_N$, and for then onwards, the paramagnetic spin-disorder scattering contribution is constant, causing the slope change. The slight curvature observed for $T > T_N$ is revealing the contribution from the crystalline field, which is the electrical field created by the ion clouds in the crystal on a given atom. In RE-intermetallics, the CEF energy is weaker than the spin-orbit interaction due to the localised character of the $4f$-shell. This character favours the mentioned spin-orbit interaction and, due to the $5p$- and $5s$-shell screening, the weakening of the CEF action. As a consequence, there is a modification of the spin disorder resistivity giving rise to a temperature-dependent term observed in the experiments [227]. In $\rho(T)$ results of bulk RECu$_2$ alloys, some curvature is also detected at $T > T_N$ [117, 228], and is only qualitatively there described on the basis of the CEF effects.
A quantitative analysis of $\rho(T)$ may start commenting two easy-to-extract parameters. On the one hand, it is frequent to evaluate the residual resistivity $\rho_0$, that is, the resistivity value at the lowest temperature. The $\rho_0$ allows to evaluate the intrinsic structural order within the samples. Hence, in perfect single crystals, $\rho_0$ is very low (surely $\rho_0 \cong 0$) and increases with the disorder of the alloys. Unluckily but expectedly, as our powder samples have been compacted, then unreliable $\rho_0$ values are extracted. Thus we will not attempt to discuss the otherwise high $\rho_0$ values, for example $\rho_0 \cong 23\mu\Omega\text{cm}$ in 0.5h TbCu$_2$. For this reason we are uniquely showing the relative values of the resistivity ($\rho/\rho_{4K}$).

On the other hand, the temperature coefficient of resistance (TCR) is another useful parameter, defined as follows:

$$\text{TCR} = \frac{1}{\rho_{300K}} \frac{d\rho}{dT} \quad (4.21)$$

which is the linear fit of the high temperature region and gives us information about the degree of amorphisation or crystallinity of the samples. The values obtained for the milled alloys are shown in Table 4.6. The TCR decreases with milling time and this must be due to the progressive increase of atomic disorder. Effectively TCR values for crystalline metals are high, reaching in bulk Cu $TCR_{Cu} = 36.2\times10^{-4} K^{-1}$ [229] and Tb $TCR_{Tb} = 10\times10^{-4} K^{-1}$ [230]. In TbCu$_2$, an extraction of TCR with data reported in Ref. [117] gives $TCR_{TbCu_2} = 33\times10^{-4} K^{-1}$. If we now turn our attention to the value of TCR found in fully disordered amorphous metals, in Co$_{75}$B$_{25}$ $TCR = 2.7\times10^{-4} K^{-1}$ [231], which lies in the regime recorded for a huge amount of amorphous compounds [232, 233]. In that report, the low values appear as $1.5\times10^{-4} K^{-1} \leq TCR_{amorphous} \leq 4\times10^{-4} K^{-1}$. Therefore, there is a universal correlation between the structural arrangement and the TCR values so that when the atoms are arranged at random, the slope of resistivity becomes smaller. It is straightforward to interpret data as a logical outcome of the increase disorder which is caused by the decrease of size favouring surface disorder and the internal microstrain. In analogous nanometallic systems of Fe nanoparticles embedded in either a Cu or Ag matrices (thin films), $TCR_{Fe_{9}Cu_{91}} = 48.7\times10^{-4} K^{-1}$ and $TCR_{Fe_{14}Ag_{86}} = 41.3\times10^{-4} K^{-1}$ [76, 234], which are close to the reported nano-TbCu$_2$ magnitudes.
Assuming the Mathiessen’s rule, the electrical resistivity is due to the sum of several independent contributions. In this case,

\[ \rho = \rho_0 + \rho_{ph} + \rho_m \]  \hspace{1cm} (4.22)

where \( \rho_0 \) is the constant residual resistivity, \( \rho_{ph} \) is the phononic contribution, defined by:

\[ \rho_{ph} = B \left( \frac{T}{\Theta_D} \right)^5 \int_0^{\Theta_D} \frac{x^5 \mathrm{d}x}{(e^x - 1)(1 - e^{-x})} \]  \hspace{1cm} (4.23)

where \( B \) is a constant that includes the electron-phonon coupling constant, the atomic masses of the different atoms and a characteristic Debye temperature, \( \Theta_D \). This \( \rho_{ph} \) behaves as \( T^5 \) at low temperatures (\( T \ll \Theta_D \)) and as \( T \) at high temperatures (\( T \gg \Theta_D \)) [82, 83]. The magnetic contribution to the electrical resistivity (\( \rho_m \)) is a consequence of the electronic scattering with the magnetic moments. At \( T = 0 \)K, all the spins are aligned and hence this contribution is zero. A detailed derivation of the specific equations has been thoroughly explained by B. Coqblin [20] using a development by de Gennes and Friedel [235]. Under those assumptions,

\[ \rho_m = \rho_{m0} \left[ 1 - \frac{\langle S \rangle^2}{S(S + 1)} \right] \]  \hspace{1cm} (4.24)

where \( \rho_{m0} \) is the constant value of the magnetic contribution to the electrical resistivity above the ordering temperature and \( \langle S \rangle \) the mean value of the spin number \( S \). This is a simple equation to explain the \( \rho_m(T) \) behaviour. When \( T \) is very low, \( \langle S \rangle \) is high and, by increasing temperature, the latter becomes smaller, reaching at the order temperature, \( \langle S \rangle \to 0 \). It is facile to see that for high temperatures \( \rho \equiv \rho_{m0} \), which is the constant value in the paramagnetic regime.

\[ \rho_{m0} = \frac{3\pi N m}{2\hbar e^2 E_F} G^2 S(S + 1) \]  \hspace{1cm} (4.25)

where \( N \) is the number of atoms by unit volume, \( G \) the interaction constant (in units of energy by volume), \( m \) the effective mass, \( e \) the electron charge and \( E_F \) the Fermi energy.

The quantitative analysis of \( \rho_m \) in antiferromagnetic intermetallics is cumbersome as the specific \( T \)-dependence is not clear and may vary according to different ranges [227, 236, 237]. The accepted understanding is to take into account the spin wave-electron scattering, which in turn depends on the \( E(q) \) energy dispersion curve for
Table 4.6: Temperature coefficient of resistance TCR, calculated from Eq. 4.21, and constants $\rho_{0, \text{rel}}$, $a$ and $b$, calculated from Eq. 4.26, for every milled alloy.

<table>
<thead>
<tr>
<th>$t$ (h)</th>
<th>TCR (K$^{-1}$)</th>
<th>$\rho_{0, \text{rel}}$</th>
<th>$a$ (K$^{-5}$)</th>
<th>$b$ (K$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>9.283$x10^{-4}$</td>
<td>0.9991(4)</td>
<td>2.24(16)$x10^{-2}$</td>
<td>7.0(5)$x10^{-8}$</td>
</tr>
<tr>
<td>2</td>
<td>6.313$x10^{-4}$</td>
<td>0.9997(1)</td>
<td>1.24(2)$x10^{-2}$</td>
<td>3.2(1)$x10^{-8}$</td>
</tr>
<tr>
<td>5</td>
<td>3.314$x10^{-4}$</td>
<td>0.9993(1)</td>
<td>0.26(3)$x10^{-2}$</td>
<td>1.2(1)$x10^{-8}$</td>
</tr>
</tbody>
</table>

the sublattice magnons. In FM metals $W(q) \propto q^2$, which is modified to $W(q) \propto q$ in the AFM case. The final dependence predicts $\rho_m \propto T^4$ [20, 237]. Other models [238] give other dependencies according to the interplay between $\theta_D$ and $T_N$ but we will work with a single dependence to remain realistic. It is helpful to remark that reports on different bulk AFM 4f-based compounds such as NdGa$_2$ [239], GdNi$_{1-x}$Cu$_x$ [236], GdGa$_5$ [240], RNi$_2$Si$_2$ [241] were able to discuss only qualitatively the $\rho_m(T)$ dependence by subtracting (in some cases) the La,Y - non magnetic counterpart.

Hence, the low temperature region of the $\rho(T)$ curves will be fitted to:

$$\frac{\rho}{\rho_{4K}} = \rho_{0, \text{rel}} + a \left( \frac{T}{\theta_D} \right)^5 \int_0^{\theta_D} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} + bT^4 \quad (4.26)$$

where $\rho_{0, \text{rel}}$ corresponds to the residual resistivity divided by $\rho_{4K}$ (electrical resistivity at $T = 4K$) and $a$ and $b$ are constants associated to the phononic and magnetic contributions, respectively. In this expression we exclude the critical scattering around $T_N$ and the eventual spin fluctuation resistivity as well.

A representative fit is shown in the inset of Fig. 4.48. The agreement between the experiment and theoretical curve is excellent, below the rounded region ($\cong T_N$), in which the alloy becomes magnetically disordered. Irrespective of our assumptions, it is crucial to express that two clear trends are found. On the one hand the electron-electron contribution ($a$-coefficient) decreases with $t$, as a result of the increase of disorder of the alloys. Equally, the magnetic $b$-coefficient ($T^4$-dependence) also becomes reduced with the decrease of $D$; this fact is beautifully connected with the decrease of AFM order in the nano-TbCu$_2$ system. Essentially, the $\rho(T)$ analysis has procured us two phenomenal partial conclusions: the nano-TbCu$_2$ are metallic
and the decrease of size favours a disordered environment affecting the electronic scattering gradually.
4.5 Magnetic Phase Diagram of Superantiferromagnetic TbCu$_2$ Nanoparticles

The high-energy milling process of bulk TbCu$_2$ results in the production of randomly grouped ensembles of particles with a nanometric size distribution, as revealed by XRD and TEM analyses. It is advisable to remind first the structural arrangement within the nanoparticles. Inside each particle, the orthorhombic $Imma$ symmetry is retained, as derived from the Rietveld refinements of both (in-house and synchrotron) XRD and ND patterns (see Table 4.1). The particle size decreases as the milling time is longer, reaching a saturation $D \approx 6\, \text{nm}$. On the other hand, particle strain increases with milling time, up to $\approx 0.4\%$, for the 5th TbCu$_2$. Consequently, with this production route it is easy to end up with a series of TbCu$_2$ nanoparticles with controlled sizes.

In this final discussion we will address two important issues. Initially we will consider the macroscopic implications of nano-TbCu$_2$ as an overall magnetic response to compare with bulk $REX_2$ systems. In a subsequent step we really deepen in the nanoscopic properties which enables us to put forward an attractive magnetic phase diagram. Let us start reviewing briefly the modifications in the magnetic behaviour of bulk TbCu$_2$ provoked by changes of the alloy (rare-earth) composition (see Fig. 4.49). Those modifications are traditionally understood by the variation of the de Gennes ($dG$) factor, which follows the existence of RKKY interactions. This factor is connected to the Landé and the total angular moment through the expression:

$$T_N = \frac{3N(E_F)^2}{kE_F}G^2(g-1)^2(J+1)\sum_{i\neq 1} F(2k_F R_{0i}\cos(\vec{q} \cdot \vec{R}_{0i})) \quad (4.27)$$

where $N(E_F)$ is the density of states at the Fermi level, $G$ the interaction constant and $F(2k_F R_{0i}\cos(\vec{q} \cdot \vec{R}_{0i}))$ the oscillatory RKKY function \[180\]. The volume increases with increasing $dG$ factor value along the $RECu_2$ bulk series, being the lowest value that for $RE=$Tm and the highest for $RE=$Gd (see Fig. 4.49). The $T_N$ and $\mu_{eff}$ parameters show a different variation, with an emerging peak for TbCu$_2$ and DyCu$_2$, respectively. This means that the RKKY interaction is not the sole origin for the variation and quadrupole and magnetoelastic interactions can also contribute to the total exchange \[13\]. Then, ignoring at this point the nanometric nature of the milled TbCu$_2$, we will comment on some key results in this macroscopic analysis. In this figure we have
added the data of our TbCu$_2$ milled alloys (all of them, of course, with the same $dG$ factor). For the $T_N$, there is a general decrease for the milled alloys values; such a finding leads to a simple thought: the behaviour tends to be closer to either DyCu$_2$ or GdCu$_2$. However, $V$ tends to increase for the $t$-intermediate milled alloys ($2 \leq t \leq 5h$), in a similar trend than the change from TbCu$_2$ to GdCu$_2$. In the case of the effective moment $\mu_{\text{eff}}$, it does present an erratic behaviour, without a marked variation. In consequence, it seems that the milling time produces a magnetic response closer to that displayed in GdCu$_2$. We should remind that GdCu$_2$ is affected by the lack of angular moment and hence of magnetic anisotropy. In addition, milled GdCu$_2$ presents an AFM ordering of the Gd$^{3+}$ moments ($b$-direction) and a cycloidal propagation along the $a$-direction [242].

