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Ferrimagnetism in $Tb_3Co_8Sn_4$ intermetallic compound

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Abstract

AC and DC magnetic measurements were performed on the ternary intermetallic phase $Tb_3Co_8Sn_4$. The compound shows a ferrimagnetic transition at $T_C = 91$ K. From the imaginary part of the AC susceptibility a second broad peak was detected at $T_g = 28$ K and ascribed to a transition to a spin glass state. Zero field cooled (ZFC) and field cooled (FC) magnetization measurements at $\mu_0 H = 0.05$ Tesla (T) confirmed the reentrant spin glass state below 30 K. The hysteresis cycle, obtained from magnetization measurements at 5 K, allows to obtain the remanence ($B_r = 0.43$ T) and the coercive field ($H_C = 159.2$ kA/m). The experimental data were analysed in the framework of the Molecular Field Theory.

Keywords: Rare Earth intermetallic compounds; Magnetic properties; Ferrimagnetism; Reentrant spin glass

1. Introduction

The study of the magnetic properties of Rare Earth (R) ternary intermetallic compounds with a transition element as iron or cobalt is at present a topical field in the physics of materials both for the technological relevance related to the possible discovery of new permanent magnets, and for the scientific interest connected with the presence of a complex magnetic behaviour, i.e. spin reorientation transitions (SRT) and first order magnetization processes (FOMP), often observed in these phases.

In a previous paper [1] a new family of Rare Earth ternary intermetallic compounds, namely $R_3Co_8Sn_4$, was synthesized and crystallographic informations were obtained by single crystal and powder X-ray diffractometry: all the phases crystallise in the $Lu_3Co_{7.77}Sn_4$ structure type (space group $P6_3mc$) with a full occupancy of the atomic positions. Preliminary magnetization measurements performed on the two intermetallic compounds $Y_3Co_8Sn_4$ and $Gd_3Co_8Sn_4$ [2], showed that the two compounds order ferro-(Y) and ferrimagnetically (Gd) below 61.5 and 102.5 K, respectively. From the experimental results, analysed in the framework of the molecular field theory [3], the exchange integrals $\mathbf{J}_{Co-Co}$ and $\mathbf{J}_{Gd-Co}$ were obtained.

Here we present results obtained from magnetization measurements as well as from high resolution AC susceptibility on the ternary intermetallic phase $Tb_3Co_8Sn_4$.

2. Experimental details

Tb 99.9 wt.%, Co 99.9 wt.% and Sn 99.999 wt.% were used for direct synthesis of the compound. Stoichiometric amounts of the elements were mixed together, pressed and melted in an induction furnace under an atmosphere of pure and dry argon. The sample was turned upside down and remelted four times in order to ensure a complete homogeneization. It was then wrapped in tantalum foil, closed in silica tube and annealed at 1073 K for 4 weeks. Micrographic analysis showed a complete homogeneity of the sample. The lattice parameters, obtained from X-ray powder analysis (Cu Kα, Guinier camera), were in complete agreement with Ref. [1].

Electrical resistivity measurements were performed, with the standard four point DC method, in the 4.2–300 K temperature range.

DC magnetization and AC magnetic susceptibility data were collected using a Maglab^{2000} platform operating in the 3–300 K temperature range in applied magnetic field up to 9 Tesla (T). The frequency used for AC measurements was 1000 Hz.

3. Results

In Fig. 1 the electrical resistivity of the $Tb_3Co_8Sn_4$ phase is reported. The electrical resistivity increases at increasing temperature, showing a metallic behaviour. From low temperature data a quite high value of the

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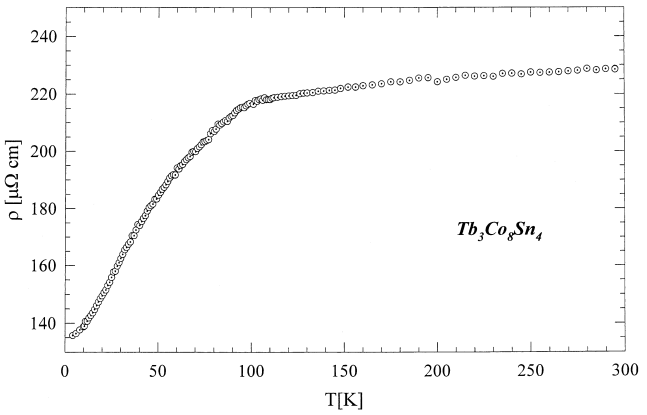

Fig. 1. Thermal dependence of the electrical resistivity of $Tb_3Co_8Sn_4$.

residual resistivity could be obtained: $\rho_0 = 135$ μΩ cm. At about 90 K a change in the slope of the electrical resistivity is observed and attributed to a magnetic transition.

