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Magnetocaloric effects in intermetallic compounds

R. TETEAN
Babes-Bolyai University, Faculty of Physics, RO-400084, Cluj-Napoca, Romania

Nowadays, there is a great deal of interest in using the magnetocaloric effect (MCE) for refrigeration, from room temperature to the temperatures of hydrogen and helium liquefaction. Owing to its high efficiency and environmental friendliness, room-temperature magnetic refrigeration has been demonstrated to be a promising alterative for conventional vapor-cycle refrigeration. It has been reported that the lanthanide (R) Laves phases (RM2, where M = Al, Co and Ni), materials exhibit an excellent magnetocaloric effect (MCE) near room temperature. The magnetic properties and MCE in $Tb_8Co_{16-X}Al_X$ compounds is reported. The cobalt behavior is analyzed in spin fluctuation model. The potential use of these materials in magnetic refrigeration is discussed.

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1. Introduction

Magnetic materials showing a large magnetocaloric effect (MCE) have attracted considerable attention for their potential application in magnetic refrigeration technology [1-3]. MCE is an isothermal magnetic entropy change or an adiabatic temperature change of a magnetic material upon application of a magnetic field. The compounds which undergo temperature driven paramagnetic to ferromagnetic transitions show relatively large "negative" MCE, in which the isothermal magnetic entropy change, $\Delta S_m = S(H,T) - S(0,T)$ is negative [4]. Refrigeration in the temperature range 250-300 K is of particular interest because of potential impact on energy savings and environmental concerns. Generally, due to their high magnetic moments, heavy rare earths elements and their compounds are considered as best candidate materials for finding a large MCE [5]. The highest MCE involving a second order transition is produced by Gd and can be used to achieve cooling between 270 and 310 K [6]. The compound $Gd_5(Si_XGe_{1-X})_4$ was discovered by Pecharsky and Gschneider in 1997 [2]. The authors report that it exceeds a reversible magnetocaloric effect, by at least a factor of around 2 comparable with any known magnetic material. This giant magnetic entropy change is due a simultaneous first order structural transition and magnetic phase transition at 276 K. There are other materials like $La(FeCo)_{11.83}Al_{1.17}$ [7], $LaFe_{11.4}Si_{1.4}$ [8], $La(Fe_{0.88}Si_{0.12})_{13}$ or $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$ [9], $La_{0.8}Ce_{0.2}Fe_{11.4}Si_{1.6}$ [10], in which were reported large magnetic entropy changes comparable with Gd. Recently was discovered that the system $MnFeP_{1-X}As_X$ exhibit a reversible giant magnetic entropy change like in $Gd_5(SiGe)_4$ [11]. The Heusler alloys Ni-Mn-Ga show large magnetic entropy changes [12,13]. These large changes were reported to appear due to an sharp change in magnetization near the structural martensite to austenite transition.

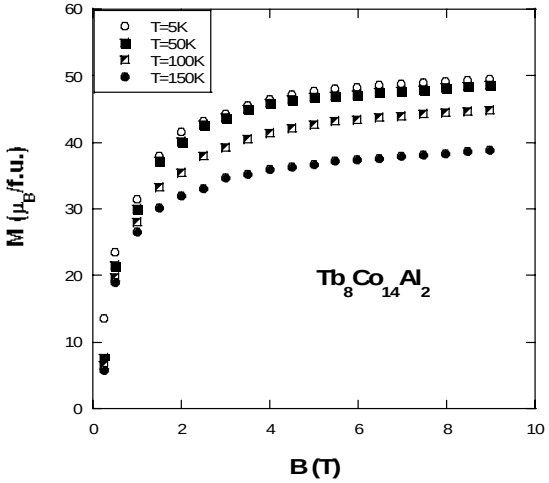

Fig. 1. Magnetization isotherms for the compound with x=2.

