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Journal of Magnetism and Magnetic Materials 258–259 (2003) 529–531
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Large crystal structure distortion in DyB_6 studied by X-ray diffraction

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Abstract

A large magnetoelastic coupling induces a lattice distortion of a rhombohedral type in DyB_6. Below the quadrupolar ordering temperature $T_Q = 31$ K the cubic and the distorted phases coexist. The cubic phase disappears at 23 K, which was identified as the magnetic ordering point T_N. In the magnetic phase the distortion $(dl/l)_{111}$ increases monotonically with decreasing temperature and reaches the value of 9×10^{-3} at 8 K, which is one of the largest value known for cubic compounds.

Keywords: Rare-earth hexaborides; Quadrupolar ordering; Magnetoelastic coupling

1. Introduction

A large variety of interesting physical properties is observed in RB_6 hexaborides with the CaCl-type cubic structure. CeB_6 is studied for more than two decades due to the Kondo-effect on the Ce-ions [1], SmB_6 is claimed to be an intermediate-valence compound showing a semiconductor behaviour at low temperatures. Recently, it has been reported that the alkaline-earth hexaboride CaB_6 doped by small amounts of La shows a weak itinerant ferromagnetic behaviour with the ordering temperature of about 600 K [2]. Due to the low work function, LaB_6 attracts much interest as a perspective material for thermo-ionic emission [3].

In the domain of multipolar interactions study, CeB_6 is an important object, since it is an archetype of a system showing antiferroquadrupolar ordering between $T_Q = 3.3$ K and $T_N = 2.4$ K. However, the mechanisms causing this ordering are to be studied more in detail [4,5]. The heavy rare-earth hexaborides RB_6 exist with R = Gd, Tb, Dy and Ho [6]. Owing to a number of problems with their synthesis, these compounds are less investigated. Quadrupolar ordering accompanied by a rhombohedral crystal structure distortion has recently been reported for HoB_6 ($T_Q = 6.1$ K, $T_N = 5.6$ K [7]). TbB_6 has a complicated magnetic phase diagram [8]. GdB_6 shows a first-order transition at $T_N = 15$ K, and another magnetic transition occurs at $T^* = 8$ K [9]. The nature of these transitions in this system with zero orbital moment still remains unknown.

DyB_6 is an antiferromagnet with $T_N = 26$ K. A second transition above T_N associated with ordering of the quadrupolar moments of Dy^{3+} has been found by specific heat and magnetic susceptibility measurements at $T_Q = 32$ K [10]. A large crystal distortion and a complicated magnetic structure have been observed by neutron diffraction [11]. The goal of the current study is to investigate the details of the distorted phase in the quadrupolar and magnetic phases in DyB_6.

2. Experimental part

Polycrystals of the rare-earth hexaborides have been obtained by melting the elemental components (99.9% purity for rare earth and 99% for "crystallic" boron) in an arc furnace under high-purity argon gas. A massive copper plate has been used as a bottom. Since all the heavy RB_6 crystallize by a peritectic reaction, the as-cast ingots obtained from the stoichiometric starting mixture

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0304-8853/03/$ - see front matter
PII: S0304-8853(02)01133-2

contained considerable amounts of RB_4 and RB_{12}, which have been found to be impossible to remove by homogenization in a standard furnace with the annealing temperature up to 1200°C. The amount of the impurity phases was minimized by a suitable tuning of the starting compositions and melting conditions. Compounds with R = Y, Tb, Dy and Ho have been synthesized and their quality has been controlled by X-ray diffraction. The X-ray patterns of the synthesized hexaborides are shown in Fig. 1. The positions of the Bragg peaks for the RB_4 (P4/mmm crystallic structure) and RB_{12} (Fm3 m) phases are indicated by arrows. The total amount of the impurity phases has been estimated as 15% in HoB_6, 7% in DyB_6, 4% in YB_6 and no foreign phases were found in TbB_6. Thus, this method has been found to be suitable for preparing samples for powder diffraction studies.

