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Single crystal growth of CrB_2 using a high-temperature image furnace

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Abstract

Single crystals of CrB_2 have been grown by the floating zone technique. A high-temperature Xenon arc lamp image furnace was used for the crystal growth. The crystals grown by this method are found to be of high quality and are readily characterised by the magnetic transition at $T \sim 88\,K$, as measured by magnetic susceptibility measurements.

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1. Introduction

Borides of transition metals and rare earths have been extensively studied especially with regard to their hardness and their highly refractory properties. A number of diborides and hexaborides have also been investigated for the extensive range of magnetic properties they exhibit [1]. Borides in general possess very high melting points and so the crystal growth of these materials by conventional techniques poses problems. CrB_2 has a melting point of around 2200 °C. Single crystals of the transition metal diborides such as CrB_2 have been grown in the past by the Al flux method [2]. The flux grown crystals are in general small, precluding their use in many investigations where large volumes are required. Larger crystals of CrB_2 have also been grown by the floating zone technique, albeit by the use of a RF induction furnace in order to achieve the high temperatures involved [3].

CrB_2 adopts the AlB_2-type hexagonal crystal structure (space group: P6/mmm) where alternative layers of Cr and B are stacked along the *c*-axis. CrB_2 is known to exhibit a helical (cycloidal)

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magnetic structure [4] and the ordered state has an itinerant magnetic character. It is therefore an interesting system to investigate further if large high-quality crystals can be grown. In this paper, we describe the growth of large high-quality single crystals of CrB_2 by the floating zone technique, making use of a high-temperature image furnace. Initial characterisation of the crystals grown by X-ray as well as by magnetisation measurements are also presented.

2. Experimental procedure

High-purity commercial CrB_2 powder was used as the starting material. This was mixed with amorphous boron powder to provide a slight excess (10–15%) of boron to compensate for any losses during crystal growth. The powders were mixed well and isostatically pressed to produce rods of ~ 6 mm diameter and 70 mm length. The rods were sintered in a flow of argon gas at 1550 °C for 1–2 h. Prior to argon flow during the sintering process, the furnace was evacuated to give a vacuum of $\sim 10^{-5}$ mbar ($\sim 10^{-3}$ Pa). The sintered rods were then used for the crystal growth. Crystal growth was carried out by the floating zone method using a four mirror image furnace equipped with Xenon arc lamps [CSI model FZT-12000-X-VI-VP] [5]. The sample chamber was evacuated to a vacuum of $\sim 10^{-6}$ mbar ($\sim 10^{-4}$ Pa) and then filled with argon gas to a pressure of 0.5 MPa. Crystal growths were performed at this argon gas pressure and the growth speeds ranged from 10 to 18 mm/h. The feed and seed rods were counter rotated at 30 rpm. A polycrystalline seed rod was used for the first growth and the crystal obtained was used as the seed for subsequent growths.

X-ray Laue photographs were taken to establish the single crystal quality of the boules grown. By the use of X-ray Laue patterns, crystals oriented along particular crystallographic axes were cut from the grown boule for various measurements.

Magnetic susceptibility (χ) measurements were carried out using a quantum design superconducting quantum interference device (SQUID) magnetometer in the temperature range 2–300 K.

3. Results and discussion

Fig. 1 shows a photograph of an as grown boule of CrB_2. The boule obtained was black with a metallic lustre. CrB_2 melts congruently, and therefore lends itself very easily to this method of crystal growth. The molten zone was not as wide as might be expected for a feed rod of 6 mm diameter, but was nevertheless stable for the growth period. The molten zone was found to be unstable when argon gas pressures less than 0.5 MPa were used for the growth process. The crystal could be cut using a low speed diamond saw and did not require the use of a spark cutter.

Fig. 2 shows the X-ray Laue photograph taken of a crystal of CrB_2 showing the *ab* plane of the hexagonal lattice. Measurements of the magnetic properties have been carried out parallel to the *ab* plane and along the *c*-axis.