Figure 4.49: Compositional dependence of $T_N$, $\mu_{\text{eff}}$ and $V$ along the bulk RECu$_2$ alloys. Our values have been inserted together to data obtained from Ref. [13].
In bulk form, it is relatively feasible to prepare pseudobinary alloys. In this sense, the evidences from the dilution of the parent alloy with non-magnetic Y-atoms, as \( \text{Tb}_x \text{Y}_{1-x} \text{Cu}_2 \), indicates a weakening of the magnetic interaction reducing the \( T_N \). This reduction follows the empirical relation 
\[
\frac{T_N(x)}{T_N(x = 1)} \propto (x - x_c)^{0.6}
\]
where \( x_c \) is the critical concentration at which the magnetic ordering disappears \[109\]. In our case, the reduction \( \Delta T_N / T_{N,\text{bulk}} \simeq -11 \% \) resulting in a \( x \sim 0.97 \) (a minute dilution) which suggests that the antiferromagnetic order is not essentially altered. Another via for compositional dilution is that established by the exchange of Cu by Ni atoms; with this, the electron concentration, which is another far-reaching parameter in Eq. 4.27, is hence altered. In the case of \( \text{Tb(Ni, Cu)}_2 \) such a replacement increases the AFM character and eventually gives rise to a FM (\( \sim 8\% \) Ni) structure \[117\]. In our nano-\( \text{TbCu}_2 \), we observe the disappearance of the AFM order which is not substituted by long-range ferromagnetism here, but by a magnetically disordered state. In addition our reduction is much smaller than that found for the former cases and we ought to reconcile that observation with another explanation. This requirement is reinforced by the evident correlation between the \( T_N \) and \( T_f \) values.

![Figure 4.50: Magnetic phase diagram of \( \text{TbCu}_2 \) nanomagnets. Lines are guides for the eye.](image)

Now we are in a position to discuss from a real macroscopic point of view. In view of the size-induced variation of key temperatures,
we propose a useful magnetic phase diagram. The release of such a magnetic phase diagram driven by size-variations constitutes a handy landmark in the understanding of the nano-TbCu$_2$. Effectively, it immediately resembles the diagrams of magnetically disordered systems, especially those of the so-called reentrant magnets. Among the latter there are paramount examples in which the compositional change is the control variable for the definition of the paramagnetic, magnetic and disordered regions. It has to be admitted that the vast majority of them present a ferromagnetic order when going from the paramagnetic to lower temperatures and then cluster or spin glass regions. In the crystalline state we can cite the AuFe system by B. R. Coles et al. [243]. As it is well-known, an amorphous atomic arrangement does not jeopardise the apparition of such reentrant behaviour. Indeed, examples based in the random dilution of amorphous FeNiBPBAI [149] or in the density variations of Fe-Fe coupling in FeZr metallic glasses have been thoroughly analysed [121, 143].

In the case of RE-alloys there are also beautiful examples, as occurs in the weak random-axis magnet (Dy$_x$Y$_{1-x}$)Al$_2$, with a Laves-phase intermetallics structure [244, 245]. Its behaviour is supported by the presence of random magnetic anisotropy, according to the HPZ model based on the single-ion anisotropy of the 4f-electron clouds and the crystal field effects [29]. This approach was also applied to understand Tb-based crystalline dilute magnets of Tb$_x$Y$_{1-x}$Al$_2$ [246]. In the case of amorphous RE-alloys, a paradigm can be represented by the then popular Dy$_6$Fe$_{74}$B$_{20}$ amorphous magnets [247] interpreted according to the onset of an easy axis which varies following the local arrangement (short-range structure) of the amorphous metal [248].

Here, a distinct fact is that the size evolution triggers a macroscopic coexistence of (super)antiferromagnetic and spin glass which is not that common. There are sparse examples on Ising Fe$_{0.55}$Mg$_{0.45}$Cl$_2$ and Fe$_{0.6}$Mn$_{0.4}$TiO$_3$ [249, 250] compounds, YBa$_2$(Cu$_{0.88}$Fe$_{0.12}$)$_3$O$_{6.5}$ semiconductors [251], insulating materials of Co$_2$(OH)(PO$_4$)$_2$ [123], and Heisenberg perovskites of Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ [110, 252], to cite a variety of material states. To our knowledge, nano-TbCu$_2$ is an original example using nanometric particles with metallic character (as proven by the electrical resistivity, see Fig. 4.48). In the few AFM systems with a reentrant SG state [110, 123, 249, 250, 251, 252], the combination of frustration and random bonds gives rise to the freezing. The Sherrington-Kirkpatrick model predicts that long-range ferromagnetism is always present but, for $T \lesssim T_f$, there exists a replica
symmetry breaking resulting in the coexistence of FM and SG states [67]. Such an explanation qualitatively supports the phase diagram in Fe$_{0.55}$Mg$_{0.45}$Cl$_2$ [249, 250]. For Pb(Fe$_{1/2}$Nb$_{1/2}$)O$_3$ both uncollinearity and clustering have been invoked [110, 252]. A very recent model has been proposed involving small clusters with AFM order, showing $\chi(T)$ resembling the one presented here, and predicting SG $\leftrightarrow$ PM transitions [73]. However, here the particle size is much larger.

Regarding the superantiferromagnetic state, this displays a connection with other supermagnetic systems. Nevertheless most of them have been worked out in superferromagnetic/super spin glass state [75, 76, 77, 215, 253, 254]. This scenario is very close to the reported in milled alloys of GdAl$_2$ [95] and TbAl$_2$ [80, 99] for which the ferromagnetic transition was disappearing at the expense of a growing spin glass state. This idea of definite coupling among nanoparticles was first proposed in antiferromagnetic goethite $\alpha$-FeOOH [78], with a very curious magnetic behaviour [255, 256]. In fact very recently it has been shown that its magnetic properties are dominated by the AFM order, followed by a lower transition in the fine particle state, and a further very low temperature magnetic coupling mode [257]. This Fe oxi-hydroxide in fact turns out as a macroscopically very similar system to nano-TbCu$_2$. Yet, there $T_N$ had the experimental drawback of appearing at $T > RT$, $T_N \approx 348K$; this is always a risk for nanoparticle systems. Furthermore, the study of AFM nanoparticles allow to extract information on the surface spins given that the particle cores have a negligible response [115]. It should also be reminded that the SG surface had been widely reported in the Fe-oxides in nanoparticle state. In this sense, there are some reports in ferrimagnetic particles $\gamma$-Fe$_2$O$_3$ scrutinised about the real origin for this effect [116, 258]. Other similar evidences were found by Mössbauer spectroscopy in metallic Fe nanoparticles (2 nm, $\approx 350$ atoms) [259] or in exchange-biased systems [27]. Here we have detected that the spin canting is governed by the reduction of particle size and a parallel existence of microstructural strain, which both are enhancing an interfacial disordered coupling between particles.
The strongly correlated electron system (SCES) YbAl$_3$ alloy has attracted much attention in the last decades due to the fact that it exhibits a great variety of cutting-edge physical phenomena, such as intermediate valence (IV), Kondo resonance and Fermi-liquid (FL) behaviour [260, 261, 262]. All these behaviours are related to the mentioned (see Chapter 2) hybridisation of the 4f-state with the conduction band electrons. Among the great variety of experiments performed in YbAl$_3$ we could cite magnetic [263] or thermoelectric [264, 265] measurements and the effect of the hydrostatic pressure [266] or the magnetic field (and disorder) [267], procuring a great deal of complementary information on the just related attractive phenomena.

In bulk form, YbAl$_3$ crystallises in a cubic AuCu$_3$-type structure, with a lattice parameter $a = 4.213\,\text{Å}$ (space group $Pm-3m$) [268]. The magnetic susceptibility $\chi(T)$ shows a maximum at $T_{\text{m, max}} \approx 120\,\text{K}$. This peak is observed in IV compounds. For $T \lesssim 40\,\text{K}$ the electrical resistivity of the bulk alloy exhibits a FL behaviour as $\rho(T) \propto T^2$ [269, 270].

In a previous analysis [15], a milling procedure was carried out in YbAl$_3$. YbAl$_3$ was selected as a starting alloy to study the downsizing effects on the electronic properties of IV compounds. These should be connected mainly to the possible variation of the Yb$^{2+}/$Yb$^{3+}$ valance. The analysis comprised the study of the magnetisation and specific heat and several changes in these properties were found. It was detected that the absolute value of the magnetic susceptibility $\chi(T)$ decreased with milling time (indicating an increase of the Yb$^{2+}$ contribution). Another finding is the increase of the slope above 160 K and excess of specific heat $C_P$ around 40 K (related as well to the downsizing of the particle size). Ultimately, completed by XRD, TEM and by X-ray Absorption Near Edge Structure (XANES), it was observed that the milled alloys were formed by a distribution of nanoparticles in which the Yb$^{2+}$ atomic state was favoured at the
surface of these nanoparticles while the atoms located in deeper layers (within the core) kept the intermediate valence state of the bulk alloy. Thus, this effect was related to the surface/volume ratio increase so the high fraction of atoms on the surface was the origin of the variation of the physical properties in the milled alloy.

In spite of the former relevant results, the lack of basic information on IV-nanoparticles prompted a challenging effort to analyse the electrical resistivity $\rho(T)$ behaviour. Therefore, in this chapter we will deepen in the effect of reducing the particle size of nanostructured YbAl$_3$, on the contributions to the electrical resistivity. Moreover, we will present and interpret other necessary measurements such as XRD, TEM, synchrotron radiation and DC-susceptibility, in order to characterise the samples comprehensively.

5.1 PREPARATION AND CRYSTALLOGRAPHY

Starting polycrystalline YbAl$_3$ pellets were prepared by arc melting suitable amounts of pure constituents Yb(3N) and Al(5N) in an arc furnace under protective Ar (99.99%) atmosphere. Considering the high vapor pressure of Yb, a 5% excess (respect to stoichiometry) of Yb mass was added prior melting. Under these circumstances, only up to a $\approx 2g$ pellet was obtained. Subsequently, the ingot was annealed at 750°C for five days. Later on, the samples were crushed and milled in the same way as the one described for nano-TbCu$_2$ (see Chapter 4).

With the aim of elucidating the presence of impurities in the resulting alloys, a compositional analysis was carried out by conventional semi-quantitative X-ray fluorescence with the assistance of Msc B. Estandía at the SERCAMAT (Universidad de Cantabria). The results show that the main metallic impurities are Mg (0.09%), Ag (0.08%), Fe (0.04%), Pt (0.02%). In any case, we are limited to the purity of Yb metal, as supplied with Pb(0.09%), Fe (0.03%) and Ti (0.02%). All these percentages are extremely low and close to the real resolution limits of the technique.
Figure 5.1: X-ray diffraction patterns for the bulk (0h) and the 20 and 70h YbAl$_3$ milled alloys. There exist some extra reflections (small peaks, marked with asterisks), corresponding to YbAl$_2$.

5.1.1 Structural characterisation

The structural characterisation was carried out in a Bruker D8 Advance diffractometer, with Cu-K$_\alpha$ radiation. The crystallographic parameters were determined using the FullProf Suite [88, 89] in order to perform Rietveld refinements taking into account the expected peak broadening.

Figure 5.1 shows the X-ray diffraction patterns for the series of YbAl$_3$ bulk and milled alloys. A progressive broadening and reduction in the intensity of the peaks, commonly related to a decrease of the particle size ($D$) and an increase in the lattice strain ($\eta$) is observed. The Rietveld refinement (Fig. 5.2) confirms this particle size reduction (Table 5.1). Several asterisks are displayed in the bulk XRD pattern in order to show those reflections corresponding to YbAl$_2$. This phase coexistence (with traces of YbAl$_3$) has also been reported when YbAl$_2$ was produced by an induction furnace [271]. It can be then accepted that it is difficult to obtain pure either YbAl$_3$ or YbAl$_2$ alloys.

