Lattice Locations of ^{12}B in CaB$_6$

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The nuclear quadrupole interaction of the short-lived β-emitter ^{12}B implanted into CaB$_6$ crystal has been studied by means of modified β-NMR (β-NQR) technique. The electric field gradient at the implanted ^{12}B was found to be $q = -(1.34 \pm 0.05)\times 10^{21}$ V/m^2 at room temperature. From this result it is concluded that the ^{12}B probe nuclei are mainly implanted in the substitutional boron site and are applicable to systematic NMR studies of ferromagnetic La doped CaB$_6$.

Key words: Recoil Implantation; β-NMR; Electric Field Gradient; CaB$_6$.

1. Introduction

Recently, Young *et al.* reported weak ferromagnetism in lightly La-doped calcium hexaboride Ca$_{1-x}$La$_x$B$_6$, in which no magnetic element is contained [1]. NMR studies, such as the observation of the local hyperfine field H_{hf} and the spin-lattice relaxation time T_1, are expected to help understanding the mechanism of the ferromagnetism in this system. The β-NMR technique has been applied to measure H_{hf} and T_1 of short-lived β-emitting nuclear probes implanted into ferromagnetic Fe, Co and Ni [2 - 6]. In this way the electronic structure of such ferromagnetic materials at the impurity sites was clarified, and from the behavior of T_1 near the Curie temperature T_C [2] the nature of the electron-spin structure in Ni was shown. In case of the ferromagnetic CaB$_6$ system, the β-NMR probe ^{12}B ($I^\pi = 1^+$, $T_{1/2} = 20.2$ ms) is quite suitable for a systematic study of H_{hf} and T_1 at the substitutional boron site. For such a study, it is important to determine the implantation site of ^{12}B in CaB$_6$.

As shown in Fig. 1, the crystal structure of calcium hexaboride is basically the CsCl simple cubic structure with calcium ions at the Cs sites and octahedra of boron atoms at the Cl sites. Therefore an axially symmetric electric field gradient exists at the boron site. If the ^{12}B nuclei are implanted in the substitutional boron site, the nuclear quadrupole effect should be observed in NMR spectra of ^{12}B in CaB$_6$. In the present study we observed the β-NMR of ^{12}B implanted into a pure CaB$_6$ crystal to identify the implantation site of ^{12}B.

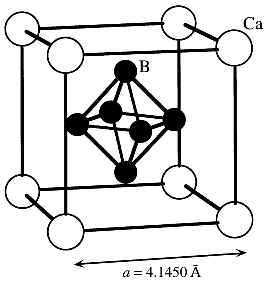

Fig. 1. Crystal structure of CaB$_6$.

2. Experimental

The experimental method is similar to previous work [2 - 6]. The short-lived β-emitter ^{12}B was produced through the ^{11}B(d, p)^{12}B reaction. A deuteron beam of 1.5 MeV, provided by the 5 MV van de Graaff accelerator at Osaka University, was used to bombard a 50 µg/cm^2 thick natural boron target, vacuum evaporated on a 0.5-mm thick water cooled Ta backing. The ^{12}B nuclei ejected from the target to angles rang-

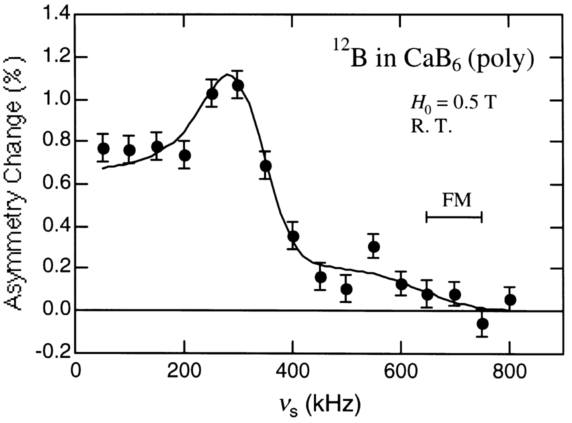

Fig. 2. β-NQR spectrum of ^{12}B in CaB$_6$. The solid curve is the best fit theoretical polycrystal pattern to the data.

