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Magnetic properties and magnetocaloric effect in $GdCo_3B_2$ compound

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ABSTRACT

The magnetic properties and magnetocaloric effect (MCE) in $GdCo_3B_2$ have been studied by the magnetization and heat capacity measurements. The compound undergoes a magnetic Co–Co ordering at ~160 K, and a second magnetic Gd–Gd ordering transition at 54 K. A reversible magnetocaloric effect has been observed accompanied by a second-order phase transition at around Gd–Gd sublattice ordering temperature. The values of maximum magnetic entropy change ($-\Delta S_M^{max}$) reach 5.0 and 11.6 J kg^{-1} K^{-1} for the field change of 2 and 7 T with no obvious hysteresis loss around 56 K, respectively. The corresponding maximum adiabatic temperature changes (ΔT_{ad}^{max}) are evaluated to be 2.8 and 6.4 K. The magnetic transition and the origin of MCE in $GdCo_3B_2$ were discussed.

1. Introduction

Magnetic materials with large magnetocaloric effect (MCE) have been extensively investigated experimentally and theoretically, not only because of their great potential for magnetic refrigeration applications but also for further understanding the fundamental physical properties of the materials [1–11]. The MCE manifests as an isothermal magnetic entropy change (ΔS_M) or an adiabatic temperature change (ΔT_{ad}) when the magnetic material is exposed to a varying magnetic field. Magnetic refrigeration based on the MCE is advantageous being an environment friendly and energy efficient refrigeration mechanism, which is expected to be an important future cooling technology [1–3]. A large value of MCE is considered to be the most important requirement of the application, and therefore it is desirable to find new materials with large MCE especially at low magnetic fields and with a wide temperature range. Recently, some rare-earth based compounds with a ferromagnetic (FM) or an antiferromagnetic (AFM) phase transition have been found to possess not only large magnetic entropy change but also a small hysteresis loss [6–11].

The ternary intermetallic compounds of the RCo_3B_2 where R is a rare earth or yttrium have attracted some attentions due to their interesting physical properties [12–19]. The RCo_3B_2 compounds are paramagnetic at room temperature and undergo a Co–Co sublattice magnetic order transition at ~160 (20) K. In addition, a second R–R sublattice magnetic order transition was also observed at 54, 47, 28 and 22 K for R = Gd, Sm, Tb and Dy, respectively [12–19]. Among all the rare-earth transition metal compounds, Gd-based systems [20–22] have been extensively investigated owning to that Gd ion has the largest spinorial moment and has the highest effective exchange coupling around room temperature. In addition, Gd ion has no orbital moment in its ground state, which makes it simple for understanding the magneto-thermal behaviour occurring in various compounds containing Gd. To further understand the physical properties of RCo_3B_2 system and search new material displaying large MCE, in this paper, the magnetic properties and MCE in $GdCo_3B_2$ were systematically studied.

2. Experimental

The polycrystalline $GdCo_3B_2$ was synthesised by an arc melting method using a tungsten electrode under an argon atmosphere. Stoichiometric amounts of high purity Tb, Co and B were melted more than six times for homogeneity on a water-

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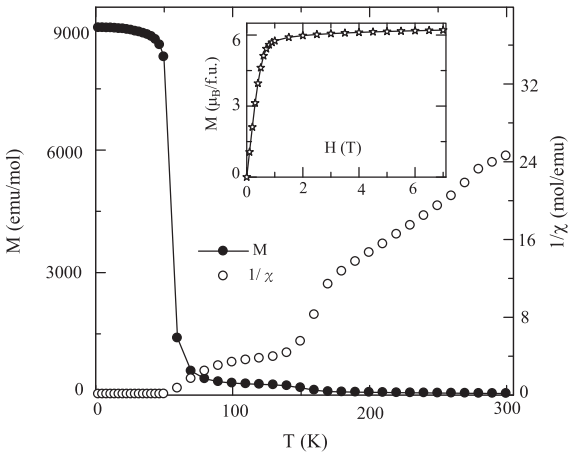