The temperature dependent X-ray measurements have been performed on a Rigaku-Denki "Geigerflex" diffractometer with 2 kW X-ray tubes using Fe-K_α or Co-K_α radiation. A flow cryostat (Oxford Instruments, CF-100) was used for cooling the sample down to 8 K, the temperature was controlled with an accuracy of 0.25 K.

For DyB_6 the (1 1 0), (2 2 0), (3 2 0) and (4 0 0) reflections were studied in the temperature range 8–35 K. With decreasing temperature, the (1 1 0), (2 2 0) and (3 2 0) reflections split gradually into doublets with equal intensities. No splitting was observed for the (4 0 0) reflection in the whole temperature range. The data obtained show that a rhombohedral crystal structure is stabilized in DyB_6 at low temperatures. In Fig. 2, the (1 1 0) reflection is shown at some characteristic temperatures as an example. The patterns at intermediate temperatures are complicated and can be interpreted as consisting of non-distorted cubic and distorted rhombohedral phases. The concentration of these phases varies with temperature.

Fig. 3 shows the temperature dependencies of the intensity of the X-ray peaks for the cubic and

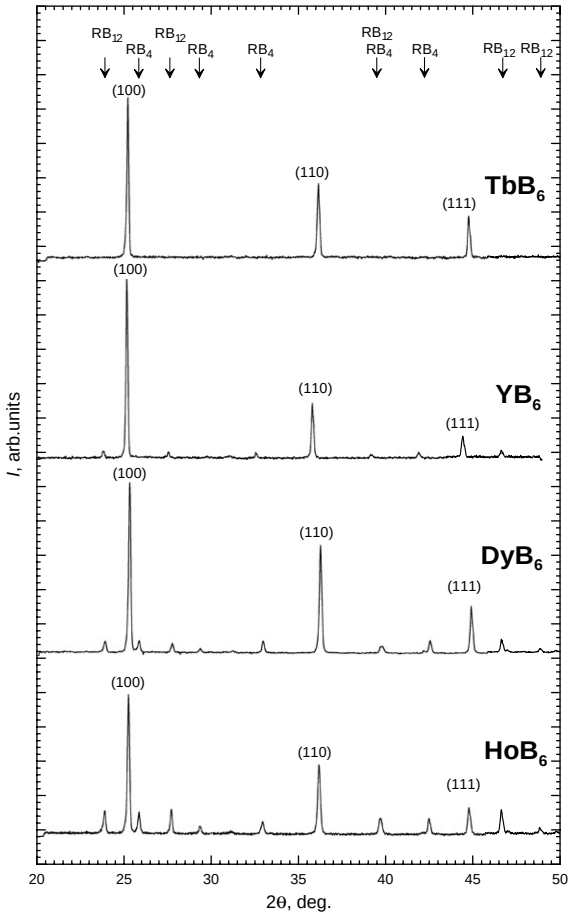

Fig. 1. X-ray diffraction patterns of the synthesized hexaborides (Co-K_α radiation). The positions of the Bragg peaks for the RB_4 and RB_{12} phases are indicated by arrows in the top of the figure.