Preliminary isothermal (300 K) magnetization measurement up to 5 T was performed on the compound in order to quantitatively evaluate the ferromagnetic Co impurity contribution. We estimated that in $Tb_3Co_8Sn_4$ the impurity content was 0.07%. The obtained data were used to correct all the experimental magnetic measurements.

Fig. 2 shows the real (χ') part of the AC susceptibility, in an AC field of 1 Oe and in zero DC magnetic field, in the 5–300 K temperature range, while, in the inset, the inverse of the magnetic susceptibility in the 50–300 K temperature range is reported. A sharp cusp, related to the magnetic ordering of the compound, is clearly observed at 91 K with a broad shoulder at 50 K. Above the transition temperature, as shown in the inset, the inverse of the magnetic susceptibility does not follow the Curie–Weiss law. A more complex equation, typical of a ferrimagnetic compound, was used to fit successfully the experimental data:

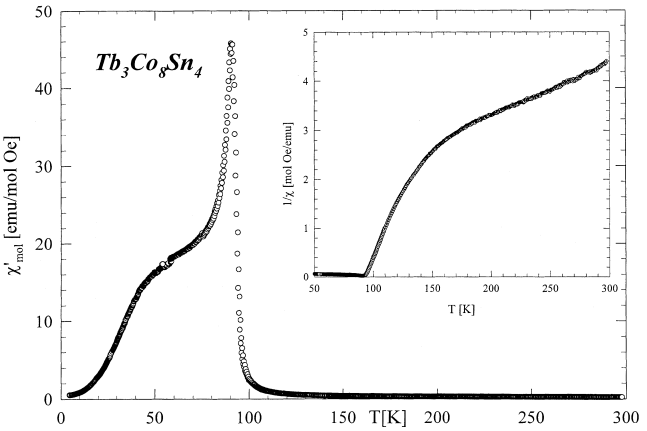

Fig. 2. Temperature dependence of the real part (χ') of the AC susceptibility of $Tb_3Co_8Sn_4$ ($H_{AC} = 1$ Oe). In the inset, the inverse of the magnetic susceptibility in the 50–300 K temperature range is reported.

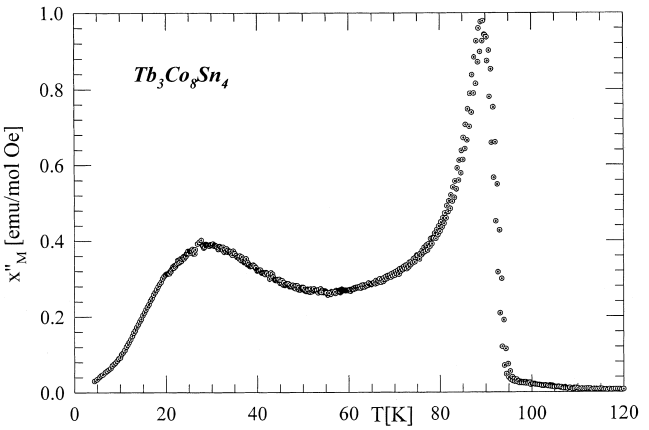

Fig. 3. Imaginary part of the AC suscptibility of $Tb_3Co_8Sn_4$ (5–120 K).

$$\chi^{-1} = \frac{T}{C} + \chi_0^{-1} + \frac{\sigma}{T-\theta}$$

We obtain $C = 248.8$ μ_BKf.u.$^{-1}$ T^{-1}, $\chi_0 =$ 3.787 μ_Bf.u.$^{-1}$ T^{-1}, $\sigma = -184.4$ TKf.u.μ_B^{-1} and $\theta = 52$ K.

The two anomalies could be more clearly observed in the imaginary part (χ'') of the AC susceptibility, reported in Fig. 3: the sharp peak, already observed in χ' at 91 K corresponds to the ferrimagnetic transition while a second broad peak between 25 and 30 K can be easily detected.

From magnetization measurements, performed at 5 K in applied magnetic fields up to 9 T (Fig. 4), a saturation magnetic moment $\mu_{sat.} = 14.8$ μ_B/f.u. was obtained. Under the hypothesis of an antiferromagnetic coupling between Tb and Co sublattices and taking the magnetic moment per Co atom in the ordered state equal to 0.32 μ_B (from Ref. [2]) we obtain $\mu_{Tb} = 5.8$ μ_B, far from the value in the ordered state ($\mu_{gj} = 9$ μ_B). Thus, the hypothesis of a non-collinear magnetic structure of the Tb sublattice seems reasonable.