Fig. 1. Temperature dependence of magnetization (M) and inverse susceptibility ($1/\chi$) for $GdCo_3B_2$ in an external magnetic field $H = 0.1$ T. Inset shows the magnetization M as a function of applied magnetic field at 2 K up to 7 T for $GdCo_3B_2$.

cooled copper hearth. The total weight loss of the sample in this step was less than 0.5%. Then the samples were finally annealed at 1073 K for one week in evacuated quartz tubes. The sample was proved to be single phase with the $CeCo_3B_2$-type hexagonal crystal structure belonging to the *P6/mmm* space group by X-ray diffraction (XRD) experimental. The lattice parameters a and c were evaluated to be 5.058 and 3.016 Å, respectively, from XRD data using Rietveld's refinement method. The magnetization measurements were done using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7) in the temperature range 2–300 K, with DC magnetic fields from 0 to 7 T. The specific heat measurements were carried out by the adiabatic heat relaxation method in the temperature range from 2 to 300 K using a physical property measurement system (PPMS-9) from Quantum Design.

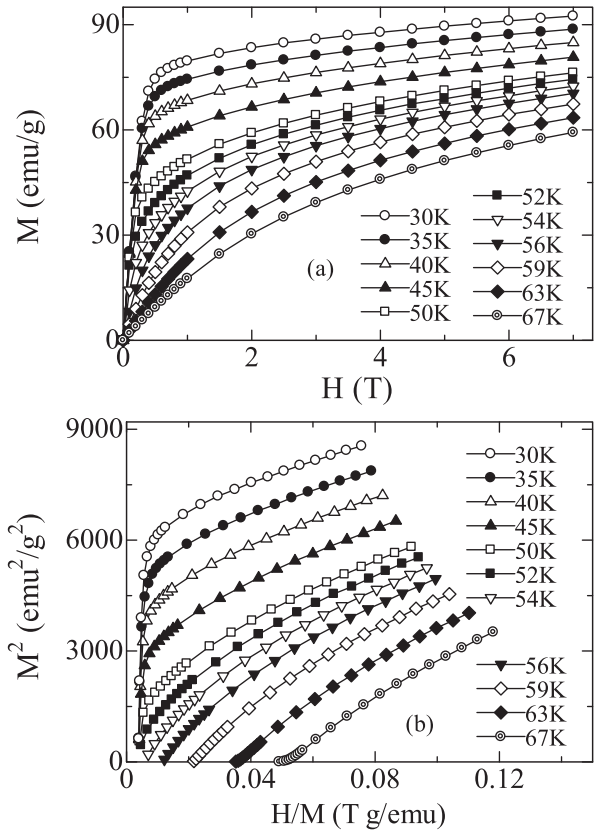

Fig. 2. (a) Magnetic field dependence of the magnetization for $GdCo_3B_2$ at some selected temperatures up to 7 T; (b) The Arrot-plot H/M vs. M^2 at some selected temperatures for $GdCo_3B_2$.

3. Results and discussion

Fig. 1 shows the temperature dependence of magnetization (M, left scale) and the reciprocal susceptibility ($1/x$, right scale) for $GdCo_3B_2$ in an external magnetic field $H = 0.1$ T. A sharp transition around 54 K and the anomaly change around 160 K were observed. These behaviours were consistent with previous reported results by Ido et al. [16] and similar with those in $TbCo_3B_2$ [14,17]. Sigalov et al. [18] studied the magnetic phase transition in YCo_3B_2 by nuclear magnetic resonance and electron resonance spectra, and they concluded that Co sublattice in RCo_3B_2 orders at 150 (20) K independent of rare earth element Dubman et al. [14] further confirmed this behaviour in $TbCo_3B_2$ by means of neutron diffraction method, i.e. the observed lower temperature transition (~54 K) and the anomaly change (~160 K) in $GdCo_3B_2$ were corresponding to the Gd–Gd sub-lattice and the Co–Co sub-lattice magnetic ordering transition, respectively. The reciprocal susceptibility shows Curie–Weiss behaviour above 200 K. The evaluated value of effective magnetic moment is 9.17 μ_B/f.u., which is obviously larger than free ion value of Gd^{3+} (7.94 μ_B). The magnetization M as a function of applied magnetic field at 2 K up to 7 T for $GdCo_3B_2$ is shown in the inset of Fig. 1. The magnetization of $GdCo_3B_2$ tends to be saturated at low field and remains almost constant up to 7 T. The saturation magnetic moment per formula unit extrapolated to infinite field is 6.2 μ_B/f.u. which is smaller than that of a free Gd^{3+} ion (7.0 μ_B). The inconsistent of the effective magnetic moment and saturation magnetic moment between $GdCo_3B_2$ and free Gd^{3+} ion probably due to the paramagnetic susceptibility includes a Pauli paramagnetic contribution from the Co–Co sub-lattice and the magnetic moment of Co is antiparallel to the Gd moment [16,19].

