Crystallographic, magnetic and magnetocaloric properties in Yb-based alloy

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ABSTRACT

The crystallographic and magnetic properties, as well as the magnetocaloric effect (MCE) of the novel polycrystalline $Yb_{0.5}Gd_{0.5}Ni_5$ alloy were investigated. The alloy crystallizes in the hexagonal $CaCu_5$ structure. We estimated the presence of less than 6 % of the impurity phase. The magnetic properties showed the transition to a ferromagnetic state at T_c = 21.8 K. The heat capacity confirmed such behaviour. The Sommerfeld coefficient yielded a heavy-fermion value of 790 mJ/mol.K^2. Moreover, we observed a $-lnT$ dependence below 3 K at zero applied magnetic field. The magnetocaloric effect yielded an asymmetric shape of the $-\Delta S_M$ dependence due to the presence of spin fluctuations.

1. Introduction

The intermetallic compounds based on ytterbium, cerium or europium are attractive due to their anomalous behaviours and very interesting properties arising from the variety of f-electrons configurations, which could occur at a low-temperature range [1, 2, 3, 4]. From the physical properties point of view, it is essential to distinguish between electronic, magnetic and transport properties in terms of physical phenomena such as the quantum criticality, the unconventional superconductivity, the heavy-fermion ground state materials or strongly correlated materials. All of the mentioned facts are associated with the ground state research on which it is crucial to establish potential application, e.g. materials suitable for technical application as magnetocaloric components or biomedical application, etc. However, whereas for the starting material $GdNi_5$ and its magnetocaloric e.g. [5] and magnetic e.g. [6] properties are relatively well-known, about $YbNi_5$ and $(Yb,Gd)Ni_5$ only scarce information-exist [7, 8].

Nowadays, it is attractive to find a magnetocaloric material as a prominent candidate in magnetic refrigeration, which is expected to replace the conventional cooling technology [9]. The quest for new materials exhibiting sizeable magnetocaloric effect (MCE) at a wide temperature range is still unending, ever since discovering MCE around sub or near room temperature in rare earth materials e.g. [10,11]. Moreover, it is important also to find new cheaper materials.

Focusing on theoretical predictions and obtained experimental results from previous studies of rare earth materials e.g. [1-9], we synthesized a new Yb-based alloy $Yb_{0.5}Gd_{0.5}Ni_5$. We present in this paper the results of the study of crystallographic, magnetic, heat capacity and MCE properties where the spin fluctuation effect was observed.

2. Experimental details

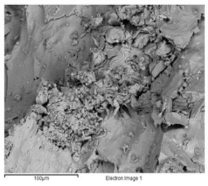
The polycrystalline sample of $Yb_{0.5}Gd_{0.5}Ni_5$ has been prepared by weighting the stoichiometric amount of elements of the following metals: ytterbium (pieces, 99.9 mass % purity), gadolinium (pieces, 99.5 mass % purity), nickel (foil, 99.9 mass % purity). The total weight of the prepared sample was 1 g, and melting was made by induction melting in a sealed tantalum crucible under a stream of pure argon. The crucible with the sample was continuously shaken to ensure homogeneity during the melting process. The sample was annealed in a resistive furnace for ten days at 800 °C and finally quenched in cold water.

After sample preparation, the structural characterization was done by using a Brucker D8 Advance diffractometer. The XRD patterns were collected from 10° to 100°, 2θ angle range, with 0.02° steps, and an integration time of 0.5 s per step. The samples were characterized by a scanning electron microscope with an energy dispersive X-ray (EDX) spectrometer.

The magnetic properties and the heat capacity measurements were performed using a DYNACOOL (Quantum Design) commercial device. The magnetic properties were measured by using a Vibrating Sample Magnetometer (VSM) in the temperature range from 2 K up to 300 K with DC applied magnetic fields from 0 T to 9 T. The magnetic susceptibility has been measured in zero-field cooling (ZFC) and field cooling (FC) mode. Heat capacity was measured by 2-τ method in the temperature range from 2 K up to 300 K with DC applied magnetic fields from 0 T to 9 T .

3. Results and discussion

The XRD pattern of $Yb_{0.5}Gd_{0.5}Ni_5$ alloy was indexed by two phases. The first phase belongs to the hexagonal $CaCu_5$-type crystal structure, with lattice parameters a = 0.4881 nm and c = 0.3971 nm. The secondary phase comes from oxides, also confirmed by SEM and EDX analysis (Figure 1). It was not possible to identify the secondary phase. However, we could estimate that it represents less than 6 %. The surface of the sample is porous and contains grains of non-regular shapes. Therefore, we are using the nominal composition for this alloy.