The hysteresis cycle, performed at 5 K and shown in Fig. 5, closes at 2 T: from the experimental data the

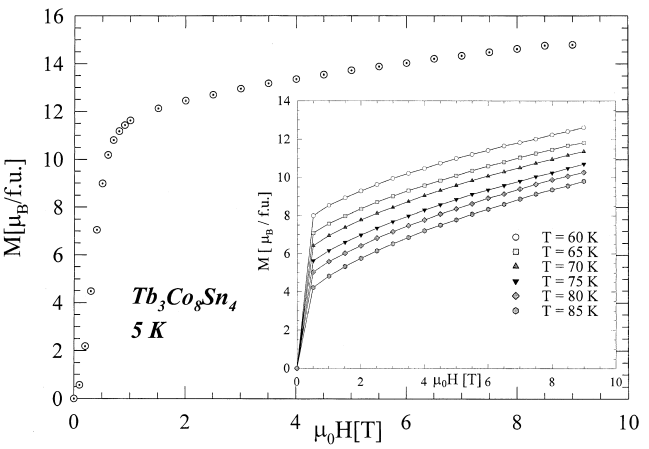

Fig. 4. Isothermal (5 K) magnetization of $Tb_3Co_8Sn_4$. In the inset the field dependence of the magnetization at different temperatures is shown.

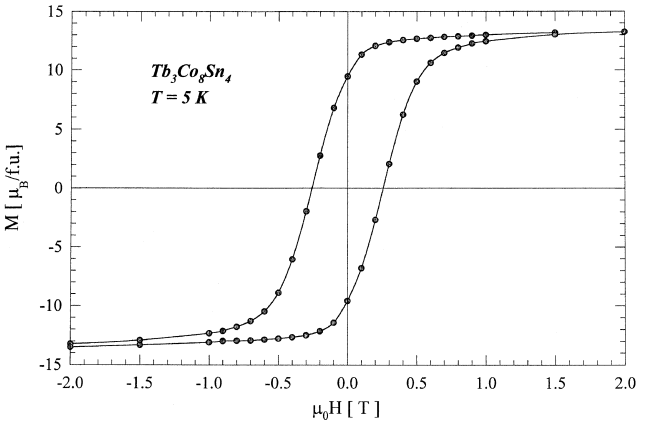

Fig. 5. Hysteresis cycle of $Tb_3Co_8Sn_4$ at 5 K.

remanence ($B_r = 0.43$ T) and the coercive field ($H_C = 159.2$ kA/m) can be calculated.

4. Discussion

In the molecular field approximation the Curie temperature is related to the three different exchange-coupling constants through the following equation [3]:

$$3k_BT_C = A_{Co-Co} + A_{Tb-Tb} + [(A_{Co-Co} - A_{Tb-Tb})^2 + 4A_{Tb-Co}A_{Co-Tb}]^{1/2}$$

where A_{x-y}, the magnetic interaction between the **x** and **y** spins is related to the corresponding coupling constant J_{x-y} through Z_{x-y} (the average number of **y** atoms around the **x** atom) and to the two moments, *i.e.* the spin moment of the Co atom and the total moment of the Tb atom. Since the R–R interaction is fairly weak (long range interaction modulated via conduction electrons), it may be neglected. Thus, following this hypothesis, the above equation can be simply written as

$$3k_BT_C = A_{Co-Co} + [A^2_{Co-Co} + 4A_{Tb-Co}A_{Co-Tb}]^{1/2}$$

Taking $A_{Co-Co} = 92.25k_B$ (from Ref. [2]), $Z_{Tb-Co} = 8$ and $Z_{Co-Tb} = 3.43$ (Ref. [1]) we obtain the exchange integral $J_{Tb-Co} = 10.1\ k_B$, which can be compared with that already obtained for $Gd_3Co_8Sn_4$, $J_{Gd-Co} = 11\ k_B$ [2]. Preliminary AC susceptibility measurements performed on the homologous $Dy_3Co_8Sn_3$ phase show the magnetic transition to be at 72 K, with an exchange integral $J_{Dy-Co} = 7\ k_B$. The above results give evidence that the exchange interaction R–Co is roughly one tenth of the Co–Co exchange constant.

The presence of a second peak in the imaginary part (χ'') of the susceptibility was at first tentatively ascribed to a magnetic process where the Tb sublattice could be involved; however the magnetization measurements performed at 5 K (Fig. 4) and at different temperatures between 60 and 85 K (see the inset of the same figure) give no evidence of an order–order magnetic transition below the ferrimagnetic transition temperature (89 K).

