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Magnetic properties and specific heat of $GdBe_{13}$

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Abstract

New magnetic as well as specific heat measurements on the $GdBe_{13}$ intermetallic compound are reported. The first-order character of the antiferromagnetic transition at $T_N = 26$ K and the overall features of the magnetization processes suggest the presence of high-order exchange interactions in addition to the usual isotropic bilinear coupling.

Keywords: Magnetization processes; First-order transition; Gadolinium compound; Rare earth intermetallics; Specific heat

1. Introduction

The binary intermetallic compounds RBe_{13} (R = rare earth), crystallise in the cubic $NaZn_{13}$-type structure (space group *Fm3c*, $a \sim 10$ Å). The unit cell contains eight formula units. The R^{3+} ions have eight equivalent positions in (1/4,1/4,1/4), whereas the Be atoms occupy two different crystallographic sites, namely 8 Be^{I} in (0,0,0) and 96 Be^{II} in (0,*y*,*z*). If only the R^{3+} ions are considered, this structure corresponds to a simple cubic one of parameter $a/2$. The local symmetry of the R^{3+} ions is cubic, but being surrounded by 24 Be atoms, they have a nearly spherical environment; thus they experience a rather small crystalline electric field. The high stability of these compounds is reflected by high melting points and congruent melting behaviour.

The magnetic structures of the RBe_{13} compounds result from the competition between exchange and magnetocrystalline anisotropy. Helical structures, commensurate and/or incommensurate, have been observed within the series (R = Gd [1], Tb [2,3], Dy [4], Ho [5] and Er [6]. Néel temperatures are rather small, the highest one occurring for $GdBe_{13}$ ($T_N = 28$ K). In $TbBe_{13}$ and $HoBe_{13}$, the periodicity of the incommensurate structure has been found to depend on the temperature, and to lock into a long period commensurate value corresponding to the propagation vector $\boldsymbol{Q}_o = (0, 0, 1/3)$, below a critical temperature T_t. Considering the rare earth sublattice, this vector corresponds to a magnetic unit cell which includes six magnetic moments. The magnetic structure of the compounds with Dy and Er are commensurate in the whole range of temperature below T_N with the same propagation vector $\boldsymbol{Q}_o$. For all the commensurate structures, a distortion from a pure regular helix has been assumed at low temperatures, in agreement with the weak fourfold magnetocrystalline anisotropy.

The compound with gadolinium is particulary interesting since Gd^{3+} is an S-state ion, insensitive to crystal field effects. Its magnetic structure was determined by neutron diffraction [1]: it is an incommensurate spiral structure below $T_N = 26$ K. The propagation vector $\boldsymbol{Q} = 0.285\boldsymbol{c}^*$ is parallel to the $\boldsymbol{c}$ axis and independent of temperature. The magnetic moments of Gd^{3+} ions are perpendicular to the $\boldsymbol{c}$ axis. The angle between magnetic moments in adjacent planes is $\psi = 2\pi c/2$, i.e. $y = 51.1°$. The paramagnetic Curie temperature $\theta_p = 25$ K is only slightly smaller than T_N [7] and this strong positive value is in contrast to the antiferromagnetic characteristic of this compound. In a previous study [8], the magnetization saturates in a field of about 4 T at 4.2 K. In another magnetic study [9], the only magnetization curve

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measured at 2 K showed a hysteresis effect and a kind of metamagnetic transition around 0.3 T. Further magnetization and specific heat measurements were then been carried out on a polycrystalline sample in order to examine the magnetic and thermodynamic properties of this compound in more detail. The results are presented below.

2. Magnetization measurements

The magnetization of $GdBe_{13}$ was measured in the temperature range from 1.5 to 50 K in a magnetic field up to 10 T, by using the extraction method, at the Laboratoire de Magnétisme Louis Néel (Grenoble). The magnetization curves as a function of the applied field are shown in Fig. 1 for different temperatures. At 1.5 K, the magnetization reaches the saturation value of $7.1\mu_B/Gd^{3+}$ above the critical magnetic field $H_s = 7$ T. This saturated value is in agreement with the theoretical Gd^{3+} free ion moment. The inset of Fig. 1 shows the detail of the curve below 5 T for increasing and decreasing field. Contrary to the $Gd_{1-x}U_xBe_{13}$-doped alloys [9], there is no noticeable hysteresis effect in the present measurements. The magnetization process is characterized by a smooth metamagnetic transition at about 2 T, then by a wide negative curvature between 2 and 7 T. This behaviour is not consistent with a helical structure for which a linear field dependence is expected (see Section 4).