A set of magnetic isothermals on increasing and decreasing field were measured for $GdCo_3B_2$ with the temperature range from 20 to 80 K up to 7 T. There is no obvious hysteresis for all the temperature range. To ensure the readable of the figure, only several isotherms with increasing field are presented in Fig. 2(a). For low temperature ones, the magnetization M tends to be saturated at low field. A large reversible MCE is expected around the transition temperature where the magnetization rapidly changes with varying temperature. Since the magnitude; temperature and magnetic field change dependence of MCE have a strong correlation with the order of the corresponding magnetic phase transition, it is important to understand the nature of magnetic transition in $GdCo_3B_2$. According to Banerjee's criterion [23,24], the magnetic transition is of a second order if all the H/M versus M^2 curves (also named as Arrott plot) have positive slope. On the other hand, if some of the H/M versus M^2 curves show negative slope at some point, the magnetic transition is of the first order. To further understand the nature of the magnetic transition in $GdCo_3B_2$, the Arrott-plots H/M vs. M^2 at some selected temperatures for $GdCo_3B_2$ are plotted in Fig. 2(b). Neither the inflection point nor negative slopes can be observed, providing the occurrence of a second order magnetic transition for $GdCo_3B_2$.

The magnetic entropy change $-\Delta S_M$ was calculated based on the results of magnetization isotherms using the integrated Maxwell relation [25]:

$$\Delta S_M(T, \Delta H) = \mu_0 \int_0^{H_{max}} \left(\frac{\partial S(H,T)}{\partial H}\right)_T dH \approx \frac{1}{\delta T}\left[\mu_0 \int_0^{H_{max}} \times M(T+\delta T, H)dH - \mu_0 \int_0^{H_{max}} M(T,H)dH\right] \quad (1)$$

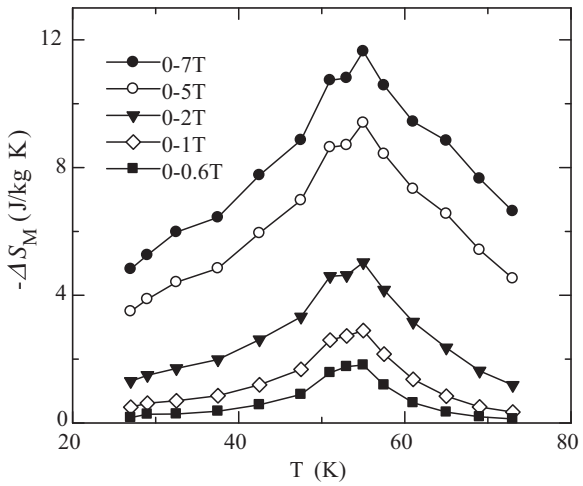

Fig. 3. The magnetic entropy change $-\Delta S_M$ as a function of temperature for various magnetic field changes up to 7 T for $GdCo_3B_2$.