Fig. 3 shows the magnetic susceptibility (χ) measured as a function of temperature for a magnetic field of 1000 Oe applied parallel to the *ab* plane of a CrB_2 crystal. The data shows a clear peak at $T = 88$ K, which has been reported earlier by Castaing et al. [6]. This peak corresponds to long-range helical magnetic order in the system. The susceptibility is found to be isotropic with respect to measurements for the field along both the *ab* and *c* directions. The inverse χ data is found to be linear above 100 K. From a Curie–Weiss fit to the data in the temperature range 100–300 K, the paramagnetic Curie temperature and the effective moments are found to be $\theta_p = -700\ (\pm 5)$ K and $p_{\text{eff}} = 2.1(\pm 0.1)\,\mu_B/\text{Cr}$, respectively.

Fig. 1. Photograph of an as grown boule of CrB_2 obtained by the floating zone technique.

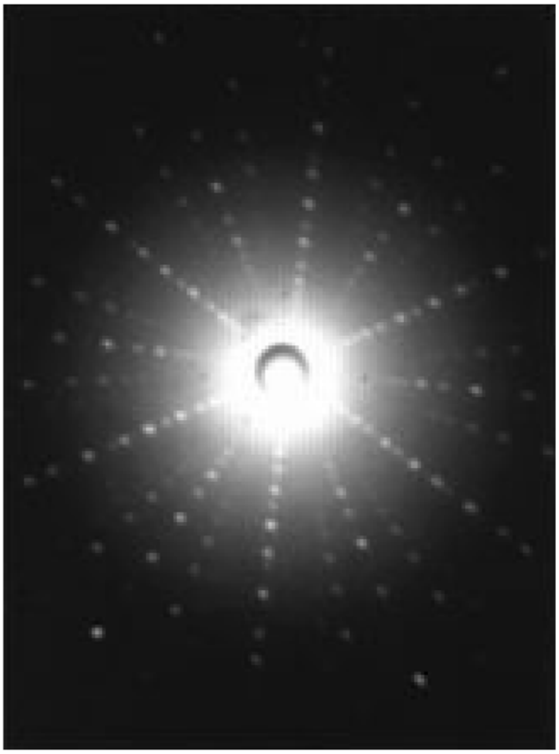

Fig. 2. X-ray Laue back reflection photograph taken of a CrB_2 crystal showing the *ab* plane of the hexagonal lattice.

4. Summary and conclusions

In summary, high-quality single crystals of the magnetic diboride CrB_2 have been obtained by the floating zone technique using a high-temperature Xenon arc image furnace. Crystals of large volume can be easily obtained by this technique. The crystals are found to exhibit the characteristic magnetic transition at $T \sim 88\,K$ as measured by magnetic susceptibility measurements. Heat capacity and more detailed investigations of the magnetic properties have been carried out and will be published separately. Further investigations of the magnetic structure are planned using neutron scattering experiments. A crystal of CrB_2 with enriched ^{11}B isotope is currently under preparation for these experiments.

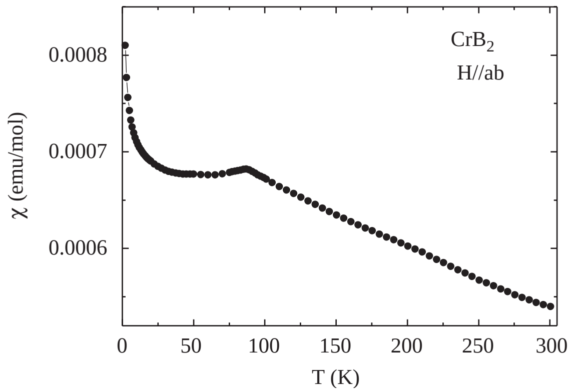

Fig. 3. Magnetic susceptibility (χ) versus temperature of a single crystal sample of CrB_2 measured with an applied field of 1000 Oe parallel to the *ab* plane.

Acknowledgements

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