The results of the most crucial parameters obtained through Rietveld refinements for the milled YbAl$_3$ alloys (see Fig. 5.2) are in-
Figure 5.2: Rietveld refinement of the XRD pattern, performed at RT, for the YbAl$_3$ milled alloys using Cu-K$_\alpha$ radiation. The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns.

Table 5.1: Lattice parameter ($a$), grain size ($D$) and strain ($\eta$) of the bulk and 20 and 70 hours YbAl$_3$ milled alloys. Standard Bragg errors are denoted by $R_B$.

<table>
<thead>
<tr>
<th>t(h)</th>
<th>$a$ (Å)</th>
<th>$D$ (nm)</th>
<th>$\eta$ (%)</th>
<th>$R_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.2014(7)</td>
<td>-</td>
<td>-</td>
<td>39.1</td>
</tr>
<tr>
<td>20</td>
<td>4.2095(1)</td>
<td>10.6(5)</td>
<td>0.30(5)</td>
<td>13.0</td>
</tr>
<tr>
<td>70</td>
<td>4.2074(2)</td>
<td>10.9(5)</td>
<td>0.33(5)</td>
<td>22.7</td>
</tr>
</tbody>
</table>
serted in Table 5.1. First, the lattice parameter is practically unmodified ($\lesssim 0.2\%$) whereas the particle size $D$ and strain $\eta$ stay practically constant for $t = 20, 70h$. It is relevant that with a low milling time, minimising the possible oxidation if large $t$ were employed, grain sizes within the nanometric range are available. The microstrain is $\eta \approx 0.3\%$, in the range of the nano-TbCu$_2$ alloys. All these parameters highlight the consistency of the synthesis route as they are practically the same as those reported in Ref. [15].

XRD characterisation was completed by synchrotron radiation, performed at ALBA Large Facility, in Barcelona (Spain), with an increased Q-range ($\lambda = 0.4126\AA$) and temperature variation (100-300K). The aim behind this is to determine better the crystallographic structure, thanks to the much better statistics. A representative pattern is shown in Fig. 5.3, at 100K.

![Rietveld refinement of the synchrotron XRD pattern of the 70h milled YbAl$_3$ alloy (at T = 100 K). The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns. Bragg positions of the possible compositions (YbAl$_3$ and YbAl$_2$) are marked in green.](image)

Figure 5.3: Rietveld refinement of the synchrotron XRD pattern of the 70h milled YbAl$_3$ alloy (at T = 100 K). The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns. Bragg positions of the possible compositions (YbAl$_3$ and YbAl$_2$) are marked in green.

The resulting structural variables deduced from the Rietveld refinements at every indicated temperature were calculated and the results are displayed in Table 5.2. There, it is feasible to observe that an excellent refinement is achieved ($R_B \approx 5\%$). Regarding the existence of
Table 5.2: Cubic cell parameter $a$ of the 70h milled alloy at different temperatures, obtained by Rietveld refinements, from results of XRD performed at MSPD instrument in ALBA synchrotron. Standard Bragg errors are denoted by $R_B$. The calculated particle size is $D = 9.3\text{nm}$, in good agreement to that obtained by conventional XRD.

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$a$ (Å)</th>
<th>$R_B$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.21080(4)</td>
<td>4.2</td>
</tr>
<tr>
<td>125</td>
<td>4.21153(4)</td>
<td>5.1</td>
</tr>
<tr>
<td>150</td>
<td>4.21227(4)</td>
<td>5.7</td>
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<tr>
<td>175</td>
<td>4.21320(4)</td>
<td>6.7</td>
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<tr>
<td>200</td>
<td>4.21357(4)</td>
<td>6.1</td>
</tr>
<tr>
<td>225</td>
<td>4.21367(4)</td>
<td>6.0</td>
</tr>
<tr>
<td>250</td>
<td>4.21390(4)</td>
<td>5.6</td>
</tr>
<tr>
<td>295</td>
<td>4.21409(4)</td>
<td>5.2</td>
</tr>
</tbody>
</table>

different crystallographic phases, the calculations indicate that more than 99% of the peak intensity is due to YbAl$_3$. Spurious phases, such as YbAl$_2$, represent only less than 1%. Thus, although it is common to find some YbAl$_3$-YbAl$_2$ phase coexistence, as mentioned before, the trouble is kept to a minimum in our samples. The cell parameter at RT is $a = 4.21409(4)$Å, which is similar to that obtained by in-house XRD ($a = 4.2074(2)$Å) and to the bulk alloy \cite{15, 268}. On the other hand, the particle size ($D \approx 9\text{nm}$) is too in very good agreement to that determined in the previous analysis by XRD. The use of a cryostat enables a description of the lattice (volume) thermal variation; there is in fact a noticeable variation of the cell parameters with temperature. This variation is plotted in Fig. 5.4. As it can be observed, two different regions exist with a definite change of slope ($\Delta a/\Delta T$). This crossover is surprising as there is not a structural phase transition in this alloy. The observed trend is worth investigating but it has not apparent influence on the low-temperature properties. In any case, it will merit future attention analysing different samples to establish tendencies.
For practical purposes, it is interesting to report the thermal expansion coefficient, that is calculated from:

\[
\alpha = \left( \frac{1}{a} \right) \frac{\Delta a}{\Delta T} \text{ at } T = 100\text{K}
\]  

(5.1)

Figure 5.4: Lattice parameter variation with temperature, for the 70h milled YbAl₃ alloy, from Table 5.2. A change of slope is observed at \( T \approx 80\text{K} \), which is not related to structural transitions [272].

As it was described, the two different regions provide a couple of thermal expansion coefficients, \( \alpha_1 = 7.54 \times 10^{-6} \text{K}^{-1} \) and \( \alpha_2 = 1.35 \times 10^{-6} \text{K}^{-1} \). The 2-zone thermal expansion does not coincide with the bulk thermal expansion [272], where \( \alpha(T) \) exhibits a monotonic behaviour within the \( 2 - 300\text{K} \) range. Regarding the order of magnitude, both bulk and nano-YbAl₃ show \( \alpha \approx 7 \times 10^{-6} \text{K}^{-1} \) at \( T = 100\text{K} \) but the values at higher temperatures differ, being much higher for bulk (at 300K, \( \alpha_{\text{bulk}} \approx 1.4 \times 10^{-5} \text{K}^{-1} \) and \( \alpha_{\text{nano}} \approx 1.35 \times 10^{-6} \text{K}^{-1} \)).

Drastic changes of \( \alpha \) have been reported in other milled alloys, although of very different electronic and magnetic state. In recent years, milled Fe-Ni alloys (for example Fe₆₄Ni₃₆) Invar alloys have displayed \( \alpha \approx 2 \times 10^{-6} \text{K}^{-1} \) in the low temperature region (\( T < T_C \approx 565\text{K} \)) whereas \( \alpha_{T>T_C} \approx 1.4 \times 10^{-5} \text{K}^{-1} \) [273]. The existence of such Invar behaviour in Fe-based milled alloys had also been reported in FeCu where \( \alpha \approx 3 \times 10^{-6} \text{K}^{-1} \) (in Fe₄₄Cu₅₆) below 350K. The latter values are clearly larger than \( \alpha_1 \) in 70h YbAl₃. It turns out that the determination of the eventual origin of the Invar character for
T > 190K in nano-YbAl$_3$ may render intriguing physics to be scrutinised in the near future. To end up and provide completeness in this work it should be reminded that for the nano-TbCu$_2$ alloys, $\alpha_{TbCu_2,2h} = 5.1 \times 10^{-5} K^{-1}$ and $\alpha_{TbCu_2,5h} = 3.78 \times 10^{-5} K^{-1}$. Both temperature regions in nano-YbAl$_3$ show lower values of the thermal expansion than in nano-TbCu$_2$ (see Section 4.4.1). In the latter alloys no change of slope was encountered whatsoever.

5.1.2 Transmission Electron Microscopy

The structural characterisation at the nanoscale was completed via Transmission Electron Microscopy (TEM), at 200 keV. Fig. 5.5 shows two bright field images of the 70h milled YbAl$_3$ nanoparticles. A high resolution detail is shown in Fig. 5.5(b), in which lattice planes are visible, confirming the crystallinity of the samples. The histogram analysis (inset Fig. 5.5) confirms the nanometric size of milled YbAl$_3$ ($D_{TEM} = 4.7(5)$ nm, from a log-normal fit) though a smaller value than in XRD is obtained ($D_{XRD} = 11(1)$ nm), as it happened in the case of TbCu$_2$. The low error in $D_{TEM}$ indicates a greater homogeneity in YbAl$_3$, compared to nano-TbCu$_2$, which should be surely related to the value of the Young’s modulus $E$ of the alloys in question, for which $E = 174$ GPa in YbAl$_3$ [274] and $E = 77.4$ GPa in TbFe$_2$ [275] bulks.

5.2 Magnetic Properties

The ZFC $M_{DC}$ curves of the 20 and 70h milled alloys are presented in insets of Fig. 5.6. The $M/H$ curve shows a marked increase towards the lowest temperature. The uprise at low temperatures is due to the presence of Yb$_2$O$_3$ oxide ($T_N = 2.3$ K), as it has been detected in previous works on nanometric YbAl$_3$ [15]. Besides, it has been reported traces of oxide occasionally in single crystal alloys [263] as well, even if the handling and storing of the samples was carried out under an Ar (99.99%) atmosphere. To extract the intrinsic nano-YbAl$_3$ magnetic susceptibility we have subtracted this contribution from the original $M(T)$ curve giving the results plotted in Fig. 5.6. This subtraction was carried out by varying the amount of the contribution from Yb$_2$O$_3$
Figure 5.5: TEM images of the 70h milled YbAl₃ sample. Inset: diameter distribution of the 70h YbAl₃ milled alloy, obtained by TEM. The black line is the fit to a log-normal distribution, centred at 4.7nm, with a standard deviation $\sigma = 0.5$nm.

(previously the magnetisation of Alfa Aesar Yb₂O₃, 99.998%, was measured), until a characteristic unambiguous plateau at low temperatures was obtained. The percentage of Yb-oxide presence is very low, with 0.8% and 1.2% for 20h and 70h YbAl₃, respectively. This should be taken as a rough estimation, much less reliable than the quantities derived from the XRD data. Another confirmation of the presence of Yb₂O₃ is visible in Figure 5.6 (inset b) where M(H) at $T = 2K$ shows a magnetisation increase with field. The values are logically lower for 20h YbAl₃ as the oxide quantity increases with higher milling times. At $T = 300K$ there appears an expected enhanced Pauli paramag-
netism with a minute contribution to the magnetisation ($\lesssim$ 1 emu/g at $H = 80$ kOe) together to a kink for $H \lesssim 2$ kOe with $M \lesssim 0.35$ emu/g. The latter kink could be due to the supplied Yb metal but it decreases with milling time, becoming negligible for further interpretation.

Effectively, the shape of the $M(T)$ curve after subtraction is similar to that of bulk alloys [15, 263, 266]. The curve is characterised by an increase of susceptibility towards a maximum at $T \approx 100$K and a subsequent decrease towards RT, ideally following a Curie-Weiss law. This maximum is one of the typical features of IV compounds [15, 263], associated to the Kondo temperature.
There exists a reduction of magnetisation from 20 to 70h, as $D$ decreases. This result is in good agreement with a previous work on nanometric YbAl$_3$ [15] in which the magnetisation decrease was related to a reduction of the Yb$^{3+}$ atoms, which are replaced by atoms in the Yb$^{2+}$ state, giving rise to Yb$^{2+}$ ions on the nanoparticle surface. The modification of the ratio of Yb$^{3+}$/Yb$^{2+}$ atoms was finely confirmed by XANES [15]. Moreover, a shift of the maximum of the magnetisation is observed for longer milling times. For 20h, the $\chi_{\text{max}}$ is found at $T \simeq 80\text{K}$ while for 70h, this maximum is observed at $T \simeq 100\text{K}$, indicating fairly an increased Kondo interaction.
5.3 TRANSPORT PROPERTIES

5.3.1 Electrical resistivity

In Fig. 5.7 the thermal variation of the electrical resistivity $\rho(T)$ of the 70h milled YbAl$_3$ is presented. As commented at the beginning, our main interest in the analysis of YbAl$_3$ alloys is to evaluate the behaviour of $\rho(T)$. Accordingly, it is patent the existence of a minimum around $\approx 15$K which is followed at $T \approx 125$K by a broad hump and a further almost linear (negative) $\rho(T)$, when approaching RT. Before going into detail about the remarkable presence of a minimum, we shall overview briefly the expected contributions to the resistivity in intermediate valence alloys.

