\textbf{\textit{11B-NMR STUDIES OF WEAKLY FERROMAGNETIC BaB}_6^*}

\textit{SH. MUSHKOLAJ, J.L. GAVILANO, D. RAU, H.R. OTT}

Laboratorium für Festkörperphysik, ETH-Hönggerberg, 8033 Zürich, Switzerland

\textit{A. BLANCHI, AND Z. FISK}

National High Magnetic Field Laboratory, Florida State University
Tallahassee, Florida 32306, USA

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\textit{BaB}_6 is a weakly ferromagnetic material with a Curie temperature \(T_C\) well above room temperature. From the results of d.c. magnetization measurements on single crystalline \(\text{BaB}_6\), the saturation magnetization at low temperatures is \(8\times10^{-4}(\mu_\text{B}/\text{f.u.})\), in line with other weak ferromagnets of the hexaboride series. The \(^{11}\text{B}-\text{NMR}\) spectra measured on a collection of single crystals of \(\text{BaB}_6\) yield a quadrupolar frequency of 472 KHz, in good agreement with calculated field gradients for this type of materials. The central \(^{11}\text{B}-\text{NMR}\) transition consists of two partially resolved signals, where the frequency displacement between them is of the order of 10 KHz. One of the signals exhibits a positive, the other a negative frequency shift, both of the order of 50 ppm. Between 7 K and room temperature these shifts do not vary with temperature. The temperature dependence of the spin-lattice relaxation rate \(T_1^{-1}(T)\) at the B sites is similar to that of other alkaline-earth hexaborides.

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Alkaline-earth hexaboride compounds XB\(_6\) (where X=Ca, Sr and Ba) adopt a simple cubic CsCl-type crystal structure containing divalent metal ions and B\(_6\)-octahedra. In spite of this simple crystal structure they show very puzzling physical properties. \textit{E.g.}, La-doped Ca\(_{1-x}\)La\(_x\)B\(_6\) with \(x=0.005\) and SrB\(_6\) exhibit weak ferromagnetism with very high Curie temperatures \([1, 2]\) of the order of 600 K or more.

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In figure 1 we show one example of a hysteresis loop of BaB$_6$, measured at 200 K, using a commercial SQUID magnetometer. From this type of measurements we found that BaB$_6$ orders ferromagnetically with a Curie temperature $T_C$ well above room temperature. The coercive field $H_C$ at 200 K is of the order of 250 Oe and the saturation magnetization at this temperature is $6.5 \times 10^{-4} (\mu_B/\text{f.u.})$. In addition to the ferromagnetic part of the magnetization, we also identify paramagnetic and diamagnetic contributions. The temperature dependence of the magnetic susceptibility $\chi (T)$, measured at 5 T, exhibits a Curie-Weiss behavior with an effective magnetic moment of $5.6 \times 10^{-2}(\mu_B/\text{f.u.})$ and a paramagnetic Curie temperature of $\theta = -6$ K. The diamagnetic offset is $-2 \times 10^{-6} (\text{emu/mol of f.u.})$ [3]. Similar results were obtained for other weak ferromagnets in the hexaboride series.

$$M_{\text{sat}} = 6.5 \times 10^{-4} (\mu_B/\text{f.u.})$$
$$H_C = 250 \text{ Oe}$$
$$T=200 \text{ K}$$

![Fig. 1. Hysteresis loop $M(H)$ of BaB$_6$ at 200K.](image)

In order to obtain additional microscopic information on the magnetic features of BaB$_6$, we made NMR measurements on $^{11}$B nuclei. For these measurements we have used two types of standard spin-echo NMR techniques: sweeping the magnetic field $H$ at a constant frequency $\nu$ and sweeping the frequency at a constant magnetic field, respectively, and by recording the spin-echo intensity as a function of $H$ or $\nu$. The wide NMR spectra which include the central line and quadrupolar wings were measured by magnetic field sweeping. High resolution measurements of the central line alone were performed at a fixed magnetic field and changing stepwise the frequency. From our measurements of the wings of the $^{11}$B-NMR (data not shown here [3]), we extract a quadrupolar frequency for the $^{11}$B nuclei of 472 KHz,
which implies an electric field gradient at the B sites of $1.09 \times 10^{21}$ V/m$^2$.

This value is in good agreement (better than 5 %) with theoretical values predicted for BaB$_6$ \[4\].

Figure 2 depicts the central transition ($-1/2 \leftrightarrow +1/2$) for $^{11}$B nuclei taken at 85 K in a field of 7.06 T. The central transition consists of two partially overlapping signals with frequency shifts of +60 ppm and -40 ppm, respectively. The frequency shifts have been measured by comparing the position of the two peaks of the $^{11}$B central line in BaB$_6$ with the resonant frequency of $^{11}$B nuclei in liquid B(OH)$_3$. Between 7 K and room temperature the $^{11}$B NMR line shifts do not vary with temperature. The width of each of the two individual $^{11}$B NMR-signals is 10 KHz and their intensities are approximately equal. One may interpret the results for the $^{11}$B NMR central line as an indication that in BaB$_6$ the B sites experience two magnetically different environments. The appearance of two peaks in the $^{11}$B central line seems to be independent of the concentration of conduction electrons, because it has also been observed in hexaborides with very different transport properties, such as CaB$_6$, La-doped CaB$_6$ (Ca$_{1-x}$La$_x$B$_6$ for $x = 0.005$, $x = 0.1$ and $x = 0.2$), BaB$_6$, LaB$_6$ and YbB$_6$ \[3, 5\].

Fig. 2. Central signal of the $^{11}$B-NMR Spectrum of BaB$_6$ at 7.2 T. The solid line represents the best fit to the data at 85 K using the sum of two Gaussian functions.
The temperature dependence of the spin-lattice relaxation rate $T_1^{-1}(T)$ measured in a constant magnetic field of 5.2 T is very different in two different $T$-regions. At temperatures above a crossover temperature of approximately 5 K, $T_1^{-1}$ is, on the average, temperature independent and at temperatures below 5 K it decreases very rapidly with decreasing temperature. These results for the spin-lattice relaxation rate are very similar to the cases of $\text{Ca}_{0.995}\text{La}_{0.005}\text{B}_6$ and $\text{SrB}_6$ [6].

REFERENCES