

NMR Studies of YbB₆

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Abstract

We report results of dc-magnetisation and ¹¹B-NMR measurements on single crystalline YbB₆. The magnetisation data at temperatures between 4 and 300 K reveal weak ferromagnetic order with a $T_C > 300\text{K}$. It involves very small ordered moments, of the order of $0.002\mu_B/f.u.$, representing only a small fraction of the effective paramagnetic moment per formula unit that is indicated by the magnetic susceptibility. The latter can be accounted for by assuming that 2% of all the Yb atoms adopt the Yb⁺³ configuration. Since almost all the Yb ions adopt the divalent configuration one expects YbB₆ to be a poor metal.

Key words: NMR; magnetism; hexaborides

1. Introduction

In 1999 Young and co-workers reported[1] that La-doped CaB₆ exhibits an unusual ferromagnetic state involving the ordering of very small magnetic moments below a surprisingly high Curie temperature. This was completely unexpected because neither B, Ca or La ions are known to carry an intrinsic magnetic moment. Subsequently it has been established[2,3,5] that this phenomenon is not an anomalous behavior of the Ca_{1-x}La_xB₆ series, but also occurs in other Alkali-Earth hexaborides such as SrB₆, BaB₆ and in some samples of CaB₆. These compounds are thought to be vacancy-doped, because a systematic study[3] of the thermal and transport properties of CaB₆ revealed that samples prepared with a starting stoichiometry slightly rich in Ca, to compensate for the tendency of the hexaborides to form with a Ca deficiency, were not ferromagnetic above 2 K. It is believed that the presence of vacancies is important for the magnetic properties of these materials, but the origin of the observed ferromagnetism in Alkali-Earth hexaborides is still not understood. Various difficulties prohibit to establish a co-

herent physical picture of these hexaborides, because clear correlations between the different observed physical properties are missing. For example, in a previous comparative NMR study of Ca_{1-x}La_xB₆ and SrB₆ we found no correlations between the NMR response, and the transport properties of these materials. Here we report preliminary magnetization and NMR data that were obtained on a collection of randomly-oriented millimeter size single crystals of YbB₆.

2. Experimental Results

Using a SQUID magnetometer we have measured the magnetization of YbB₆ as a function of temperature and applied magnetic field. We found that the magnetization M may be written as $M = M_{ferro} + M_{para} + M_{dia}$, where M_{ferro} , M_{para} and M_{dia} are a ferromagnetic, paramagnetic and diamagnetic contributions, respectively. In Fig. 1 we display one example of a hysteresis loop $M(H)$ for YbB₆ measured at a temperature of 6 K. The observation of similar $M(H)$ curves for YbB₆ persists up to 300 K. This is a clear evidence for YbB₆ to be ferromagnetic with a Curie temperature well above 300 K. From the paramagnetic contri-

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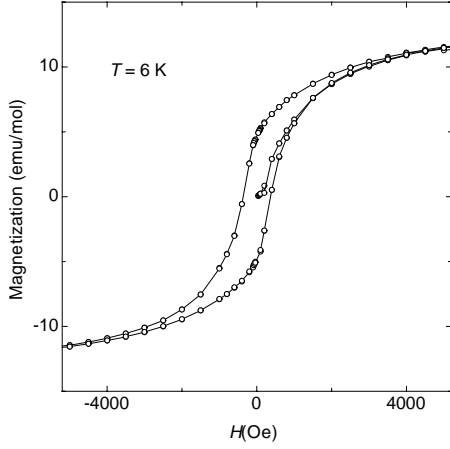


Fig. 1. $M(H)$ hysteresis loop of YbB_6 , measured at 6 K.

bution one infers the presence of localized moments of the order of $0.1\mu_B$ per formula unit. Only Yb^{+3} carry a moment of the order of $4\mu_B$ pro ion. The experimental value of M_{para} implies that 2% of all the Yb atoms adopt the Yb^{+3} configuration, the rest is divalent.

Using standard spin-echo techniques we have measured ^{11}B -NMR spectra at a fixed field of 7.01 T. To enhance the frequency resolution of these measurements we used very long, up to 40 μs , rf pulses. In Fig. 1 we show one example of the ^{11}B central transition measured at 3 K. The ^{11}B -NMR spectra also contain extended wings (not shown here) arising from the quadrupolar perturbation of the Zeeman line.

The main feature of the ^{11}B -central line is the presence of two partially resolved signals. The best fits to this part of the spectrum, using two Gaussian functions, are represented by the solid line in Fig.1. From the center of the Gaussians we extracted the corresponding NMR line shifts which are +34 ppm and -76 ppm, respectively. These shifts have been determined with respect to liquid $\text{B}(\text{OH})_3$ and are approximately temperature independent. Similar results have been observed[5] in other hexaborides both ferro- and non-ferromagnetic, and have been interpreted as evidence for the presence of two different B environments. Considering the crystalline structure, this is definitely an unexpected feature.

3. Discussion

The results for both the magnetization and the NMR spectra of YbB_6 is very similar to those found for other hexaborides[5]. However, taking into account that the Yb ions in YbB_6 are predominantly in a valence state of +2 one may expect that YbB_6 is a nonmagnetic semiconductor, as it was considered for a long time. If, as

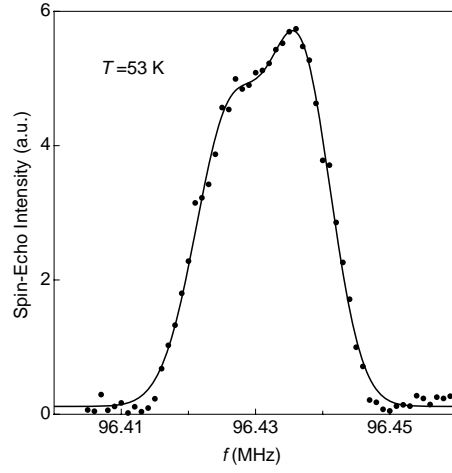


Fig. 2. ^{11}B -NMR central transition of YbB_6 at 7.01 T. Note the two partially resolved signals (see text).

implied by the results of the magnetization, 2% of the Yb ions in YbB_6 are in a trivalent state, the compound is expected to be a poor metal. This conclusion is supported by the temperature dependence of the electrical resistivity $\rho(T)$ of our material[6], which displays a monotonic decrease with decreasing temperatures, by a factor of about 3 between room temperature and 4.2 K.

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- [6] The electrical resistivity of our sample was measured in collaboration with Ch. Bergemann, M. Chiao and G. Wigger.