To start with, the resistivity is a electronic scattering process normally ascribed to the presence of disorder, whatever the origin of such is. In ordinary magnetic metals, we already explained in Section 4.4.4 the common assumption of the Mathiessen’s rule (see Eqn. 4.22) and the role played by the electron-phonon (Eqn. 4.23) and the electron-magnon interactions (Eqn. 4.24 and 4.26).

Since YbAl$_3$ is a moderate heavy fermion, there should exist a contribution due to the Fermi-Liquid (FL)-scattering, as $\rho_{FL} \propto T^2$. Then:

$$\rho(T) = \rho_0 + \rho_{ph} + \rho_{FL} \quad (5.2)$$

The shape of the electrical resistivity should then be a drastic $\rho(T)$ increase at low temperatures, from a $\rho_0$ constant value, followed by a smooth variation for $T \gg \theta_D$. However we observe here two important features that get away from this *typical* shape.

At high temperatures, a broad hump, above described, is observed with a maximum of the $\rho(T)$ at $T \approx 125$K. The presence of this maximum is a striking result as it does not appear in bulk YbAl$_3$ [269]. However, other heavy fermion compounds do show similar high temperature maximum (CeCu$_6$, CeCu$_2$ or CeAl$_3$ [276]). For these, the maximum has been explained on the basis of the Wachter and Marabelli theory [277]. This model supposes the existence of two energy bands separated by a gap, influenced by the hybridisation of states. The Fermi energy is located in one of these bands (see sketch in Fig.
Figure 5.7: Electrical resistivity dependence with temperature of the 70h YbAl$_3$ milled alloy. At low temperatures (red dashed-circle) there exists a marked and unexpected minimum followed by an increase of the resistivity, up to a broad maximum, observed in IV compounds.

Both bands are assumed to follow a gaussian shape, with the same FWHM. The fact that the Fermi energy is semi-filling the upper band results in a high density of states (DOS), which in turn explains the high $\gamma$-coefficient of the specific heat in these alloys. Depending on the separation between both bands and their FWHM, different behaviours are expected which for archetypal UPt$_3$ appears as nearly gapless with wide peaks whereas for CeCu$_2$Si$_2$ the shape of DOS is represented by two very sharp peaks [276]. When the FWHM of the bands is small compared to its separation, there appears a maximum in the electrical resistivity. This can be understood in an extremely simplified view as the consequence of modifying the density of carriers due to interband electronic transition across the gap.

An alternative point of view is to consider the effect of the Kondo interaction here. In this sense, it should be noted that the magnetic resistivity of Kondo systems may show up a maximum at high temperatures. This has been well-established in Kondo systems in which there was an evolution from a magnetically ordered CePt to an IV CeNi, following a Ni-dilution in CeNi$_x$Pt$_{1-x}$ intermetallics [50]. The explanation for the observed resistivity was given by the application of
The nanometric YbAl\textsubscript{3} system

resistivity calculations by Cornut and Coqblin, dependent on the density of states at the Fermi level, the number of occupied states and a coupling constant between the \textit{qf} shell and the conduction band [278]. However, this calculation was developed taking into account a definite magnetic moment and the existence of CEF effects. In IV YbAl\textsubscript{3}, it is not expected an (or at least there is a negligible) influence from both facts. In consequence, the interpretation of the maximum on the Kondo interaction basis should be slightly different; in this alloy such an interaction is large and therefore, an increase of the resistivity is expected moving from high to lower temperatures (−\ln T). However, there is a tendency for coherence effects, as expected for a Kondo lattice system when decreasing the temperature; that is to say, the resistivity decreases below the coherence temperature (around 100 K in YbAl\textsubscript{3}). Around the maximum, and on going to lower temperatures, this coherence begins to appear, and the resistivity decreases going gradually towards a Fermi liquid behaviour (40 K in YbAl\textsubscript{3}) when approaching lower temperatures. It is though rather disgusting that the difficulty of applying a proper subtraction of the phonon term refrains for a more definitive interpretation of this result. It may merit to perform future dilutions in the nanocrystalline state to provide a quantitative evaluation.

![Energy levels scheme](image)

Figure 5.8: Energy levels scheme, as proposed in the Wachter and Marabelli theory [277], where \( \rho_D(E) \) represents the density of states.

Another observable feature is the high value of the residual resistivity \( \rho_0 \). The value here, \( \rho_0 \approx 16000 \mu \Omega \text{cm} \) is much higher than in other systems, such as the intermetallic compound Mg\textsubscript{1−x}Zn\textsubscript{x}
(\(\rho_0 \approx 50\mu\Omega\text{cm}\)) \([279]\), the ferromagnetic SmNiC\(_2\) (\(\rho_0 \approx 25\mu\Omega\text{cm}\)) \([280]\), or naturally in single crystal YbAl\(_3\) (\(\rho_0 \approx 1.5\mu\Omega\text{cm}\)) \([265]\). The reason why this \(\rho_0\) is that high is due to the fact that we have measured \(\rho(T)\) in a cold-pressed powder bar instead of in bulk. Thus, it is not a crystalline lattice where the atoms are \textit{perfectly} located in their positions along the whole compound; by contrast there might be some disorder at grain boundaries. Because of this, there exists an important electron scattering implying a lower conduction of these electrons. In another cold-pressed powder sample, Bismuth-Silica composites, a similar value, \(\rho_0 \approx 1200\mu\Omega\text{cm}\), was obtained \([281]\). Then again, the compaction process is surely affected by the metallurgical properties of the alloy. In particular, for nano-TbCu\(_2\) the values of \(\rho_0\) were much smaller than here. This fact might be ascribed to the different ductility of both RE-alloys, which was already commented in the TEM results.

On the other hand, the temperature coefficient of resistance (TCR) (see Eq. 4.21) is independent of the bar section (geometry) and can account for whether a material is crystalline or amorphous. In our case, taking the (linear) high-temperature range, a value of \(TCR = -2.16\times10^{-4}\text{K}^{-1}\) is obtained. In conventional metals, the negative TCRs are related to high values of resistivity. This phenomenological fact was collected and proposed in the so-called Mooij’s correlation \([232]\). The extracted TCR YbAl\(_3\) value would mean that the \textit{real residual resistivity} should lie \(\rho \approx 300\mu\Omega\text{cm}\). For instance, the metallic glass \(Y_{0.45}Al_{0.55}\) with \(\rho_{300K} = 280\mu\Omega\text{cm}\) and \(TCR = -10^{-4}\text{K}^{-1}\) \([282]\). This can solely be referred as an indication as we have just commented the influence of the DOS hybridisation, altering the \(\rho(T)\) and TCR in the proximity of RT.

Let us now proceed with the thorough analysis respect to the astonishing existence of a minimum at \(T \approx 15\text{K}\). Minima in \(\rho(T)\) have been reported in crystalline metallic systems since the 30s \([36, 283]\), and have been later interpreted in terms of the well-known Kondo theory \([38]\) (see Chapter 2). Not surprisingly, in the early 70s, there was also evidence of a \(\rho(T)\) minimum in amorphous metals. The debate of the origin of the latter minima was controversial for a number of years until quantum interference theories \([233, 284, 285]\) were successfully applied in the interpretation. In the case of nanoparticle metallic systems, it is rather surprising that in spite of the strenuous efforts to understand the giant magnetoresistance phenomena
[286, 287, 288], much less experimental evidence and analysis of $\rho(T)$ has been delivered. In particular, recent reports in Fe$_x$M$_{100-x}$ (M = Au, Ag, Cu) films of Fe nanoparticles in a metallic matrix showed no resistivity minimum [76] whereas CoCu immiscible nanoparticle alloys do, here interpreted with the aid of a Kondo-like interaction [289]. It is facile to realise that the latter analysis is controversial but, on the plus side, rendering new fundamental physics.

In consequence, the whole curve will be deeply studied in the following in order to determine which interactions are playing a role. To analyse the origin of this minimum in $\rho(T)$ it was ought to measure the electrical resistivity in : (i) YbAl$_3$ milled for lower times (20 hours) and (ii) LuAl$_3$ milled for 70h, for reasons given below. The rationale behind this is to discuss all possible origins for the minimum, following a comprehensive appraisal.

The electrical resistivity for the 20h milled alloy is shown in Fig. 5.9, in order to check if the milling time affects the existence of the minimum. Visually, it seems to follow a Fermi-liquid variation. In this sense, when $\rho$ vs. $T^2$ is plotted, the variation is obeyed (see inset Fig. 5.9) but for very low temperatures ($T < 5K$), it can be observed that there exists a weak minimum ($T_{min} = 3.63K$) in the electrical resistivity. This minimum is shallow in comparison to that in YbAl$_3$ 70h. Thus, the contribution provoking the electrical resistivity minimum in YbAl$_3$ 20h is not as strong as in YbAl$_3$ 70h.

As mentioned above, the electrical resistivity of LuAl$_3$ 70h was also measured. It is neccessary to test whether the minimum is observed in a conventional metallic alloy of a similar structure. In this case, the curve is that of a typical metal, but curiously it also displays a minimum at $T \approx 15K$, again shallower than that in YbAl$_3$ 70h. Its residual resistivity, possesses also a large value, $\rho_{2K} = 1300\mu\Omega cm$, but an order of magnitude lower than in YbAl$_3$ 70h and similar to YbAl$_3$ 20h. The $TCR_{LuAl_3} = 3.84x10^{-4}K^{-1}$ (positive), indicating in this conventional metal that $\rho_{300K} \approx 1\mu\Omega cm$, according to the formerly mentioned Mooij’s correlation. This milled (70h) LuAl$_3$ alloy also results in a collection of nanoparticles (space group $Pm-3m$) with an average size $\langle D \rangle \approx 10nm$, as calculated by Rietveld refinements (see Fig. 5.11) ($R_B = 7.0\%$), keeping a similar lattice parameter ($a = 4.1892(1)\AA$) respect to that in the bulk alloy ($a = 4.191\AA$) [290].
Once the qualitative description is finished, we will start to analyse the YbAl₃ 70h and LuAl₃ 70h curves in order to elucidate which is the reason is for the electrical resistivity minimum appearance. Following Eq. 5.2, different contributions will be taken into account as follows:

\[
\rho = \rho_0 + AT^2 + B \left( \frac{T}{\theta_D} \right)^5 \int_0^{\theta_D} \frac{x^5 dx}{[e^x - 1](1 - e^{-x})}
\]

(5.3)

where the Fermi-Liquid (FL) scattering follows the \( T^2 \) and the electron-phonon term, including the Grüneisen-Bloch integral, evolves to \( \rho \propto T \) when \( T > \theta_D \) and to \( \rho \propto T^5 \) when \( T \ll \theta_D \). Finally, \( \rho_0, A \) and \( B \) are constants. If we try to fit our curves to this equation, we observe that it fits perfectly for most of the curve (\( T > 50 \)K) in LuAl₃ 70h (see Fig. 5.10), but at low temperatures there is a missing contribution providing the increasing resistivity when reducing the temperature, which Eq. 5.3 cannot reproduce, obviously (see bottom right inset of Fig. 5.10). In the case of YbAl₃ 70h it does not fit at all, due to the \( \rho \)-maximum appearing at \( \approx 125 \)K.

There exist several mechanisms that could provide a reasonable interpretation for the increase of the electrical resistivity at low temperatures for these alloys. We will first take into account changes in
the density of carriers, which are considered commonly in semiconducting materials. Then, following electron-electron interaction and weak localisation, there will be a study on the quantum interference effects which can be reminiscent of the Mott metal-insulator transition. Finally, an approach to quantify an eventual Kondo effect will be discussed as another extra (possible) source for electron localisation.