Several Laves phase compounds have been investigated for magnetocaloric effect because of simply crystal structure [14-16]. The RCo_2 intermetallic compounds (R= rare earth metal) were intensively studied due to the metamagnetic character of its cobalt sublattice [17-18]. When R is nonmagnetic there are necessary high fields (> 70 T in Yco_2) in order to induce magnetic moments on cobalt atoms and giving rise to metamagnetic transitions. If R is a magnetic atom the internal field is high enough to induce and polarize the cobalt moments. The compounds with light rare earths are ordered ferromagnetically, the rare earth and cobalt moments being parallel oriented while the compounds with heavy rare earths are ferrimagnetically ordered the R and Co moments being antiparallel oriented. It was reported that in the compounds with R = Dy, Ho or Er the ferromagnetic state is coupled to a structural transition,

leading to a first order transition at the critical temperature [19-21]. Due to the high value of the R magnetic moment a large entropy changes at the transition temperature were reported [see excellent reviews 22-23].

Many of these materials are potential candidates for the magnetic cooling in different temperature ranges. The materials to be applied in magnetic refrigeration must present a series of properties: (i) a first order field induced transition near the working temperature, in order to use the entropy changes associated with this transition; (ii) a high refrigerant capacity: $q = \int_{T_{cold}}^{T_{hot}} \Delta S(T)_{\Delta H} dT$; (iii) a low magnetic hysteresis in order to avoid the losses due to domains rotations in a magnetic refrigeration cycle; (iv) a low heat capacity; (v) low costs and harmless. The best magnetic refrigerants in the whole temperature range are rare earths based compounds.

The physical properties of the RM_2 intermetallic compounds, where R is a rare earth or yttrium and M a transition metal, were intensively investigated [24]. The f electrons of R elements have a small spatial extent, and generally one can assume that they are well localized. The 3d electrons give rise to a wide range of behaviors from well established magnetism with high ordering temperatures to paramagnetism by crossing the situation in which magnetism is close to an onset or a collapse. The Rco_2 compounds crystallize in a cubic Laves phase structure of C15 type. In this structure the R and M atoms, respectively, occupy each one type of site only. Because of the high symmetry of this lattice, the study of these compounds may give useful information on the magnetic behavior of the constituent atoms [24,25]. The $TbCo_2$ compound was reported to be ferrimagnetically ordered, the Tb magnetization being antiparallel oriented to that of iron. In the paramagnetic region a non-linear temperature dependence of the reciprocal susceptibility was reported.

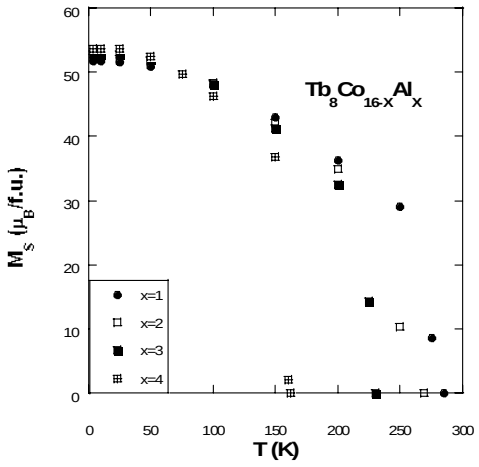

Fig. 2. Composition dependences of saturation magnetizations.

Previously, we have studied the magnetocaloric effect in $TbCo_{3-X}Al_X$ compounds in the region where a rhombohedral structure having $R\bar{3}m$ space group is formed [26]. Large magnetic entropy changes has been observed for all concentrations with a maximum at x=0.99. It was found that transition temperature can be tuned via Al concentration. It was shown that the cobalt magnetic moment is sensitive to the local environment. In order to obtain additional information on transition metals behavior in pseudobinary compounds we study the magnetic properties of cobalt in $Tb_8Co_{16-X}Al_X$ system in the rich cobalt composition range. In all cases the magnetic entropy changes around transition temperatures were evaluated.

2. Experimental

The $Tb_8Co_{16-X}Al_X$ compounds were prepared by arc melting the constituent elements in a purified argon atmosphere. A small excess of rare earth element was used in order to compensate for losses during melting. The ingots were remelted several times in order to ensure a good homogeneity. The samples were heat treated in vacuum, at 1000°C, for 5 days.