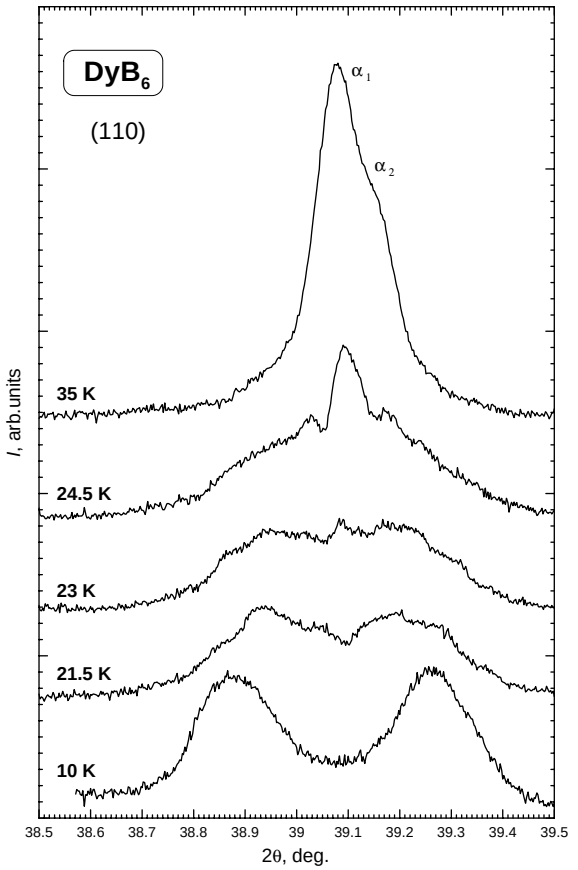

Fig. 2. X ray patterns of the (1 1 0) reflection of DyB_6 at different temperatures (Fe-K_α radiation). Asymmetry of the X-ray peak arises from non-resolved $\alpha_1 + \alpha_2$ doublet as indicated at $T = 35$ K.

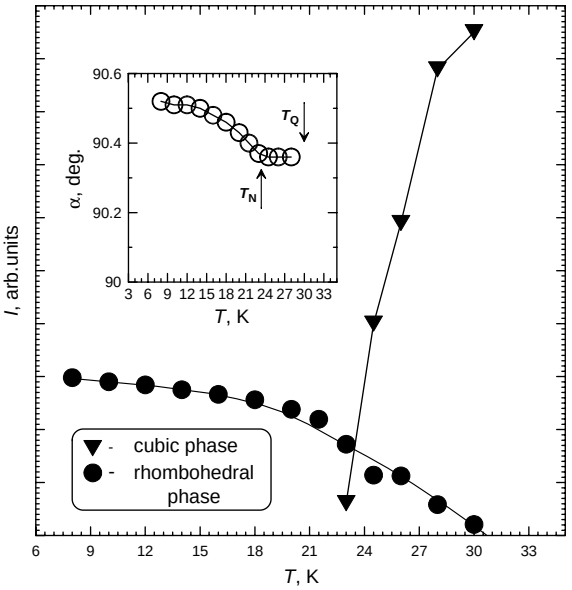

Fig. 3. Temperature dependence of the intensity of the X-ray peaks for the cubic and rhombohedral phases of DyB_6. The inset shows the temperature dependence of the calculated rhombohedral angle. The quadrupolar and magnetic transition temperatures are indicated by arrows.

rhombohedral phases of DyB_6. They correspond to the content of these phases in the material. As can be seen from this figure, the quadrupolar ordering temperature T_Q is about 31 K (in good agreement with [10,11]). The magnetic ordering temperature T_N, at which the non-distorted phase disappears completely, is estimated as 23 K (26 K according to the specific heat data [10]). The inset in Fig. 3 shows the temperature variation of the rhombohedral angle, α, of DyB_6. The jump-like appearance of the lattice distortion proves that the transition at T_Q is of a first-order type. This angle is weakly temperature dependent in the quadrupolar range and corresponds to $(\Delta l/l)_{111} \approx 6 \times 10^{-3}$. Below T_N, this parameter increases monotonically and reaches $\approx 9 \times 10^{-3}$ at 8 K. This value is among the largest one known for cubic compounds: $(\Delta l/l)_{111} \approx 4.5 \times 10^{-3}$ for $TbFe_2$ and $TbCo_2$, 7.0×10^{-3} for US and 8.0×10^{-3} for $NpFe_2$ [12]. Note, in the heavy rare-earth hexaboride series a large value of $(\Delta l/l)_{111}$ (5×10^{-3}) has been found for HoB_6, too [7]. Our X-ray measurements have shown that the lattice distortions in TbB_6 do not exceed 10^{-4}.

Acknowledgements

This work was supported by RFBR, Project No. 00-02-17844, 02-02-06022.

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