1. Semiconducting behaviour.

In semiconducting materials, the electrical resistivity can suffer large variations with temperature (for example, $\gtrsim 10$ orders of magnitude in Sb-doped Ge [291]). These variations in the intrinsic case, can be largely controlled by $E_g/K_B T$, the ratio of the band gap ($E_g$) to the temperature. When this ratio is large, the concentration of intrinsic carriers will be low and the resistivity will concomitantly grow. Hence, there is a mechanism for the existence of a minimum. The actual variation is usually taken as a simple exponential with $\rho \approx e^{E_g/2k_B T}$ [83, 291]. For this reason, we have plotted the LuAl$_3$ 70h and YbAl$_3$ 70h as...
Figure 5.11: Rietveld refinement of the XRD of the 70h LuAl\textsubscript{3}, using Cu-K\textsubscript{α} radiation. The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns. The nanoparticle structure (space group Pm-3m) is remarkably well reproduced ($R_B = 7.0\%$).

\[ \ln[\rho(T)] \text{ vs. } 1/T \] (see Fig. 5.12). It can be observed that none of both curves follow a straight line ruling out such an explanation. Moreover, in semiconductors, the voltage ($V$) vs. intensity ($I$) response is not ohmic and then, there exists tunneling at very low temperatures (below $T_{\text{min}}$). In the inset of Fig. 5.12 it is visible that $V$ vs. $I$ is absolutely ohmic ($R = 0.99985$) at $T = 2K$, below the minimum. This constitutes another clear-cut evidence to conclude that this mechanism is not the one governing the extra scattering of $\rho(T)$ at low temperatures. In other words, the mentioned ohmic behaviour is an overwhelming evidence for a metallic conductivity. This fact not only discards the semiconducting behaviour, but also eliminates the possibility of hopping conductivity, based on Mott metal-insulator transition, with an exponential dependence anyway [83].

2. Quantum interference effects.

An electrical resistivity minimum has been been widely observed in amorphous materials of high $\rho_0$ ($\gtrsim 80\mu\Omega\text{cm}$). As it was
shown in TEM images (see Fig. 5.5), our nanoparticles are not amorphous or surrounded by amorphous environments, but milling could have led to lattice strains and deformations, giving rise to a poorly crystallised environment at a very local range. Therefore, it would not be surprising to detect an influence in $\rho(T)$.

The $\rho(T)$ minima found in disordered metallic glasses in the early 70s [292] have been explained with the use of very different approaches. An experimental generalised interpretation [293] was supported by the existence of a 2-level system ($\approx -\ln(T^2 + \Delta^2), \Delta \equiv$ level splitting) which follows previous Anderson models [294]. The basic underlying idea is that there exists a tunneling effect between energy level in a double-well potential. The main advantage of this view was that it also explained the lack of influence in the minimum by the magnetic field.

In subsequent years, a definitive answer was encountered by applying the so-called quantum corrections to conductivity or,
more simply, quantum interference effects (QIE) [284, 285]. The use of QIE is understood by considering the extremely small mean-free paths associated to very high ρ₀ values, resulting in unphysical magnitudes below the interatomic distances. Thereby, the electrical transport could be likely diffusive rather than ballistic. QIE theories [284, 295] put forward two corrections, namely the electron-electron interaction (EEI) [296] and the weak localisation (WL) [297]. In the following, we will briefly comment on both effects. Assuming the existence of EEI, Altshuler and Aronov [296] described the modification of electronic potentials which effectively alter the density of states at the Fermi level. The correction to conductivity (σ) was derived as:

\[
\Delta \sigma_{ee} = \frac{1.3}{\sqrt{2}} \frac{e^2}{2\pi h} F_0 \sqrt{\frac{2\pi k_B T}{\hbar D'}}
\]

where \( D' = \frac{V_F^2}{2} \) is the diffusion constant, in terms of the Fermi velocity \( v_F \) and the relaxation time \( \tau \). \( F_0 \) is a screening term which turns to \( 4/3 \) in the case of the absence of an applied magnetic field. Experimental reports revealing the \( \rho \propto -\sqrt{T} \) dependence have been extensively published for disordered metals [295, 298, 299]. On the other hand, the electron wave propagation, away from a classical interpretation, allows a variety of paths with the existence of loops of interference between the electron waves giving rise to a factual localisation. If all particles returned back to the origin, then \( \rho \rightarrow \infty \) and the full localisation would be achieved. In a less restricted WL regime, the electrons are not entirely bounded by the scattering probability and a finite increase of \( \rho \) is expected. With the aid of assumptions by Kaveh and Mott [300] and Howson [285] calculations, a generalised expression for \( \rho(T) \) has been provided. An asymptotic extrapolation results in \( \rho(T) \) to some power of \( T \) dependence on the spin-orbit and inelastic scattering lifetimes [298]. Hence, both EEI and WL introduce an extra scattering term which is temperature dependent. However, it has been shown that at zero magnetic field, the QIE are dominated solely by the EEI correction [301].

An ideal approach to determine the influence of QIE is then to include \( \rho \propto -\sqrt{T} \) which should be added to Eqn. 5.3:

\[
\rho = \rho_0 + A T^2 + B \left( \frac{T}{\theta_D} \right)^5 \int_0^{\theta_D} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} - C \sqrt{T} \quad (5.5)
\]
where $C$ is a constant. However, in LuAl$_3$ 70h the $\rho(T)$ minimum is weak, and then it has not been possible to fit, with Eq. 5.5 the whole curve (2-300K), taking into account the low temperature region ($T < 20$K). Therefore, we will first fit the high temperature region ($T > T_{\text{min}}$) to Eqn. 5.3 (without the QIE term) to obtain $\rho_0$, $A$, $B$, and $\theta_D$, and then subtract this curve from the experimental data. Later, this subtraction, representing $\rho_{\text{TOTAL}} - \rho_{\text{FL}} - \rho_{\text{ph}} - \rho_0$, is plotted against $\sqrt{T}$ in order to check whether it follows or not a straight line. Left inset of Fig. 5.10 shows the mentioned subtracted resistivity as a function of $\sqrt{T}$. It is clearly observed that it is possible to fit a linear variation supporting experimentally that the mechanism related to the electrical resistivity minimum in LuAl$_3$ is the weak localisation or electron-electron interaction, i.e. the quantum corrections. In the case of YbAl$_3$ 20h, it is not possible to fit the low temperature region, as $T_{\text{min}} = 3.63$K and there are no enough data points at $T < T_{\text{min}}$ to provide an unambiguous result. Therefore, no more analysis on this alloy will be presented.

By contrast, the minimum in YbAl$_3$ 70h is perfectly defined and we can attempt to fit to Eq. 5.5 directly on the minimum region ($T < 45$K), where the high temperature maximum contribution could be considered negligible. In Fig. 5.13, an example of a fitted curve is presented along the experimental data (blue line). Clearly there is a lack of agreement for a combination of parameters which describe well the $T > T_{\text{min}}$ but fail to explain the increasing $\rho(T)$ for $T < T_{\text{min}}$. The study has involved the sampling of the different parameters choosing a variety of initial values to minimise the possibility of landing onto local minima in the error function ($\chi^2$). The algorithm was performed with an in-house integral program using the Levenberg-Marquardt approach and the ProFit commercial software. The outcome of these efforts is that an extra contribution is required to account for the experimental data.


Another possible cause may rely on the existence of a contribution stemming from the Kondo effect. Within this interpretation,
the electrical resistivity $\rho \propto \ln(T)$. In consequence, the Kondo term is included in the following expression:

$$
\rho = \rho_0 + AT^2 + B \left( \frac{T}{\theta_D} \right)^5 \int_0^{\theta_D} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})} - C\sqrt{T} - D\ln T
$$

where $D$ is the constant of the logarithmic dependence.

![Figure 5.13: Electrical resistivity of the YbAl$_3$ 70h alloy, together with the fit to the Eqn. 5.6 ($\chi^2 = 1.26 \times 10^{-10}$). The blue curve shows an unsuccessful fit to Eq. 5.5.](image)

As it has been commented previously, the $\rho(T)$ curve of YbAl$_3$ exhibits a hump at high temperatures, $T \approx 125K$. For this reason, we will restrict the range of fit (ROF), with an upper limit far from this maximum, and up to $\approx 2T_{\text{min}}$. This enables a long enough ROF in order to achieve a reliable result. In these conditions, a remarkably good fit is exhibited in Fig. 5.13. The values for the set of the 6 parameters include: $\rho_0 = 1.6039(1) \times 10^{-2} \Omega \text{cm}$, $A = 1.329(5) \times 10^{-11} \Omega \text{cmK}^{-2}$, $B = 4.0(2) \times 10^{-2} \Omega \text{cmK}^{-5}$, $C = 1.0694(6) \times 10^{-5} \Omega \text{cmK}^{-1/2}$, $D = 4.15(3) \times 10^{-5} \Omega \text{cm}$ and $\theta_D = 50(5)K$. The error function gives a small $\chi^2 = 1.26 \times 10^{-10}$. The number of free parameters is admittedly numerous but we have to stress that it has resulted the only successful methodology to reproduce the whole temperature range. In this sense, it is worth noting that it is a seldom finding to account for the whole
minima variation; in a vast number of reports, the analysis is restricted to either side (branch) of the minimum [299, 301, 302, 303]. Had it been an addition of different contributions without justified physical meaning, the validity of the results could be questioned. By contrast, our rationale has allowed to establish the importance and role of the contributions for the electronic scattering in Eq. 5.6.

Without trends handed in by the use of several samples, it is hard to evaluate the contribution from each term. Nevertheless, it looks clear that the electron-phonon scattering is a major source in comparison with the rest of terms. In addition, the $\theta_D$ value ($\theta_D = 50K$) is quite low, compared to other intermetallic compounds, such as CuAu ($\theta_D = 220K$ [304]), ThNi5 ($\theta_D = 365K$ [305]) or TbNi2 ($\theta_D = 262K$ [306]). Moreover, the value of the Debye temperature for the bulk YbAl3 found in literature is $\theta_D = 257K$ [307]. Therefore, $\theta_D$ has considerably decreased with the milling process. Such a reduction can be connected with a decrease of the bonding strength of the vibrating atoms, which is expected, considering that the (surface) atomic coordination in an ensemble of nanoparticles is certainly diminished. Indeed, a microscopic evidence for the changes in the phonon spectrum in nanostructures is reflected in a modified density of states, as reported in Ref. [308]. Following the nano-TbCu2 particles discussion presented elsewhere, it should be reminded the onset of a peak around 50K in the $C_p$ in nanoparticles, confirming strong modifications in the vibration spectrum [98].

Regarding the contributions which increase $\rho(T)$ for $T \rightarrow 0$, both QIE (C-coefficient) and the Kondo interaction (D-coefficient), in Eq. 5.6, display a similar importance. The first contribution is a logical continuation of the finding for LuAl3 70h and YbAl3 20h; there is a quantum behaviour in the electronic conduction due to high degree of disorder, as was thoroughly discussed earlier. On the other hand, a couple of considerations should be brought to the fore as a final evaluation respect to the Kondo interaction.

An issue to evaluate is the possible presence of magnetic impurities in the milled YbAl3 alloy which could give rise to a $\rho$-minimum. This question has been addressed by milling a
bulk YbAl$_3$ alloy in ZrO$_2$ containers. These containers are naturally free of metals and were immaculate before attempting any milling. It should be reminded that the WC containers were used for the samples so far discussed. Under similar milling conditions, after $t = 10\text{h}$ and with YbAl$_3$ nanoparticles (ZrO$_2$) of $D \approx 10\text{nm}$, it was possible to detect an electrical resistivity minimum at low temperatures ($T \approx 4\text{K}$) and the maximum around 150K (see Fig. 5.14) is still present as well. In short, apart from some modification in the magnitude of the scattering, the general features of YbAl$_3$ are maintained. Hence, the experimental evidence in a magnetic impurity-free environment confirms the existence of the minimum as an intrinsic feature.