ing from 32 to 48 degree relative to the direction of the d-beam were selected with a collimator to introduce polarization. The polarized ^{12}B nuclei were implanted into a CaB$_6$ powder sample placed in a static magnetic field H_0 = 0.5 T applied parallel to the normal of the reaction plane to maintain the polarization and to detect NMR. The initial polarization created through the nuclear reaction was about 10%. The ^{12}B nuclei were distributed over a 0 - 1 µ m implantation depth. The CaB$_6$ powder was supplied with a purity of 99% and a typical grain size of about 50 µm. It was adhered on a PET plate of 0.2 × 22 × 25 mm^3 using an adhesive tape. The simple cubic structure with the proper lattice constant for CaB$_6$ was confirmed by X-ray powder diffraction. The β-rays emitted from the ^{12}B nuclei were detected by two sets of plastic-scintillation-counter telescopes located above and below the sample relative to the reaction plane to detect the asymmetry in the β-ray angular distribution. The asymmetry changes were detected as NMR effects by applying the radiofrequency (rf) of the magnetic field H_1 perpendicular to H_0.

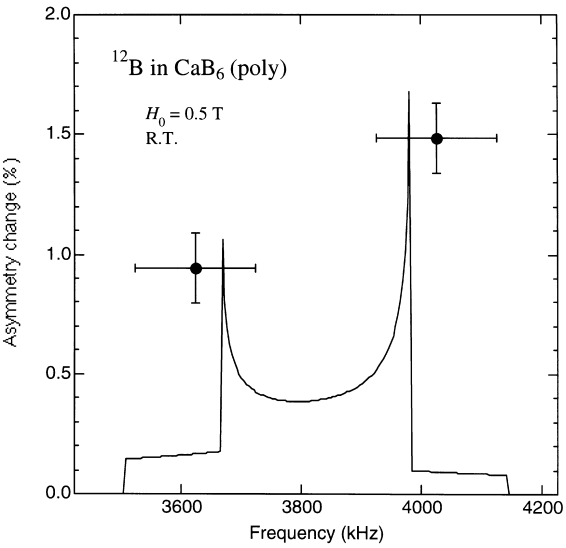

Fig. 3. β-NMR spectrum of ^{12}B in CaB$_6$. The solid curve is the schematic polycrystal pattern in case of negative eqQ/h under the present experimental conditions. The horizontal bars indicate the frequency-modulation range over which the line shape is integrated.

3. Results and Discussion

We observed electric quadrupole splitting at room temperature. For the efficient NMR detection of quadrupole splitting, the β-nuclear quadrupole resonance (β-NQR) technique was performed, in which the adiabatic fast passage (AFP) was used to invert the polarization, applying a set of 3-rf oscillating fields on the 2 frequencies split by the electric quadrupole interaction for nuclear spin I = 1. Figure 2 shows the obtained β-NQR spectrum of ^{12}B in CaB$_6$. The horizontal axis ν_s is the separation frequency which is the full split between the transition frequencies corresponding to the m = +1 $\leftrightarrow$ 0 and –1 $\leftrightarrow$ 0 transitions. Assuming a symmetric electric field gradient, i. e. an asymmetry parameter η = 0 due to the crystal structure of CaB$_6$, the separation frequency ν_s is given as $\nu_s = |\nu_Q(3\cos^2\theta - 1)|$, where $\nu_Q = \frac{3}{4}eqQ/h$ and θ is the angle between H_0 and the electric field gradient q. Random orientation of the field gradient for a powder sample gives a polycrystal pattern $f(\nu_s)$ described as

$$f(\nu_s) \propto \begin{cases} 1/\sqrt{\frac{\nu_s}{\nu_Q}+1} + 1/\sqrt{1-\frac{\nu_s}{\nu_Q}}, & 0 \le \nu_s < \nu_Q, \\ 1/\sqrt{\frac{\nu_s}{\nu_Q}+1}, & \nu_Q \le \nu_s < 2\nu_Q. \end{cases}$$

