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ScienceDirect
Journal of Solid State Chemistry 179 (2006) 2748–2750
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Magnetic structure of rare-earth dodecaborides

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Received 19 September 2005; accepted 26 October 2005
Available online 19 December 2005

Abstract

We have investigated the magnetic structure of HoB_{12}, ErB_{12} and TmB_{12} by neutron diffraction on isotopically enriched single-crystalline samples. Results in zero field as well as in magnetic field up to 5 T reveal modulated incommensurate magnetic structures in these compounds. The basic reflections can be indexed with $q = (1/2\pm\delta,\ 1/2\pm\delta,\ 1/2\pm\delta)$, where $\delta = 0.035$ both for HoB_{12} and TmB_{12} and with $q = (3/2\pm\delta,\ 1/2\pm\delta,\ 1/2\pm\delta)$, where $\delta = 0.035$, for ErB_{12}. In an applied magnetic field, new phases are observed. The complex magnetic structure of these materials seems to result from the interplay between the RKKY and dipole–dipole interaction. The role of frustration due to the *fcc* symmetry of dodecaborides and the crystalline electric field effect is also considered.

PACS: 61.12.–q; 75.40.–s; 75.50.Ee

Keywords: Dodecaborides; Neutron scattering; Magnetic-phase diagram

Magnetic properties of B_{12} cluster compounds have attracted considerable interest in recent years [1,2]. This is above all due to the unique combination of their physical properties, such as high melting point, hardness, thermal and chemical stability, and rich magnetic properties [1–3]. Among them, the rare-earth dodecaborides, which crystallise in the NaCl-based *fcc* structure, exhibit a variety of physical properties which result mainly from the 4*f* occupancy of their rare-earth ions [3]. Thus e.g., LuB_{12} with a fully occupied 4*f* shell is a metal which becomes superconducting below 0.4 K, YbB_{12} is a Kondo insulator, and TmB_{12}, ErB_{12}, HoB_{12} and DyB_{12} are metals which order antiferromagnetic in the Kelvin temperature range. For the magnetic dodecaborides it was shown that the indirect exchange interaction of the RKKY type is the dominating mechanism leading to the observed antiferromagnetic order [1]. However, recent specific heat and magnetisation measurements on small HoB_{12} single crystals and neutron diffraction measurements on powder samples of HoB_{12} [3] have shown that the magnetic structure of some of them exhibits rather complex features. Three magnetic phases were observed e.g. in HoB_{12} below T_N in an applied magnetic field. In zero field the obtained results pointed to an incommensurate amplitude-modulated magnetic structure [3,4]. Therefore, except the RKKY, also other interactions have to be taken into account.

In order to receive more information about the magnetic structure of HoB_{12}, ErB_{12} and TmB_{12}, which order at 7.4, 6.6 and 3.3 K, respectively [1], we investigated them by neutron scattering in magnetic fields up to 5 T and in the temperature range between 1.5 and 15 K.

Neutron scattering experiments were performed at the BER II reactor at the Hahn Meitner Institute, Berlin. Data were taken at a wavelength of 2.45 and 4.5 Å. A 5 T cryomagnet with a variable temperature insert was used to set the temperature and magnetic field. The isotopically enriched single-crystalline samples of HoB_{12}, ErB_{12} and TmB_{12} were prepared by inductive zone melting [3]. All samples have been characterised by a Laue picture which has shown *fcc* symmetry from opposite sides of the slabs. Neutron diffraction revealed the high sample quality, all reflections from the chemical structure are resolution limited.

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0022-4596/$ - see front matter
doi:10.1016/j.jssc.2005.10.046

Fig. 1 shows the reciprocal space map of reflections observed at 2 K and in zero magnetic field for HoB_{12}. These neutron data can be well described assuming an incommensurate magnetic structure with a propagation vector $q=(1/2\pm\delta,\ 1/2\pm\delta,\ 1/2\pm\delta)$, where $\delta=0.035$. The formation of this structure can be understood taking into account the interplay between the indirect RKKY interaction, which favours antiferromagnetic ordering with $q_{AF}=(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and the dipole–dipole interaction that splits this basic propagation vector.