$Yb_{0.5}Gd_{0.5}Ni_5$	required atomic %	real atomic %
Yb	8.34	Yb = 10.01
Gd	8.34	Gd = 7.54
Ni	83.32	Ni = 76.11
		O = 6.33
TOTAL	100.00	100.00

Figure 1 SEM images together with EDX analysis. The results show that a small number of oxides besides required elements are present.

Figure 2 shows the temperature dependence of the magnetization in two different modes, ZFC-FC, for two different applied magnetic fields (B = 0.1 T and B = 1 T). It is possible to appreciate the increase of the magnetization without thermal hysteresis at low temperatures, which is characteristic of ferromagnetic behaviour. The transition temperature to the ferromagnetic state is at T_c = 21.8 K. This value can be better defined from the derivative of the magnetization, as shown in the inset of Fig. 2. In addition, one could see in the temperature range between 50 and 150 K some minor anomalies, which could be due to the impurity phase or the possible presence of spin fluctuations [12]. When the applied magnetic field is increasesed, the anomaly is partially depressed. In order to estimate the effective paramagnetic moment, μ_{eff}, and the paramagnetic Curie temperature, Θ_P, we fitted the inverse DC-magnetic susceptibility $1/\chi(T)$ with a Curie-Weis law at high temperatures. The paramagnetic Curie temperature Θ_P = -67.95 K was determined. This value indicates an antiferromagnetic exchange interaction, as was published for the $YbNi_5$ compound [7]. However, to explain the observed value of μ_{eff}, we have to consider a situation similar to that of $CeNi_5$ [13], where magnetism comes from Ni atoms. On the other hand, in $GdNi_5$, magnetism comes from Gd. Therefore, we suppose that the observed μ_{eff} value comes from Yb, Gd and Ni atoms, and we determined μ_{eff} = 3.03 μ_B/f.u., which is lower than the calculated from the free ions values, μ_{eff} = 3.4 μ_B/f.u.. Taking only into account the contribution from Ni atoms, the experimental value is higher. We suppose that neutron diffraction could help to explain the situation.

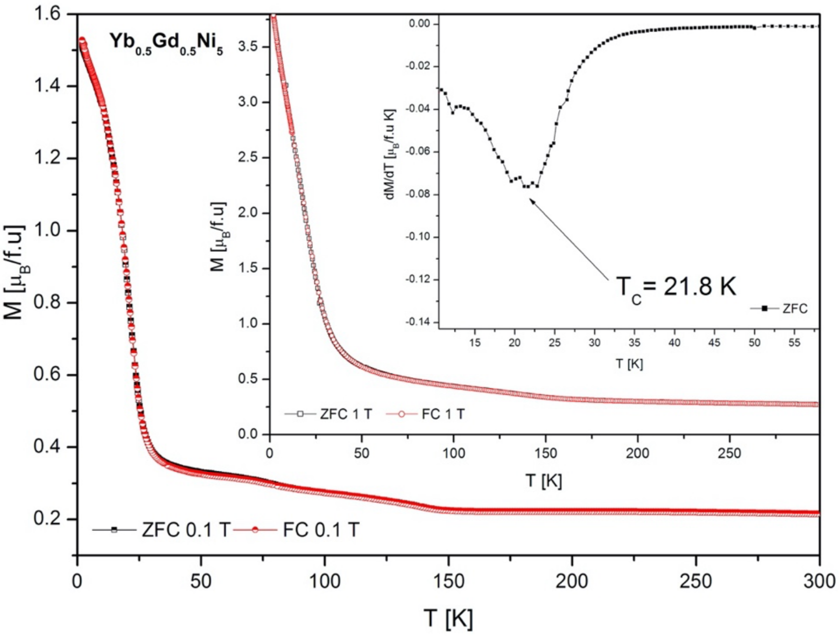


Figure 2 DC-magnetization dependencies at ZFC (the black line) FC (the red line) mode at low applied magnetic field B = 0.1 T and high applied magnetic field B = 1 T (inset). The second inset shows the dM/dT derivative, fixing the magnetic transition temperature.

In Figure 3, the magnetization as a function of the applied magnetic field at different temperatures is presented. The saturated magnetization value for the studied alloy at 2 K is close to the full free-ion Yb^{3+} magnetic moment, and it confirms the magnetic ordering in the alloy below 2 K.