The crystal structure was studied by X-ray diffraction measurements, at room temperature, using the Cu Kα radiation with a Brucker D8 X Advance diffractometer.

The magnetic measurements were performed in the temperature range 4.2-900 K and external fields up to 9T using a Maglab 2000 Oxford Instruments equipment.. The spontaneous magnetizations, M_s, were determined from magnetization isotherms according to approach to saturation law, $M = M_s(1 - b/H) + \chi_o H$. We denoted by b the coefficient of magnetic hardness and χ_o is a Pauli-type contribution. Above the Curie points, the susceptibilities were determined by using a Faraday type balance, the samples being sealed in vacuum. In order to avoid any possible alteration of magnetic susceptibilities as result of the presence of small quantities of magnetic ordered impurities, the susceptibilities, χ, were determined from Honda-Arrott plots according to the relation $\chi_m = \chi + dM_s' H^{-1}$ by extrapolation to $H^{-1} \to 0$, [27]. By d we denoted a presumed impurity content and M_s' is their saturation magnetization.

The entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation:

$$\Delta S_m(T, H_0) = S_m(T, H_0) - S_m(T,0) = \frac{1}{\Delta T}\int_0^{H_0} [M(T + \Delta T, H) - M(T, H)]dH$$

where ΔT is the temperature increment between measured magnetization isotherms ($\Delta T = 5K$ for our data).

3. Results and discussion

The X-ray analysis shows, in the limit of experimental errors, the presence of one phase only, for $x \leq 4$, of C15 type. The lattice parameters decrease slightly when Al content increases, fact attributed to smaller radius of Al ion compared with Co one

Some magnetization isotherms for the $Tb_8Co_{14}Al_2$ compound are plotted in Fig.1. One can see that the saturation is not attended even in 9 T magnetic external field. Similar behavior were obtained in all cases. The thermal variations of spontaneous magnetizations are plotted in Fig. 2. The magnetizations, at 4.2 K, increase from 50.51 μ_B/f.u. at x = 0 to 53.878 μ_B/f.u. at x = 4. The above behavior is in agreement with the presence of a ferrimagnetic type ordering, the cobalt and terbium magnetic moments being antiparallely oriented. Assuming that the terbium mean magnetic moment, at 4.2 K, is the same like that determined on $TbCo_2$ compound by neutron diffraction study [19] the cobalt contributions to magnetizations were determined. The cobalt moments are little dependent on aluminum content having values in the range 1.15±0.09 μ_B/atom. The Curie temperatures increase slowly and than decrease when aluminum content increase – Fig.3. The ordered-paramagnetic transitions are of second order.

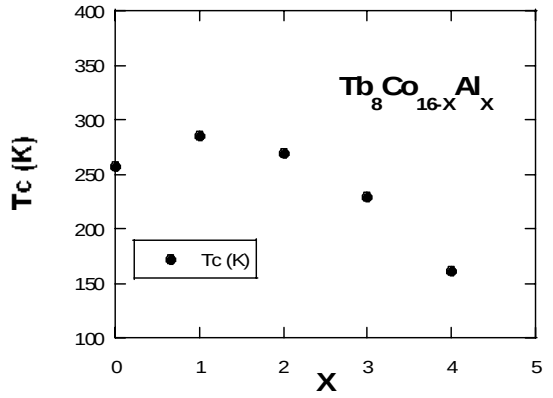

Fig. 3. The composition dependences of the Curie temperatures.

The temperature dependences of reciprocal susceptibilities, χ^{-1}, follow a hyperbolic law of Néel- type, characteristic for ferrimagnetic ordering. At high temperatures, the χ^{-1} vs. T plots shows linear dependences. The Curie constants, determined in the above temperature ranges, are higher than the characteristic values for Tb^{3+} ion suggesting the presence of contributions from the cobalt atoms. According to addition law of susceptibilities and supposing that the Curie constant of terbium is the same as that of Tb^{3+} ion, we determined the contributions of Co, to the Curie constants and the effective cobalt moments, M_{eff}(Co), respectively. The M_{eff}(Co) values are only slightly composition dependent being 2.81±0.12 μ_B/atom. The ratio $r=S_P/S_0$ between the number of spins obtained from effective iron moments, S_P, and saturation moments, S_0, is quite constant having values around 1.73. In the local moment limit we have r=1.0. For a weak ferromagnet the r values increase considerably. In case of $TbCo_2$ compound the r=1.73 value suggest that cobalt have rather high degree of itinerancy.