In an exhaustive review [4], Maletta and Zinn examined the stimulating phenomenon of the 'spin glass': the peculiar state of a diluted magnetic system where, below a characteristic temperature, the spins order in a non-periodic structure, i.e. the magnetic moments of the system are frozen in random directions. If the concentration of the magnetic moments increases, the exchange interactions become stronger, so an interplay between spin glass state and long range magnetic order is possible: this is the 'reentrant spin glass state' (RSG). In the RSG, with decreasing temperature, the system first becomes ferromagnetic, then goes in a mixed state where ferromagnetism and spin glass states can coexist; finally it freezes below a characteristic temperature. The imaginary (χ') part (Fig. 3) of the AC susceptibility of the $Tb_3Co_8Sn_4$ compound clearly reflects this trend: with decreasing temperature the AC susceptibility first peaks at the ferromagnetic transition temperature, then it decreases to a non-zero value, in agreement with a picture of disordered ferromagnetic domains; at last a second peak, due to the transition to the spin glass state, can be detected. The above picture agrees very well with zero-field cooled (ZFC) and field cooled (FC) magnetization measurements, performed between 5 and 100 K in an applied filed of 0.05 T and reported in Fig. 6. Below the ferrimagnetic transition temperature, the ZFC curve exhibits a weakly temperature-dependent plateau, comparable with that observed in the χ'' curve (mixed state) down to about 30 K, then it decreases sharply around the transition temperature $T_g = 28$ K (the first maximum in χ''). The FC curve goes together with the ZFC curve down to 65 K: at this temperature magnetic irreversibilities parts the two curves (mixed state). The FC curve increases monotonically with decreasing temperature down to 10 K, then it saturates. A careful analysis of a magnetic system showing reentrant spin glass behaviour has been recently proposed [5]. Similar results, where a magnetic order can coexist with a spin glass state, were

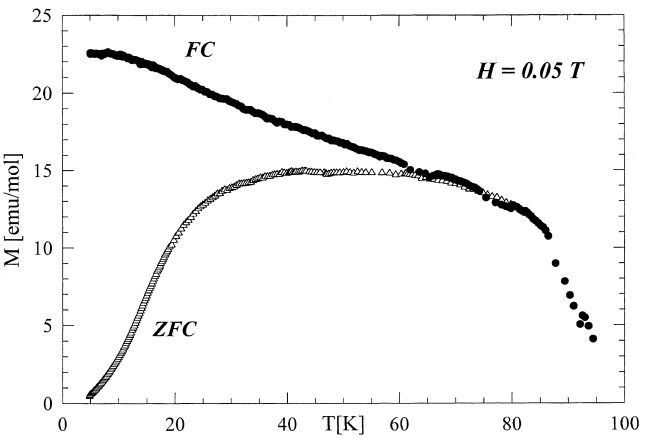

Fig. 6. ZFC and FC magnetization of $Tb_3Co_8Sn_4$ between 5 and 100 K.

already observed in other intermetallic phases as $DyCo_2$ [6], TbPdIn and DyPdIn [7], $Fe_{80-x}Ni_xCr_{20}$ [8].

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References

[1] F. Canepa, S. Cirafici, M.L. Fornasini, P. Manfrinetti, F. Merlo, A. Palenzona, M. Pani, J. Alloys Comp. 297 (2000) 109.
[2] F. Canepa, M. Napoletano, P. Manfrinetti, A. Palenzona, S. Cirafici, F. Merlo, J. Magn. Magn. Mater. 220 (2000) 39–44.
[3] K.H.J. Buschow, in: E.P. Wohlfarth, K.H.J. Buschow (Eds.), Ferromagnetic Materials, Vol. 4, North Holland, Amsterdam, 1988.
[4] H. Maletta, W. Zinn, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 12, Elsevier Sciences Publ, North Holland, 1989.
[5] E. Vincent, V. Dupuis, M. Alba, J. Hammann, J.-P. Bouchaud, Europhys. Lett. 29 (6) (1999) 1.
[6] A. Kowalczyk, J. Baszyński, A. Szajek, J. Kovàč, I. Ŝkorvànek, J. Magn. Magn. Mater. 152 (1996) L279.
[7] S. Nishigori, Y. Hirooka, T. Ito, J. Magn. Magn. Mater. 177–181 (1998) 137.
[8] G. Sinha, A.K. Majumdar, J. Magn. Magn. Mater. 185 (1998) 18.