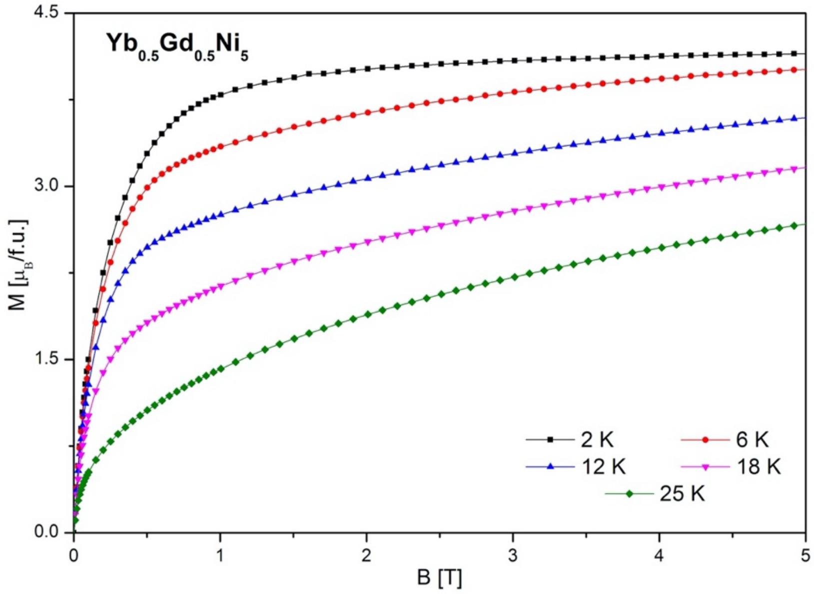


Figure 3 Characteristic behaviour of the magnetic field dependence of the magnetization for $Yb_{0.5}Gd_{0.5}Ni_5$ measured at different temperatures.

In Figure 4, the measurement of the heat capacity of $Yb_{0.5}Gd_{0.5}Ni_5$ as a function of the temperature and the applied magnetic fields is presented. One could see that, in the temperature range below 50 K, an anomaly connected with T_c was observed. This anomaly is depressed with the magnetic field (see Figure 5). It is noteworthy that, at zero applied magnetic field, between 2 and 3 K, a $-lnT$ behaviour was observed, which could be due to the heavy fermion behaviour or the proximity of quantum criticality. The observed value of the Sommerfeld coefficient, γ = 790 mJ/mol.K^2, would support the heavy fermion behaviour. Under an applied magnetic field of 9 T, the value is γ = 113 mJ/mol.K^2, which gives a modest heavy-fermion behaviour.

The low temperature details are better observed in Figure 5, in which, at zero applied magnetic field, a small maximum at around 22.5 K is observed, which is connected to the transition temperature T_c. Moreover, there is another small shoulder at around 18 K, which is probably connected with the impurity phase in our alloy. This figure also displayed the effect of increasing the magnetic field on the low temperature (below 3 K) $-lnT$ dependence, which is depressed.

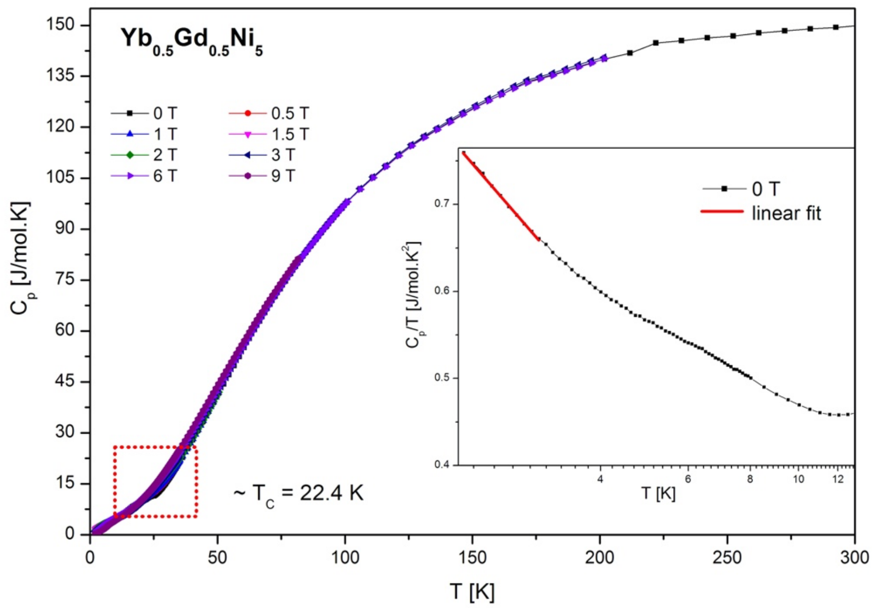


Figure 4 The heat capacity measurements at different applied magnetic fields for the $Yb_{0.5}Gd_{0.5}Ni_5$ alloy with transition temperature. The inset shows the Cp/Tvs.log(T) plot at zero field.