![Figure 5.14: Electrical resistivity of the 10h YbAl$_3$ alloy, milled in a ZrO$_2$ container. Inset: low temperature region of the electrical resistivity, where a minimum is detected.](image)

The outcome of the former discussion is that the experimental evidence is explained by both QIE and Kondo interaction, which act simultaneously. The milling of the bulk YbAl$_3$ results in an ensemble of nanoparticles randomly dispersed and in contact, forming a granular alloy. On the one hand, the nanometric size of the particles favours the presence of surface shells in which the atomic coordination is reduced whereas the microstrain is enhanced. This results, as in the case of nano-TbCu$_2$, in a subtle core-shell structure. For the nano-TbCu$_2$ this appropriate arrangement of spherical particles gives rise to a change in the
magnetic state with AFM moments in the core and SG moments in the outer shell. Here, we have a parallel situation which incides in the electronic structure rather in the magnetic state as YbAl$_3$ is a non magnetic IV alloy. In consequence, firstly, the nanoparticles are connected by a disordered interface which is a result of the combined external shells of each particle. In this situation the nanostructure becomes more and more disordered, affecting the electrical resistivity. Therefore, such a high disorder is the basic element supporting the QIE.

Now we turn the attention to the supplementary Kondo interaction. In bulk YbAl$_3$, the $f$-electron atoms are forming a periodic array which lie in the so-called Kondo lattice systems, as in single crystal Yb$_3$Ni$_{15}$Al$_{19}$ [309]. If by chance there is a parameter favouring the transition to a more dilute situation respect to the Yb-ions, the Kondo interaction becomes modified and a single impurity approach explains the electronic state [267, 310]. It has been shown that the reduction of size in nano-YbAl$_3$ promotes the ion valence reduction as a consequence of the increasing atoms located at the surface (Yb$^{2+}$) [15]. In Ce-based alloys [311], this situation is interpreted (mirror-like) as an opposite effect and with the aid of the Doniach diagram [44], a qualitative picture can be traced out. In Yb-alloys, the Doniach diagram is less indicative but in any case, our finding would mean that the nanometric system is moving towards an increased Kondo interaction (that is, moving rightwards in the diagram). Irrespective of this qualitative interpretation, what is clear is that by reducing the size, the minimum is appearing as a single impurity effect. A reasonable interpretation is then put forward as follows: the electronic shell is forming a disordered interface which contributes to a randomisation and a reduction of the core influence, hence breaking down the Kondo lattice coherence. The consequence is that there exists a factual increase of disorder and, as always happens in the electronic conduction, there is a concomitant increase of resistivity. Thus, the presence of an extra low $T$ scattering is favoured. As a matter of fact, this situation resembles the cases in which by adding non-magnetic rare-earh atoms (Y and La for Ce-based and Lu for Yb-based compounds) there is a dilution of the alloys with an evolution from a Kondo ferromagnet to intermediate valence; this is the case of Ce$_x$Y$_{1-x}$Ni$_{0.8}$Pt$_{0.2}$, where for $x = 1$ the resistivity shows
5.3 Transport Properties

a ferromagnetic transition at $T_C$, visible as a change of slope in $\rho(T)$, and at $x = 0.5$, a minimum is observed at $T \approx 15K$ [312]. In Yb$_x$Lu$_{1-x}$Al$_3$ alloys it has been confirmed the sensitivity of the coherence of the Kondo lattice effects [310] and confirmed by X-ray photoelectron spectroscopy. In short, it seems that the size is again a magnificent driving parameter now for the electronic changes. In this sense and to extend the universality of the former assert, it is widely known that particles of noble metals at the nanocrystalline state can suffer serious changes in the DOS as have been recently reported [313, 314, 315]. Therefore, our finding is naturally connected with a more general physical situation.

5.3.1.1 Magnetoresistance: Effect of the magnetic field.

The analysis of magnetoresistance is an important tool which is used to extract quantitative information on the fine details of the QIE in disordered alloys [299, 316]. Such details are connected to the evaluation of inelastic-scattering relaxation time and the spin-orbit time, both playing an important role in the electron conduction. Generally speaking it requires a very detailed work to be in a position to distinguish unambiguously between those time parameters. However, it is feasible to provide supplementary information on whether the EEI or WL is the leading origin for the extra scattering due to disorder. In the following, we will present experimental evidence to select the most plausible explanation.

The magnetoresistance (MR) of the 70h YbAl$_3$ milled alloy is presented in Fig. 5.15. The MR is small (up to 0.4%) and positive for every temperature below 50K. Above this temperature, MR becomes flat. As it has been commented above, the $-\sqrt{T}$ term that we have included in the fit of the $\rho(T)$ for both milled LuAl$_3$ and YbAl$_3$ is related to the quantum corrections.

The WL and EEI contributions to the total quantum corrections can be distinguished if a magnetic field is applied since the localisation effect should be suppressed by a certain field $H > H_{\text{crit}} = \frac{\hbar c}{2el^2}$ ($l \equiv$ elastic free path) [317]. We can then evaluate both contributions through the fit of the magnetoresistance. If:

$$MR = \frac{\rho(T, H) - \rho(T, 0)}{\rho(T, 0)}$$  \hspace{1cm} (5.7)
Figure 5.15: Magnetoresistance curves for the 7th YbAl$_3$ milled alloy. The low and high field dependence are shown in the left inset for the curve at T=2K. Right inset: low temperature region of the electrical resistivity for the YbAl$_3$ 7th, with magnetic fields H = 0T (black) and H = 5T (red). The $\rho$-minimum is shifted to higher temperatures with increasing magnetic fields.

can be fitted to $H^2$ (for low fields) and $H^{1/2}$ (for high fields) then the result is in good agreement with the predictions of a major influence of the electron-electron interaction effects [296]. This difference between low and high fields is given by $H_{\text{crit}}$ and is frequently taken $H \approx 1T$ [302].

In our case, we can fit the low and high field regions of the MR to $H^2$ and $H^{1/2}$ respectively, as shown in the inset of Fig. 5.15, at $T = 2K$, with a very good result (for both regions $R > 0.98$). This result is similar to that found in the non-magnetic amorphous (Ni$_{0.5}$Zr$_{0.5}$)$_{1-x}$Al$_x$ alloy [302] and explains the MR behaviour at low temperatures satisfactorily in terms of the electron-electron interaction effects. Another indication of the nature of the low scattering terms can be derived from the inspection of $\rho(T)$ at $H = 5T$. Inset of Fig. 5.15 shows the influence of the field in the shape of $\rho(T)$. It can be seen that the $T_{\text{min}}$ shifts slightly upwards. It is well-known that the magnetic field suppresses the Kondo minimum and therefore the described modification should be ascribed to the EEI contribution.
To summarise, the overall scrutiny of the electrical resistivity in nano-YbAl$_3$ has revealed the presence of a low temperature minimum which is due to the combined effect of electron-electron interaction and favoured by the presence of a disordered collection of nanoparticles, which also trigger a change of regime from a Kondo-lattice to a single impurity behaviour.
CONCLUSIONS

The production of nanometric RE-alloys has provided evidences of novel magnetic arrangements and modifications in the electronic state. This has been possible thanks to a careful selection of samples, namely TbCu$_2$ with an ordering temperature below RT (in contrast with usual 3$d$-compounds) and YbAl$_3$ close to electronic instabilities due to its IV character.

Among the most relevant results we can indicate:

- Tb- and Yb-based nanometric RE-intermetallic alloys have been produced by high-energy planetary ball milling. The required grinding time to reach a nanometric size strongly depends on the particular alloy, from 0.5h for TbCu$_2$ ($D \approx 23\text{nm}$) to 20h in YbAl$_3$ ($D \approx 10\text{nm}$) as revealed by (in-house and synchrotron) XRD and TEM. The lowest particle size achieved is $D \approx 6\text{nm}$ for TbCu$_2$ and $D \approx 10\text{nm}$ for YbAl$_3$.

- A nano-TbCu$_2$ series has been produced. A superantiferromagnetic state has been established in these nano-TbCu$_2$. This coexists with a spin-glass behaviour, at low temperatures. Neutron diffraction has unambiguously confirmed the local and macroscopic magnetic arrangements. The SG state, not present in the bulk alloy, roots its origin in the spin disorder at the shell of the nanoparticles. When the milling time is increased, i.e. the particle size is lowered, the antiferromagnetic arrangement tends to disappear, leading to a much more pronounced SG behaviour. For longer milling times ($t \geq 10\text{h}$), the AFM transition in the DC-susceptibility is practically absent. The nano-TbCu$_2$ particles are understood to contain an AFM core surrounded by a shell of disordered spins. The core/shell ratio decreases with longer milling times. As the particle size decreases, the antiferromagnetic Néel transition temperature $T_N$ shifts down to lower $T$ whereas the freezing temperature $T_f$, corresponding to the onset of the spin-glass behaviour, appears at higher $T$. 
• The metallic behaviour has been confirmed by the electrical resistivity, in which the magnetic contribution to $\rho(T)$ decreased for longer times as a consequence of the interfacial disorder.

• The PM $\rightarrow$ AFM $\rightarrow$ SG reentrant phase constitutes a very attractive and barely studied landscape. A magnetic phase diagram is proposed, in which the variation of both $T_N$ and $T_f$ are key landmarks, and the states PM, SAFM and SAFM+SG have been distinguished.

• The magnetic characterisation of YbAl$_3$ fine particles turned out in the typical curve for an intermediate valence compound. A broad maximum is evident whose magnitude was decreased for longer milling times.

• A maximum in the electrical resistivity of nano-YbAl$_3$ is observed around 125K. Its interpretation could be associated to the modification of the carriers density, due to the interband transitions across the gap, in the density of states, and to a coherence effect appearing in Kondo lattice systems. Furthermore, the electrical resistivity shows a thrilling minimum at low temperatures. The most plausible interpretation is a combination of Quantum Interference effect (electron-electron interaction) in the electronic conduction, due to the disorder induced by milling and a Kondo-like interaction as a result of the hybridisation enhancement of the 4f-shell and the Fermi level. Moreover, an interface is created as a consequence of milling. This interface corresponds to a shell of atoms with a major Yb$^{2+}$ atomic coordination, instead of the intermediate valence of the core. Therefore, the core of the particles could see the system as diluted, evolving from a Kondo lattice to a Kondo single impurity.

In consequence, the production of well-characterised nanoparticles of rare-earth alloys opens up a relatively unexplored path in which magnetic and electronic arrangements, out of reach in bulk state, are modified in a controlled manner.
CONCLUSIONES

La producción de aleaciones nanoestructuradas de tierras raras ha proporcionado evidencias de nuevos órdenes magnéticos y modificaciones en el estado electrónico de estos materiales. Esto ha sido posible gracias a una cuidadosa selección de muestras como ocurre en el TbCu$_2$, con una temperatura de orden por debajo de la temperatura ambiente (en contraste con lo que pasa en los habituales compuestos formados por metales 3d) y el YbAl$_3$, cuyo carácter como aleación de valencia intermedia hace que se encuentre cerca de fenómenos asociados a inestabilidades electrónicas.

Entre las conclusiones más relevantes podemos destacar:

- Se han producido aleaciones nanométricas de tierras raras basadas en Tb e Yb mediante molienda mecánica en un molino planetario de bolas. El tiempo requerido para la obtención de nanopartículas depende fuertemente del material en sí; 0.5h para TbCu$_2$ ($D \approx 23\,\text{nm}$) y 20h para YbAl$_3$ ($D \approx 10\,\text{nm}$), tal y como revelan la difracción de rayos X (en el laboratorio y en sincrotrón) y la microscopía electrónica de transmisión TEM. El menor tamaño obtenido es $D \approx 6\,\text{nm}$ para TbCu$_2$ y $D \approx 10\,\text{nm}$ para YbAl$_3$.

- Se ha producido una serie de nano-TbCu$_2$. Se ha establecido un estado superantiferromagnético (SAFM) en esta serie nano-TbCu$_2$. Este SAFM coexiste con un comportamiento tipo vidrio de espín (spin glass, SG) a bajas temperaturas ($\leq 10\,\text{K}$). La difracción de neutrones ha confirmado inequívocamente el orden magnético local y macroscópico. Esta fase de vidrio de espín no está presente en el compuesto masivo y tiene su origen en el desorden de los espines de la superficie de las partículas. A medida que aumenta el tiempo de molienda (esto es, que disminuye el tamaño de partícula), el orden antiferromagnético (AFM) tiende a desaparecer dando lugar a un incremento de la contribución de vidrio de espín, hasta llegar a $t \approx 10\,\text{h}$, cuando ya no se detecta orden AFM en la susceptibilidad magnética. Entendemos,
por tanto, nuestras partículas como un núcleo AFM rodeado de una capa de espines desordenados. La proporción núcleo/superficie va disminuyendo con la molienda. A medida que el tamaño de partícula disminuye, la temperatura de la transición AFM (temperatura de Néel, $T_N$) se desplaza a menores temperaturas mientras que la temperatura de congelación, $T_f$, correspondiente al comportamiento de vidrio de espín, se desplaza hacia una temperatura mayor.