The electric quadrupole coupling constant eqQ/h was deduced from the χ^2-fitting basically with this line shape function. The effect of the frequency modulation was taken into account in the analysis by integrating $f(\nu_s)$ over the modulation range. This way the coupling constant was determined to be $eqQ[^{12}\mathrm{B}]/h$ = –(427 ± 13) kHz. By integrating the spectrum it turned out that 60 - 90% of the total polarization produced in the reaction was kept in the crystal. The sign of the coupling constant was found to be negative

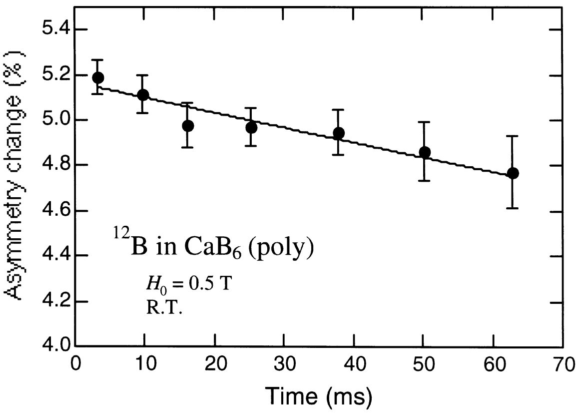

Fig. 4. Time dependence of the polarization of ^{12}B in CaB$_6$ at room temperature. The straight line is a fitting result with an exponential function.

by use of the positive initial alignment of ^{12}B created through the nuclear reaction [7], which gives an asymmetric line shape in the single rf β-NMR spectrum of ^{12}B in CaB$_6$ as shown in Figure 3. Considering the negative initial polarization relative to H_0 and the positive magnetic moment of ^{12}B, the negative sign of eqQ/h can be deduced. Using the known value of the quadrupole moment of ^{12}B; $Q[^{12}\text{B}]$ = (13.21 ± 0.26) mb [8, 9], the electric field gradient q was determined to be $q = -(1.34 \pm 0.05) \cdot 10^{21}$ V/m^2, which agrees well with the data from the ^{11}B-NMR measurement of CaB$_6$ at room temperature; $|q| = (1.28 \pm 0.02) \cdot 10^{21}$ V/m^2 [10, 11], and also Ca$_{0.995}$La$_{0.005}$B$_6$ at 3.12 K; $|q| = 1.40 \cdot 10^{21}$ V/m^2 [12]. Although the Ca$_{0.995}$La$_{0.005}$B$_6$ exhibits ferromagnetic order, the results in [12] have shown the quite small hyperfine field of $\sim 5 \cdot 10^{-4}$ T at the boron site. The theoretical value of $q = -1.36 \cdot 10^{21}$ V/m^2 by Schwarz *et al.* [11] is consistent with the present result. From the present experiment, it is strongly supported that the ^{12}B nuclei are mainly implanted in the substitutional boron site. The other implantation site could not be identified.

The spin-lattice relaxation rate $1/T_1$ of ^{12}B in CaB$_6$ was also measured at room temperature. From the time dependence of the detected polarization shown in Fig. 4, the relaxation rate $1/T_1 = 1.3 \pm 0.4$ s^{-1} was deduced. The present relaxation rate cannot be explained by the contact interaction of conduction electrons. According to the ^{11}B-NMR measurement on LaB$_6$, $(T_1T)^{-1}$ was deduced as $\sim 7 \cdot 10^{-4}$ (Ks)$^{-1}$, which is consistent with the observed NMR line shift [12]. The corresponding relaxation rate of ^{12}B in LaB$_6$ at room temperature is $\sim$0.06 s^{-1}. The present $1/T_1$ for ^{12}B in CaB$_6$ is much larger than this value, though the electric conductivity for CaB$_6$ is about three orders of magnitude smaller than that for LaB$_6$. So the present result implies that another mechanism than the contact interaction contributes more to the spin-lattice relaxation in CaB$_6$.

We are now preparing the next step to observe β-NMR with both pure and La-doped CaB$_6$ single crystal samples as functions of temperature and La concentration.

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