where *S*, *M*, *H*, and *T* are the magnetic entropy, magnetization of the material, applied magnetic field, and the temperature of the system, respectively. The resulting changes of magnetic entropy ΔS_M as a function of temperature for different magnetic field variations up to 7 T are shown in Fig. 3. A considerable magnetocaloric effect was observed around 55 K. The maximum values of magnetic entropy change ($-\Delta S_M^{max}$) reach 9.4 and 11.6 J kg^{-1} K^{-1} for a field change of 5 and 7 T, respectively. The MCE is related to a second order Gd–Gd sublattice magnetic phase transition. The refrigerant capacity or relative cooling power (*RCP*) is an important quality factor of a refrigerant material which is a measure of the amount of heat transfer between the cold and hot reservoirs in an ideal refrigeration cycle. The *RCP* is defined as the product of as the product of the maximum magnetic entropy change $-\Delta S_M^{max}$ and full width at half maximum in ΔS_M (*T*) curve δT_{FWHM}. The *RCP* values for $GdCo_3B_2$ are 110 and 357 J/kg for a field change of 2 and 5 T, respectively. Another important parameter for a MCE material is the temperature dependence of adiabatic temperature change ΔT_{ad}, which was also evaluated. Keeping this context in mind, the temperature dependence of ΔT_{ad} (shown in Fig. 4) for various magnetic field changes up to 7 T has been calculated using the ΔS_M (*T*) and zero-field specific heat results (inset of Fig. 4). The overall nature of ΔT_{ad} as a function of temperature is remarkably similar to that of ΔS_M (*T*). The maximum values of adiabatic temperature change (ΔT_{ad}^{max}) reach 5.2 and 6.4 K for a field change of 5 and 7 T, respectively.

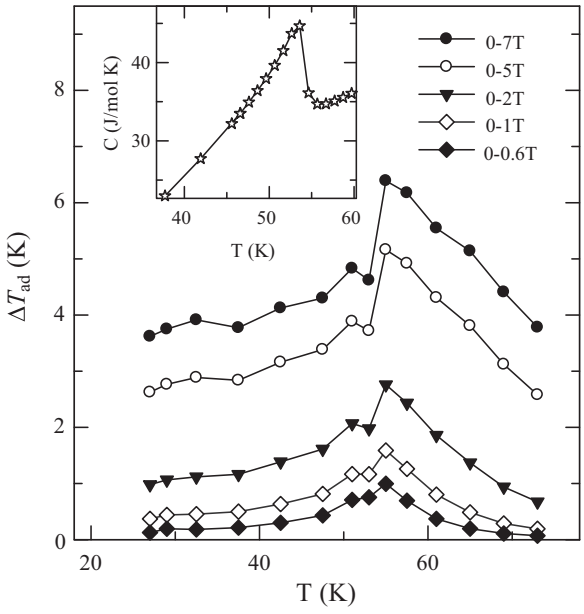

Fig. 4. The adiabatic temperature change ΔT_{ad} as a function of temperature for various magnetic field changes up to 7 T for $GdCo_3B_2$. Inset shows the temperature dependence of zero field specific heat (*C*) for $GdCo_3B_2$.

4. Conclusions

In summary, a single-phased $GdCo_3B_2$ compound has been prepared by an arc-melting method and its magnetic properties and magnetocaloric effect (MCE) of $GdCo_3B_2$ by determining the magnetization and heat capacity. A sharp transition around 54 K and an anomaly change around 170 K has been observed which was corresponding to the Gd–Gd and the Co–Co sublattice magnetic order transition, respectively. The observed reversible MCE around 56 K is related to a second-order Gd–Gd sublattice magnetic phase transition. The maximum values of magnetic entropy change ($-\Delta S_M^{max}$) reach 5.0 and 9.4 J kg^{-1} K^{-1} for the field change of 2 and 5 T, respectively. The corresponding maximum adiabatic temperature changes (ΔT_{ad}^{max}) are evaluated to be 2.8 and 5.2 K. The values of relative cooling power for $GdCo_3B_2$ are 110 and 357 J/kg for a field change of 2 and 5 T, respectively.

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