- El comportamiento metálico de la serie de nano-TbCu$_2$ ha sido confirmado mediante la medida de la resistividad eléctrica, cuya contribución magnética disminuye a medida que aumenta el tiempo de molienda.

- La fase reentrante PM $\rightarrow$ AFM $\rightarrow$ SG en nano-TbCu$_2$ constituye un sistema muy atractivo y poco estudiado. Se propone un diagrama de fases magnético en el que se muestra la dependencia de las temperaturas de orden AFM y de congelación del SG, $T_N$ y $T_f$, respectivamente, en función del tamaño de partícula. Asimismo, se han diferenciado los estados PM, SAFM y la coexistencia de SAFM y SG.

- La caracterización magnética de las nanopartículas de YbAl$_3$ ha mostrado la típica curva de un compuesto de valencia intermedia, como es el YbAl$_3$ masivo. Aparece un ancho máximo en la susceptibilidad, cuya magnitud decrece en las moliendas más prolongadas.

- Se observa un máximo en la resistividad eléctrica de la serie nano-YbAl$_3$, en aproximadamente 125K, cuya interpretación podría estar asociada a la modificación de la densidad de portadores de carga, debido a transiciones interbanda a través del *gap* en la densidad de estados, y a un efecto de coherencia que aparece en sistemas de Kondo red. Además de observar un mínimo en la resistividad eléctrica. La interpretación más plausible es una combinación de efectos cuánticos de interferencia (interacción electrón-electrón) en la conductividad electrónica (devido al desorden inducido con la molienda) y de una interacción tipo Kondo que también aumenta con la molienda, como consecuencia del aumento de la hibridación entre el nivel de Fermi y la banda 4f. Además, al moler creamos una interfase entre las partículas que se corresponde con la corteza de átomos que fa-
vorece la configuración electrónica Yb$^{2+}$, en lugar de la valencia intermedia del núcleo (la misma que el compuesto masivo). De esta manera, se podría entender que los núcleos de las partículas ven el sistema como diluido y entonces se pasa de un *Kondo red* a un *Kondo impureza*.

En consecuencia, la producción y caracterización de aleaciones de tierras raras nanoestructuradas abre un camino relativamente inexplorado en el cual los órdenes magnéticos o estados electrónicos pueden verse modificados de una manera controlada.
A.1 Rietveld Method. Fullprof Suite.

The Rietveld method allows the refinement of crystallographic and/or magnetic structures by a fit of the complete profile of the experimental powder diffractograms (either X-ray or neutrons) to a theoretical profile that is modeled by the equation A.1:

\[ y_{ci} = \sum_{\phi} S_{\phi} \sum_{\vec{h}} I_{\phi,\vec{h}} \cdot \Omega \left( 2\theta_{i} - 2\theta_{\phi,\vec{h}} \right) + y_{bi} \]  \hspace{1cm} (A.1)

where the subindex \( \phi \) represents the phase and varies from 1 and the number of existence phases in the model; \( \vec{h} = \vec{H} + \vec{k} \); \( S_{\phi} \) is the scale factor of the phase \( \phi \); \( \Omega \) is the function that models the instrumental and the sample effects (gaussian, lorentzian ...). \( y_{bi} \) is the background intensity in the position \( i \) and:

\[ I_{\phi,\vec{h}} = (L \cdot F^{2} \cdot A \cdot T \cdot P \cdot C)_{\phi,\vec{h}} \]  \hspace{1cm} (A.2)

is the integrated intensity, where \( L_{\phi,\vec{h}} \) contains the Lorentz, polarisation and multiplicity factors; \( F_{\phi,\vec{h}} \) is the structure factor; \( A_{\phi,\vec{h}} \) is the asymmetry function; \( T_{\phi,\vec{h}} \) is the transmission factor; \( P_{\phi,\vec{h}} \) is preferential orientation function; and \( C_{\phi,\vec{h}} \) is correction defined by the user.

The structure factor \( F_{\phi,\vec{h}} \) relates the intensity with the atomic order in the unit cell. So, the expression for this parameter would be defined by:

\[ F_{\phi,\vec{h}} = \sum_{l=1}^{n.o.at.} O_{l} b_{l} \exp \left( -B_{l} \frac{\sin^{2} \theta_{\vec{h}}}{\lambda^{2}} \right) \sum_{s=1}^{m} T_{ls}(\vec{r}) \exp \left[ 2\pi i \left( \vec{r}^{T}(g|\vec{t})_{s} \vec{r}_{l} \right) \right] \]  \hspace{1cm} (A.3)

where \( O_{l} \) is the occupation factor, \( \vec{r} = (x_{l}, y_{l}, z_{l}) \) is the position vector for the atom \( i \) in the elementary cell; \( \vec{h} = (h, k, l) \) are the reflection Miller indices; \( b_{l} \) is the Fermi or scattering length for the neutron diffraction, depending on the isotope but not on the atom (for XRD,
this parameter coincides with the scattering atomic factor). \( B_i \) is the Debye-Waller factor (Å\(^2\)); \( m \) is the number of symmetry operators of a certain spatial group; and \((g\vec{t})_s\) is a symmetry operator.

We will define:

\[
T_i(\text{iso}) = \exp\left(-B_i \frac{\sin^2(\theta \vec{h})}{\lambda^2}\right) \tag{A.4}
\]

as the isotropic temperature factor. The anisotropic temperature factor will be defined by:

\[
T_i(\vec{h}) = \exp\left(-\vec{h}^T S_s \beta_i S_s^T \vec{h}\right) \tag{A.5}
\]

where \( \beta_i \) represents the anisotropic temperature parameters of the atom \( i \).

For a magnetic material, the resulting intensity coming from the nuclear (depending only on the nature and position of the scattering centers) and magnetic contributions (depending on the magnetic moment position and orientation with respect to the crystallographic axis) are additive only if the incident neutron beam is not polarised. If we consider only periodic spin configurations, the magnetic moment of the atom \( i \) in the cell \( s \) (\( \vec{R}_{i,s} = \vec{R}_S + \vec{r}_i \)) can be written as a Fourier series expansion:

\[
\vec{\mu}_{i,s} = \sum_{\vec{k}} \vec{S}_{\vec{k}i} \cdot \exp\left(-2\pi i \vec{k} \cdot \vec{R}_s\right) = \sum_{\vec{k}} \vec{T}_{\vec{k}i} \cdot \exp\left(-2\pi i \vec{k} \cdot \vec{R}_{i,s}\right) \tag{A.6}
\]

where \( \vec{R}_s \) is a whole translation of the direct lattice and \( \vec{r}_i \) is the position of the atom \( i \) inside the elemental lattice. Due to the fact that both magnetic and crystalline periodicities are not necessarily coincidental, the propagation vector \( \vec{k} \) does not have to be a whole vector of the reciprocal lattice, though it can be restricted to the first Brillouin zone since \( \exp\left[i \left( \vec{\vec{k}} + \vec{H}\right) \cdot \vec{R}_s\right] = \exp\left(i \vec{k} \cdot \vec{R}_s\right) \), with \( \vec{H} \) a whole vector of the reciprocal lattice.

The total structure factor, \( F_{\vec{h}} \) is determined through the expression proposed by Halpern and Johnson [318]:

\[
\vec{F}_{\vec{h}}^2 = \left| \vec{F}_{\perp}(\vec{h}) \right|^2 = \left| \vec{F}_{m\vec{h}}(\vec{h}) \right|^2 - \left| \vec{eF}_{m\vec{h}}(\vec{h}) \right|^2 \tag{A.7}
\]
where $\vec{e}$ is a unitary vector along the $\vec{h}$ direction and $\vec{F}_{m\vec{h}}$ is the magnetic structure factor, used in FullProf Suite and defined by:

$$
\vec{F}_{m\vec{h}} = p \sum_{i=1}^{n.o.a.t.} O_i f_{ih} T_i(\text{iso}) \sum_s R_{is} \vec{S}_{ki} T_{is}(\vec{h}) \cdot \exp \left\{ 2\pi i \left[ \vec{h} \cdot (g|\vec{t}|) s \vec{r}_i - \psi_{kis} \right] \right\}
$$

(A.8)

where $p = (r_e\gamma/2) = 0.2695$; $\vec{h} = \vec{H} + \vec{k}$ is the scattering vector; $f_{ih}$ is the magnetic form factor that describes the spatial distribution of the magnetic moment carrier electrons; the sum on $s$ is related to the different symmetry operators of the spatial group that the crystal nuclear structure belongs to ($g$ and $t$ are rotation and translation operators, respectively); $R_{is}$ is the matrix that transforms the coefficients of the Fourier series expansion of the magnetic moment $S_{k,i}$ of the first atom $il$ to the atom $is$ in the position $i$; $\psi_{kis}$ is a phase factor that consists of two components, $\psi_{koi} = \phi_{kis} + \Phi_{kis}$, in which the first of them is defined by the symmetry and the second one is refifiable and only is significative for an independent set of magnetic atoms between them. Thereby, the Fourier component $S_{k,ki}$ of the magnetic moment of the atom $i$ in the cell $s$ is defined by:

$$
\vec{S}_{kis} = R_{is} \vec{S}_{kli} \cdot \exp (-2\pi i \phi_{kis})
$$

(A.9)

The matrices $R_{is}$ and the phases $\phi_{kis}$ can be derived from the atomic base functions that correspond to the irreducible representation of the group $G_k$ related to the propagation vector $\vec{k}$.

In general, $\vec{S}_{k,li}$ will be a complex vector with six components. These components constitute the parameters to be refined from the diffraction data. The symmetries may allow to reduce the number of free parameters to determine.

The value not only of this propagation vector $\vec{h}$ but also of the Fourier coefficients (accessible in a diffraction experiment) will let determine the different magnetic structures present in a crystal. Therefore, for a ferromagnetic structure, the propagation vector $\vec{k} = 0$, while $\vec{k} \neq 0$ for a uncommensurable structure.

It is important to note that the expression in Eq. A.7 indicates that the magnetic intensity is proportional to the square of the projection of the structure factor on the perpendicular plane to the scattering vector $\vec{h}$ (Fig. A.1)
Finally, the fit of the structural and magnetic parameters in FullProf is performed minimising the Eq. A.10:

$$\chi^2 = \sum_i \omega_i (y_{\text{obs},i} - y_{\text{cal},i})^2$$  

(A.10)

where $\omega_i$ is the inverse of the variance related to the observed intensity, $y_{\text{obs},i}$ in the position $i$. The accordance factor between the experimental and the calculated pattern is given, amongst other, by the minimisation of the Bragg factor, $R_B$, defined by:

$$R_B = 100 \frac{\sum_i |y_{i}^{\text{obs}} - y_{i}^{\text{cal}}|}{\sum_i |y_i^{\text{obs}}|}$$  

(A.11)

A.2 GENERAL DISPOSITIONS ABOUT FULLPROF SUITE

Although the foundations in which Rietveld method is based are rock solid, the correct use of this technique by FullProf Suite requires a special care since it employs a refinement by least squares, that can easily fall into false or local minima. Moreover, due to the correlation that exists between several parameters of this model, this can easily diverge in the first steps of the refinement. The FullProf Suite has been designed specifically to resolve these problems and there are two ways to do this.

A.2.1 Profile Matching

This procedure does not require any structural information except an approximate value of the lattice parameters. With this option, we can remove any contribution of the motif to the structure providing...
a much simpler data treatment and spreading considerably out the
application field of the powder pattern patterns.

To fit our data with this Profile Matching, with a constant scale factor,
it is only necessary to give (as long as it is possible) proper lattice parameters,
propagation vectors (only in the case of magnetic structure refinement),
asymmetries ...

### A.2.2 Simulated Annealing

FullProf has also developed a method to perform refinements of integrated
intensities of powder patterns. The Simulated Annealing mode
does not need any information about the profile, increasing considerably
the possibilities of FullProf as an analysis tool. The file of the
integrated intensities of the powder pattern is generated as a result
of the previous mode, and its fit is not performed making use of the
least squares algorithm but the Montecarlo one from an initial config-
uration.