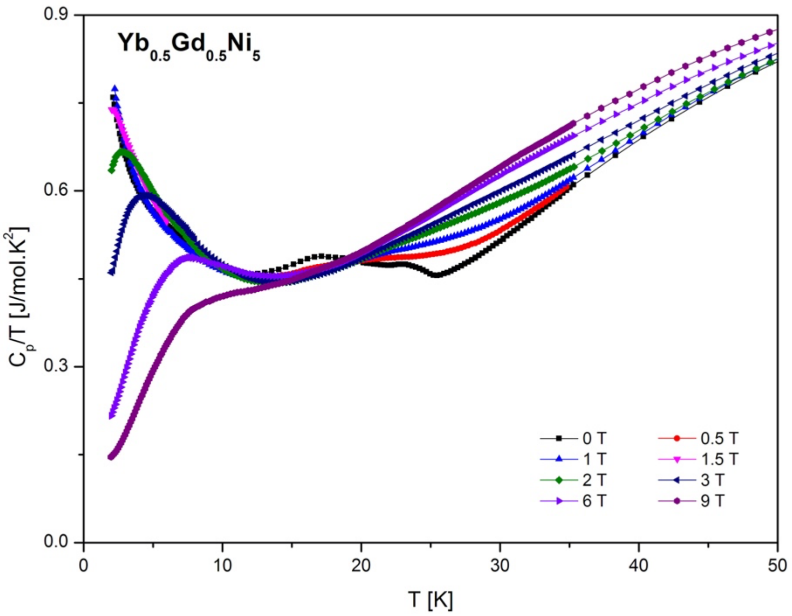


Figure 5 Low temperature detail of the heat capacity measurements at different applied magnetic fields for the $Yb_{0.5}Gd_{0.5}Ni_5$ alloy in Cp(T)/T vs. T.

To explore the possibilities of $Yb_{0.5}Gd_{0.5}Ni_5$ as a MCE material, the isothermal magnetization measurements in the neighbourhood of the ordering temperature have been performed. We observed a linear increase of the magnetization at low fields and a lack of saturation at higher magnetic fields.

In Figure 6, the determined magnetic entropy as a function of the applied magnetic field is presented. The magnetic entropy change S_M was determined from the isothermal magnetization data using the Maxwell relation:

$$\boldsymbol{S_M(T) = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB}$$

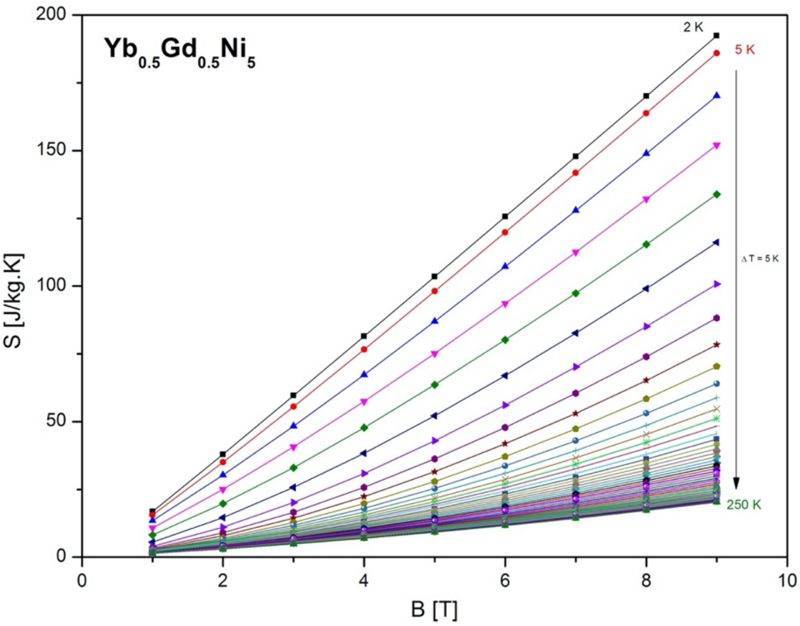


Figure 6 Field dependence of the magnetic entropy at different temperatures for $Yb_{0.5}Gd_{0.5}Ni_5$.