The temperature dependence of magnetic reflections below T_N (Fig. 2) shows a linear increase of the intensity. As the intensity has a square dependence on the order parameter Φ (the sublattice magnetisation), close to T_N the order parameter depends on the reduced temperature as $\Phi \sim t^{1/2}$, which corresponds to a classical behaviour. Note also that the "kink" seen in the temperature dependence at 6.6 K. The temperature of this anomaly coincides with the maximum of the specific heat which in HoB_{12} appear well below T_N [3].

Based on heat capacity measurements [3], in addition to incommensurable form, it was shown that the magnetic structure of HoB_{12} is also amplitude modulated. Such a structure with modulation of the magnetic moment is not likely to be stable. Therefore, towards lower temperature a tendency of "squaring" is expected, so that the different moment values (magnitudes) of the magnetic structure get compensated. In this case, harmonics of basic reflections should appear. The observed (3rd) harmonic satellites are displayed in Fig. 3. The distribution of harmonic satellites at various reflections (e.g. at $(1/2-\delta,\ 1/2+\delta,\ 1/2+\delta)$ and $(1/2-\delta,\ 1/2+3\delta,\ 1/2+3\delta)$ indicate that there is no "simple" amplitude modulation, and that likely a multiple q-structure of the type $\pm(1/2-\delta,\ 1/2-\delta,\ 1/2-\delta)$ has to be considered. The temperature dependence of their intensity (c.f. Fig. 2) shows that the harmonics appear only well below T_N. With available data, for HoB_{12} this temperature is about 6 K.

With increasing magnetic field up to 5 T the basic propagation vector $q=(1/2-\delta,\ 1/2-\delta,\ 1/2-\delta)$ remain. In fields below about 2 T the intensity of the basic reflection reduces only very slightly. In fields higher than 2 T (i.e. in the "higher magnetic field phase") the intensity reduces significantly and an induced ferromagnetic component is observed. This resembles the situation in spin–flop transitions. In absence of a strong "single-ion" anisotropy in dodecaborides (as the *fcc* crystal structure is very symmetric) probably only the dipole interaction can account for a very pronounced induction of a ferromagnetic component. Thus the dipole–dipole interaction seems to manifests itself not only in the magnetic structure (which is incommensurate), but also in the magnetic phase diagram. The sudden change of the reflection intensity with magnetic field at 2 T then can be explained through the repopulation of magnetic domains with different q vectors.

Neutron diffraction investigations of TmB_{12} have shown that within experimental resolution the magnetic structure is the same as in HoB_{12}. On the other hand, the magnetic structure of ErB_{12} differs from the magnetic structure of

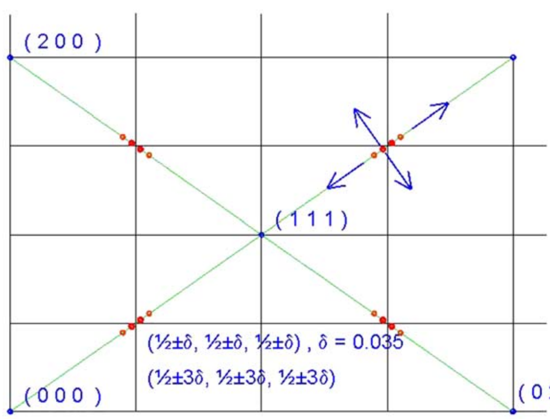

Fig. 1. Reciprocal space map of neutron scattering reflections observed for HoB_{12} at 2 K and in zero field. The points show the observed magnetic reflections. The lines show the scan directions.

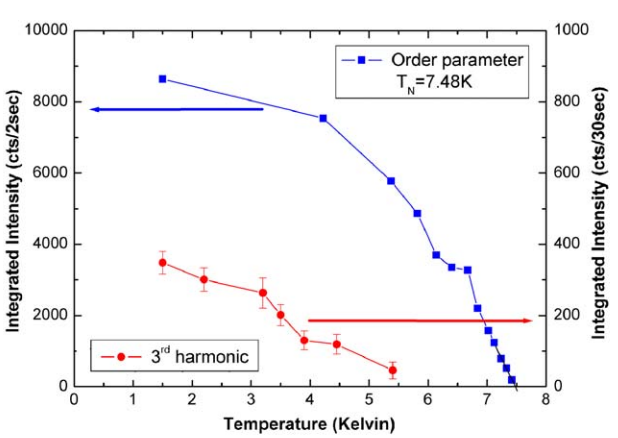

Fig. 2. The temperature dependence of the magnetic reflection $(3/2-\delta,\ 3/2-\delta,\ 3/2-\delta)$ (left scale) and of the 3rd-order harmonics (right scale).