This mode eliminates the problem of the divergence and it is very
useful for the uncommensurable magnetic structure refinement, in
which the high number of parameters to be varied makes the Rietveld
refinement very complex.

### A.3 Microstructure Analysis by FullProf

In order to determine the sample microstructure through the Bragg
diffraction peaks profile, associated to a certain crystalline structure,
it is necessary to separate first the instrumental contribution, \( g(x) \),
and the intrinsic function, \( f(x) \), from the total observed profile, \( \Omega(x) \).
Cagliotti (1958) \[319\] established the Bragg peaks profile of a ND
pattern, measured in a low-resolution diffractometer, as a Gaussian
function, in which the full width at half maximum (FWHM) varied,
with the \( \theta \) diffraction angle, as:

\[
\text{FWHM}^2 = Utan^2\theta + Vtan\theta + W
\]  

(A.12)

where \( U \), \( V \) and \( W \) are the Cagliotti parameters. However, the Bragg
peaks in the XRD pattern showed a more Lorentzian profile, with a
Figure A.2: Rietveld refinements of the XRD patterns of LaB$_6$ in our Bruker D8 Advance diffractometer with Cu-K$_\alpha$ (a) or Mo-K$_\alpha$ (b) radiations. The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns.

strong asymmetry at low angles and the FWHM presented a variation that could only be fitted to Eq. A.12 if the term $Z/\cos^2\theta$ was added. Thus the Voigt function [320] is the convolution of both Gaussian and Lorentzian functions, defining the instrumental contribution.

Several studies have been performed in order to obtain the instrumental function theoretically, but there exists an easy and practical method to determine experimentally this function depending on our diffractometer characteristics. An ideal sample, with no microstructure (so its instrinsic function $f(x)$ can be approximated by a Dirac delta) is chosen. Thus, the observed powder diffraction pattern of this standard sample, $\Omega(x)$, will coincide with the instrumental function $g(x)$. In our case, the standard sample is LaB$_6$ (Alfa Aesar, 99.5%), usually used for the calibration of the Bragg peaks profile. This material is annealed in order to eliminate inner strains and, afterwards, sieved by a filter of 15$\mu$m. Its crystalline structure (see Fig. A.2) belongs to the spatial group $Pm\bar{3}m$ and the lattice parameter is $a = 4.15692(1)\text{Å}$, as published by NIST [321].
Fig. A.2 presents the XRD patterns of LaB$_6$, measured at RT with both Cu-Kα (a) and Mo-Kα (b) radiations. The diffractograms have been analysed using the FullProf Suite program, where those parameters related to the diffractometer ($U, V, W, X, Y, Z$) have been allowed to vary, keeping those related to the sample constant (lattice parameter, atoms positions ...). The resulting instrumental parameters are saved in an instrumental resolution file (.IRF). This procedure has to be repeated from time to time, as this values can slightly vary with the use of the diffractometer (monochromator, slits ...).

The effects of the sample microstructure on the broadening of the Bragg peaks have been studied from, practically, the beginning of the diffraction theory, when Paul Scherrer (1918) observed a broadening of the Bragg peaks related to the crystallite size [322]. This study was developed afterwards by Stokes and Wilson [323] who established that this broadening by a size effect, $\beta_S$, is related to the crystalline mean size $\langle D \rangle$, by the Scherrer formula:

$$\beta_S = \frac{\lambda}{\langle D \rangle \cos \theta} \quad (A.13)$$

where $\lambda$ is the used wavelength in the diffraction experiment. On the other hand, the distortion produced by the atom positions fluctuations leads additionally to a broadening, from Bragg law:

$$\beta_D = k \epsilon \tan \theta \quad (A.14)$$

where $k$ is a constant that depends on the definition used for microstrain (for example, from residual strain coming from the presence of defects in the lattice).

From the different dependences on the diffraction angle $\theta$ in both effects, the two contributions can be separated in the $f(x)$ function. Moreover, at first sight we can know if a peak is broadened by size or distortion, as their profiles are Lorentzian or Gaussian, respectively.

The microstructure analysis, through the diffractograms, was performed by the FullProf Suite program, using the Thompson - Cox - Hastings Voigt profile [106].
A.4 Determination of Magnetic Structures by FullProf

When a neutron beam go through a crystal in which there exists a magnetic ordering, we get information not only about the atomic positions of the crystalline lattice but also about the orientation and magnitude of the atomic magnetic moments, i.e. the magnetic structure of the crystal. The resulting diffraction pattern is formed by the superposition of the diffraction processes with individual atoms through strong interaction and with the atomic magnetic moments.

In the case of a non-polarised neutron beam, the nuclear and magnetic effective sections are additive, what allows us to distinguish between the two contributions and to study the magnetic diffraction independently.

In this case, we have only performed diffraction experiments on a commensurate (collinear) antiferromagnetic magnetic structure. If the periodicity is \( n \) times \((n \in \mathbb{N})\) the crystalline lattice, the propagation vector will be \( \mathbf{k} = 1/n \) in the corresponding direction. Thus, the magnetic ordering modifies the symmetries so that there will appear additional peaks in the diffraction pattern. In our case we have two propagation vectors, \( \mathbf{k}_1 = (0,0,0) \) and \( \mathbf{k}_2 = (1/3,0,0) \), as explained in Section 4.3.3.

In our ND experiment, our milled sample retained the magnetic structure of the bulk alloy, and thus it was no necessary to determine the propagation vector, the irreducible representations (irreps) or the basis functions. In any case, we performed a refinement of the magnetic structure, through the FullProf Suite program, which allows to refine the Fourier components of the atomic magnetic moments. In order to do this, we have to introduce the components of the magnetic moment of the reference atom which come from the mixture of the two propagation vectors existing within the structure.
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Figure 5.4  Lattice parameter variation with temperature, for the 70h milled YbAl$_3$ alloy, from Table 5.2. A change of slope is observed at $T \approx 80$K, which is not related to structural transitions [272].
Figure 5.5  TEM images of the 70h milled YbAl$_3$ sample. Inset: diameter distribution of the 70h YbAl$_3$ milled alloy, obtained by TEM. The black line is the fit to a log-normal distribution, centred at 4.7nm, with a standard deviation $\sigma = 0.5$nm.  

Figure 5.6  Magnetic susceptibility dependence with temperature for $H = 1T$ of the 20h and 70h YbAl$_3$ milled alloys. The oxide contribution reveals a major Curie-Weiss behaviour. Insets a and c: Original curve of the magnetisation of 20h and 70h YbAl$_3$ milled alloys, before subtracting the oxide contribution, respectively. Inset b: Magnetic susceptibility dependence with magnetic fields for different temperatures (2 and 300K) for the 20h and the 70h YbAl$_3$ milled alloy.  

Figure 5.7  Electrical resistivity dependence with temperature of the 70h YbAl$_3$ milled alloy. At low temperatures (red dashed-circle) there exists a marked and unexpected minimum followed by an increase of the resistivity, up to a broad maximum, observed in IV compounds.  

Figure 5.8  Energy levels scheme, as proposed in the Wachter and Marabelli theory [277], where $\rho_D(E)$ represents the density of states.  

Figure 5.9  Electrical resistivity dependence with temperature of the 20h YbAl$_3$ milled alloy. Inset: Fermi liquid dependence which can not explain the $T < 5K$ resistivity upturn.  

Figure 5.10  Electrical resistivity dependence with temperature of the 70h LuAl$_3$ milled alloy. The continuous red line marks the fit to Eq. 5.3. Inset bottom right: low temperature region showing the uncorrect fit (continuous red line). Inset top left: difference between experimental and calculated resistivity, with Eq. 5.3. The continuous red line is a fit to $\rho \propto -\sqrt{T}$ (see text).
Figure 5.11 Rietveld refinement of the XRD of the 70h LuAl₃, using Cu-Kα radiation. The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns. The nanoparticle structure (space group Pm-3m) is remarkably well reproduced ($R_B = 7.0\%$).

Figure 5.12 Logarithmic representation of the electrical resistivity of LuAl₃ 70h and YbAl₃ 70h with the inverse of the temperature, below the minimum $T_{\text{min}}$. Inset: ohmic response of the YbAl₃ 70h at $T = 2K$. R is the standard coefficient of linear regression.

Figure 5.13 Electrical resistivity of the YbAl₃ 70h alloy, together with the fit to the Eqn. 5.6 ($\chi^2 = 1.26 \times 10^{-10}$). The blue curve shows an unsuccessful fit to Eq. 5.5.

Figure 5.14 Electrical resistivity of the 10h YbAl₃ alloy, milled in a ZrO₂ container. Inset: low temperature region of the electrical resistivity, where a minimum is detected.

Figure 5.15 Magnetoresistance curves for the 70h YbAl₃ milled alloy. The low and high field dependence are shown in the left inset for the curve at $T=2K$. Right inset: low temperature region of the electrical resistivity for the YbAl₃ 70h, with magnetic fields $H = 0T$ (black) and $H = 5T$ (red). The $\rho$-minimum is shifted to higher temperatures with increasing magnetic fields.

Figure A.1 Structure factor projection on the perpendicular plane to the scattering vector $\mathbf{h}$ direction.
Figure A.2  Rietveld refinements of the XRD patterns of LaB₆ in our Bruker D8 Advance diffractometer with Cu-Kα (a) or Mo-Kα (b) radiations. The theoretical calculation is depicted as a continuous (black) line and the experimental data as points (in red). The (blue) line below the spectra represents the difference between the calculated and experimental patterns.
Table 4.2 Orthorhombic cell parameters $a$, $b$ and $c$ of the 2h milled alloy at different temperatures, obtained by Rietveld refinement, from results of XRD performed at MSPD instrument in ALBA synchrotron. Standard Bragg errors are denoted by $R_B$. The calculated particle size is $D = 8.8(5)$nm, in good agreement to that obtained by conventional XRD.

Table 4.3 Orthorhombic cell parameters $a$, $b$ and $c$ of the 5h milled alloy at different temperatures, obtained by Rietveld refinement, from results of XRD performed at MSPD instrument in ALBA synchrotron. Standard Bragg errors are denoted by $R_B$. The calculated particle size is $D = 6.4(5)$nm, in good agreement to that obtained by conventional XRD.

Table 4.4 Parameter values of $\delta$, $\tau_0$, $z\nu$ and $T_0$ for different milling times $t$(h), calculated using Eqs. 4.12 and 2.13.

Table 4.5 The Debye temperature and the electronic coefficient to the specific heat for the milled TbCu$_2$ alloys, as a result of the fit of the specific heat curves to Eq. 4.20.

Table 4.6 Temperature coefficient of resistance TCR, calculated from Eq. 4.21, and constants $\rho_0$, $\rho_{rel}$, $a$ and $b$, calculated from Eq. 4.26, for every milled alloy.

Table 5.1 Lattice parameter ($a$), grain size ($D$) and strain ($\eta$) of the bulk and 20 and 70 hours YbAl$_3$ milled alloys. Standard Bragg errors are denoted by $R_B$.

Table 5.2 Cubic cell parameter $a$ of the 70h milled alloy at different temperatures, obtained by Rietveld refinements, from results of XRD performed at MSPD instrument in ALBA synchrotron. Standard Bragg errors are denoted by $R_B$. The calculated particle size is $D = 9.3$nm, in good agreement to that obtained by conventional XRD.


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DECLARATION

Dr. Luis Fernández Barquín, Profesor Titular de la Universidad de Cantabria y Dr. Daniel Rojas Pupo, Profesor Ayudante Doctor de la Universidad Politécnica de Madrid, certifican:

Que la presente Memoria, titulada “Size induced electronic and magnetic changes in nanometric rare earth alloys” ha sido realizada bajo nuestra dirección, por Cristina Echevarría Bonet, y constituye su Tesis para optar al grado de Doctor por la Universidad de Cantabria. Asimismo emitimos nuestra conformidad para que dicha Memoria sea presentada y tenga lugar, posteriormente, la correspondiente Lectura y Defensa.

Santander, March 2014

Fdo.: Dr. Luis Fernández Barquín

Fdo.: Dr. Daniel Rojas Pupo