3. Specific heat measurements

The specific heat measurements were performed in the temperature range from 1.5 to 40 K by the adiabatic method at Strasbourg. A lattice contribution

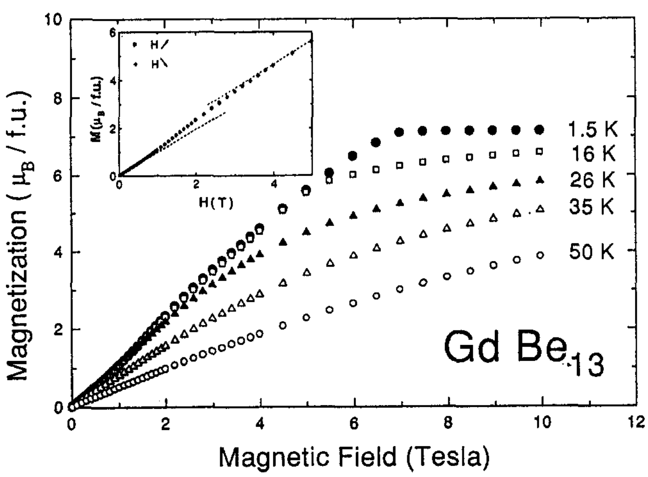

Fig. 1. Magnetization curves of $GdBe_{13}$ at different temperatures. The inset shows the 1.5 K curve for (o) increasing and (+) decreasing field.

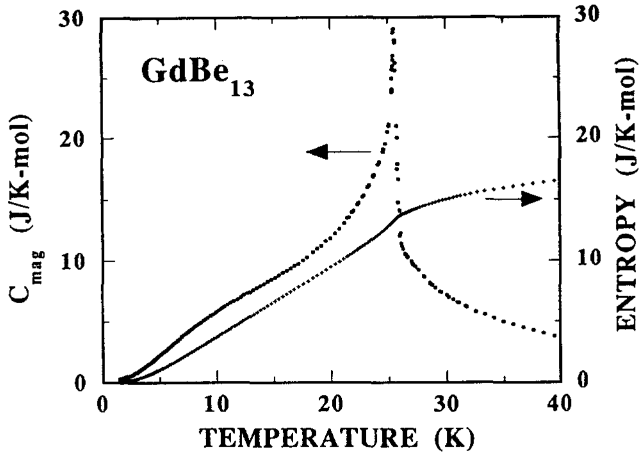

Fig. 2. Magnetic contribution to the specific heat (left scale) and entropy (right scale) of $GdBe_{13}$.

corresponding to a Debye temperature $\theta_D = 600$ K has been considered to deduce the magnetic contribution. This latter is reported in Fig 2: it shows a well-defined cusp-like discontinuity with a height of about 30 J K^{-1} mol^{-1} at $T_N = 25.7$ K. This anomaly is associated with the antiferromagnetic transition. However, the height and shape of this transition suggest a first-order magnetic transition, since the maximum value expected for a Gd^{3+} compound exhibiting a helical structure is only 20.15 J K^{-1} mol^{-1}. By integrating the C/T curve, the entropy has been deduced (see Fig.;2): it reaches 16.5 J K^{-1} mol^{-1}, i.e. about $R\ln8$ at 40 K, in full agreement with Gd behaviour ($J = 7/2$). The entropy at T_N reaches only 82% of the full value $R\ln8$, because of the existence of spin fluctuations above the ordering temperature. This behaviour is quite usual in Gd compounds [10].

4. Conclusion

The present thermodynamic study shows that the antiferromagnetic ordering is of first-order type in $GdBe_{13}$, suggesting the presence of additional higher-order interactions besides the usual bilinear exchange coupling. This characteristic prevents us from determining the type of magnetic ordering from the height of the jump of specific heat at T_N [11]; indeed, for a second-order transition and in the mean-field approximation, the height of the λ-anomaly is expected to reach 20.15 J K^{-1} mol^{-1} at T_N for a helical structure, while it should be reduced to 13.4 J K^{-1} mol^{-1} in the case of an amplitude modulated structure. The only indication in favour of a non-helical magnetic structure is the absence of linearity in the magnetization process at 1.5 K. However, the additional interactions quoted above could also lead to non-linearity effects. Therefore, the helical configuration cannot be definitely ruled out from the present experimental results.

The second point to be emphasized is the small difference $(T_N - \theta_p) \sim 1$ K, compared with the saturation critical field $H_s = 7$ T. Indeed, both values should be connected through the following relation [12]:

$$H_s = \frac{J[J(\boldsymbol{Q}_o) - J(0)]}{g_J \mu_B)}$$

where $J(\boldsymbol{q})$ is the Fourier transform of the exchange interactions. From this expression the critical field is then calculated as $H_s^{calc} = 0.5$ T, a value much smaller than the experimental one. Then it can be assumed that the coupling responsible for the first-order nature of the magnetic ordering should also explain this disagreement. Further investigations are needed to solve this problem, in particular on a single crystal, in order to see to what extent the anisotropy of the exchange couplings affects the magnetic properties of $GdBe_{13}$.

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