The above behaviour can be analyzed in spin fluctuation model [28,29]. When the amplitude of local spin fluctuations (LSF) is large and fixed, there is a local moment limit, where only the transverse components of LSF are important. As the amplitude of LSF is small, there is the weakly ferromagnet limit, where the longitudinal components of LSF or temperature variation of amplitude of LSF play an important role. From the r values in $Tb_8Co_{16-X}Al_X$ system we conclude that there are significant contributions from longitudinal components of LSF. The cobalt behavior in these compounds can be described as a weak ferromagnet. The effective cobalt moments determined in $Tb_8Co_{16-X}Al_X$ system are smaller than in YCo_2 compound. This fact may be attributed to partial quenching of spin fluctuation by internal field [30]. If the exchange field is sufficiently large so that the Zeeman splitting energy of opposite spin states is comparable or larger than the characteristic spin fluctuation energy, the paramagnons no longer have sufficient energy to flip spins and therefore the inelastic spin flip scattering is quenched. A magnetic field of the order of the characteristic spin fluctuation temperature is needed to quench the spin fluctuation enhancement [31-33]. Similar behavior was reported on $GdCo_{2-X}Si_X$ and $GdCo_{2-X}Cu_X$ compounds [34-35].

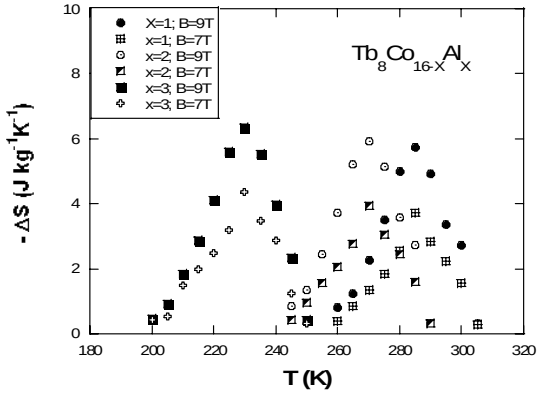

Fig. 4. Magnetic entropy change of the compounds with x=1, 2, respectively 3 as function of temperature in 7T and 9T.

The temperature dependence of magnetic entropy change in 7 and 9T external applied field for the compound with x = 1, 2 respectively 3 are plotted in Fig.4. The maximum values of entropy change occur almost at the Curie temperature for all the compounds. The maximum value is around 6.5 J/kg K in a 9T magnetic field for the compound with sharper transition (x = 3). The magnetic entropy change decreases with approximately 2 J/kg K in field of 7T. These values are somewhat smaller

than those evidenced in $TbCo_{3-X}Al_X$ compounds where as function of x values changes from 8.5 to 6.9 J/kg K were evidenced in field of 9T. The determined ΔS values in $Tb_8Co_{16-X}Al_X$ are rather high for compounds showing a second order type transition. Around 63 % of the heat is absorbed in a temperature range ±12 K, centered at the Curie point.

The origin of the large magnetic entropy change in the compound with x =3 could be attributed to the considerable variation of the magnetization near the transition temperature.

4. Conclusions

We have studied the magnetocaloric effect in $Tb_8Co_{16-X}Al_X$ compounds with Laves phase structure. Large magnetic entropy changes has been observed for all concentrations with a maximum at x = 3. The transition temperature can be tuned via Al concentration. These suggest that $Tb_8Co_{16-X}Al_X$ has a potential application as a working substance of magnetic refrigeration in the temperature range 150-295 K. Unfortunately there are necessary large magnetic fields which can be attended with superconductor electromagnets and the costs are rather high.

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*Corresponding author: rote@phys.ubbcluj.ro