The MCE determined in terms of the $-\Delta S_M$ for various field changes and the temperature dependencies is shown in Figure 7. A maximum value of $-\Delta S_M$ is 3.75 $J.kg^{-1}K^{-}$ for a field change from 1 T to 9 T. The refrigerant capacity (RC) has been calculated using the equation $RC = -\Delta S_M^{max}$ x ΔT_{FWHM}, where ΔS_M^{max} is the maximum value of the magnetic entropy change and ΔT_{FWHM} is the full width at half maximum of the ΔS_M^{max} peak. The RC values so obtained for $Yb_{0.5}Gd_{0.5}Ni_5$ are 58 J/kg and 124.6 J/kg for magnetic field changes 0 – 4 T and 0 – 9 T. A broad maximum is visible at temperatures close to 24 K, which is in good agreement with the observed T_c. This behaviour is also in agreement with [8]. Moreover, the asymmetric shape of the maxima, with a tail at higher temperatures, is due to the spin fluctuation effect [14]. The observed characteristic values are about twice smaller than those of pure $GdNi_5$ [5] and they are similar to the one obtained in reference [8].

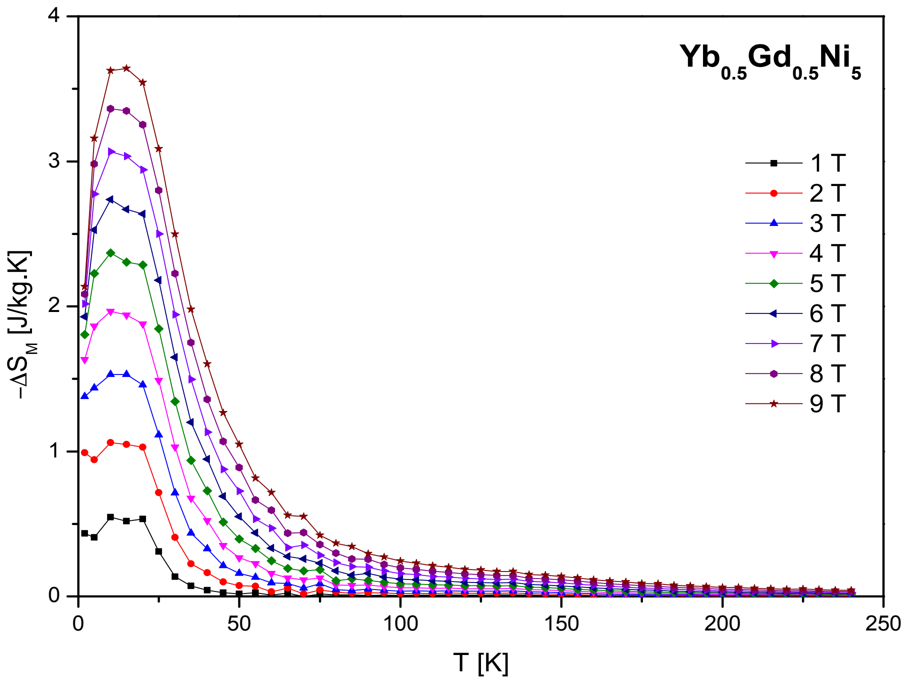


Figure 7 $-\Delta S_M(T)$ *for the* $Yb_{0.5}Gd_{0.5}Ni_5$ *alloy for various magnetic field changes.*

The materials with multiple magnetic transitions may create new avenues to attain magnetic refrigeration technology in a wider temperature range than traditional materials. The alloys and compounds with multiple magnetic transitions might help to create new materials to attain magnetic refrigeration technology in a broad temperature range compared to classical materials.

4. Conclusion

The polycrystalline $Yb_{0.5}Gd_{0.5}Ni_5$ alloy, with a major phase crystallizing in the $CaCu_5$ phase, has been prepared by inducting melting process. We have experimentally studied the present material's structural, magnetic and magnetocaloric properties and we have calculated its $-\Delta S_M$ value, which are in agreement with previous data. From the magnetic susceptibility measurements, the effective paramagnetic moment and paramagnetic Curie temperature and their values indicate antiferromagnetic exchange interactions. The heat capacity measurements showed a $-lnT$ behaviour in the temperature range below 3 K and zero applied magnetic field. Moreover, the observed Sommerfeld coefficient, γ = 790 mJ/mol.K^2, indicates that the $Yb_{0.5}Gd_{0.5}Ni_5$ alloy belongs to the category of heavy fermion materials. In order to determine more precisely other parameters, it is necessary to measure physical properties as much as possible below 2 K and clarify the issues that have been identified in this rare-earth material research.

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