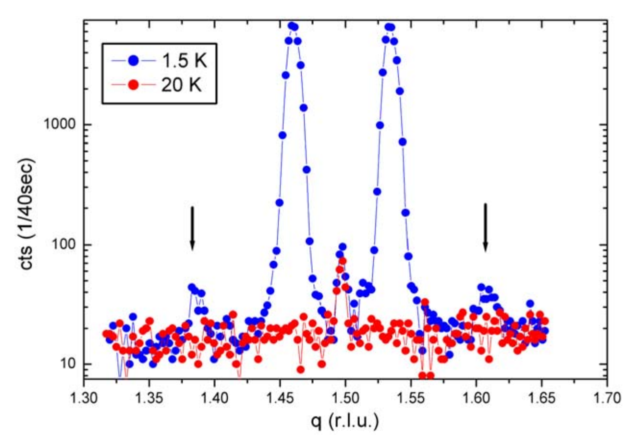

Fig. 3. The magnetic reflections and their third harmonics (arrows). The central peak at (3/2,3/2,3/2) arises from the structural (3,3,3) reflection seen with the remaining $\lambda/2$ contamination of the beam. Note the log scale of the y-axis.

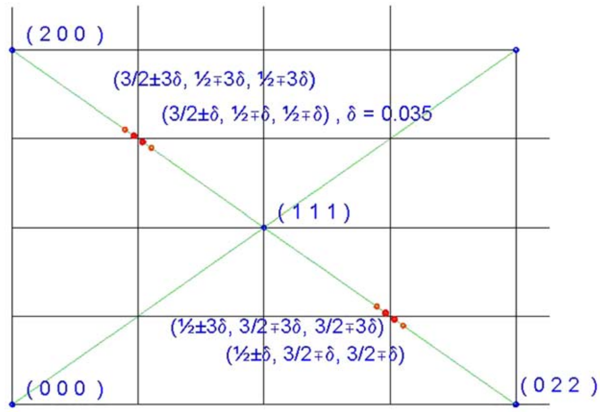

Fig. 4. The reciprocal space map of neutron scattering reflections observed for ErB_{12} at 2 K and in zero magnetic field.

HoB_{12} and TmB_{12}. In ErB_{12} only antiferromagnetic reflections of the type $q = (3/2 \pm \delta,\ 1/2 \pm \delta,\ 1/2 \pm \delta)$ could be observed (Fig. 4). The reason for this difference may be related with the change of the crystallographic structure (symmetry breaking) in this material (from *fcc* to *tetragonal*), which appears at temperatures well above T_N.

In summary, TmB_{12}, ErB_{12} and above all HoB_{12} exhibit very complex magnetic structures. As it was shown, they can result from the interplay between the RKKY and dipole–dipole interaction. There are, however, other effects possible: First, the strong frustration of antiferromagnetic order in the *fcc* symmetry of the dodecaborides could play an important role [5]. The comparison to HoB_6 or other magnetic hexaborides, which crystallise in the *bcc* symmetry, shows that these compounds exhibit a standard antiferromagnetic ordering below T_N [6]. Second, crystalline electric field effects find a rather impressive manifestation, above T_N they are observed in the thermal properties of rare-earth dodecaborides [7]. To determine exactly the role of particular interactions further, experimental investigations and rigorous theoretical studies of this class of materials are needed.

The work was supported by the EC through Access to Research Infrastructures of Human Potential Programme under the 6th Framework Program (Phys-01-641), by the International Association for the Promotion of Cooperation with Scientists from New Independent States INTAS 3036, by the German exchange agency DAAD, by the Slovak Scientific Grant Agency VEGA under Contract 4061 and APVT under Contract 0317, and by the Contract I/2/2003 of the Slovak Academy of Sciences for the Centres of Excellence.

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