Possible weak magnetism in MB₆ (M:Ca, Ba) probed by muon spin relaxation and muon level-crossing resonance

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Abstract

The temperature dependence of muon spin relaxation rate exhibits a significant increase below ~130 K in CaB₆ and ~110 K in BaB₆, while no sign of spontaneous muon precession signal under a zero field is observed. Moreover, the electric field gradient at the boron site measured by muon level-crossing resonance (μLCR) exhibits a step-like change at ~110 K in CaB₆. These results suggest a change in electronic state and the associated emergence of weak random magnetism below 110–130 K in these alkaline earth hexaborides.

Keywords: Hexaboride; CaB₆; BaB₆; Muon spin relaxation (μSR); Muon level-crossing resonance (μLCR)

1. Introduction

Rare-earth hexaborides LnB₆ (Ln: rare-earth ions) crystalize to a CsCl-type crystal structure with Pm₃m symmetry, in which Ln ions and B₆ octahedra are located on the Cs and Cl sites, respectively. They exhibit a variety of physical properties, depending on the rare-earth ions. For example, cerium hexaboride (CeB₆) is a well-known example of typical ‘Kondo lattice’ systems in which a long-range ordering of quadrupolar moments is strongly suggested both experimentally and theoretically, and SmB₆ is a classical mixed-valence compound. The inclusion of YB₆ may add ‘superconductivity’ to the variety as it falls into a superconducting state with a modest critical temperature Tc = 7.1 K.

While the rare-earth hexaborides have been serving for decades as testing grounds for the understanding of electronic correlation in the f-electron systems, it is only very recently when Young et al. reported ferromagnetism in a lightly doped divalent hexaboride Ca₁₋ₓLaₓB₆ [1] that the alkaline earth hexaborides MB₆ (M = Ca, Sr, Ba, which are presumed to be nonmagnetic and semiconducting) have become a focus of much attention. They reported a number of unprecedented characters in Ca₁₋ₓLaₓB₆ over a narrow range of carrier concentration (0 < x < 0.01), most notably the ferromagnetic behavior with a small magnetic moment (~0.07 μB/La) and a high Curie temperature (Tc = 600 K), which prompted various experimental and theoretical investigations to elucidate the origin of the weak ferromagnetism in such a nonmagnetic compound [2–8]. However, none of these has been successful to provide convincing evidence in the microscopic scale for the occurrence of the ferromagnetism originally reported for Ca₁₋ₓLaₓB₆ (including the case for x = 0). This strongly suggests that the magnetism in question might be characterized by very small moments and/or a short range, making it difficult to probe by conventional techniques such as neutron diffraction or nuclear magnetic resonance. It is clear that the muon spin rotation/relaxation (μSR) technique is uniquely suited for studying such a weak magnetism.

In this paper, we report our μSR study on polycrystalline MB₆ (M = Ca, Ba) to investigate the magnetic ground state of the parent compounds for doped hexaborides. Considering our preliminary result that the weak magnetism appears as an increase in dipolar width (Δ) in the Gaussian distribution of local fields, great care has been taken to extract the parameters...
in the Kubo–Toyabe relaxation function in a reliable manner; we have performed μSR measurements under both zero-field (ZF) and longitudinal-field (LF) conditions at a temperature so that the two parameters, Δ and the fluctuation rate for the local field ν (to that due to muon diffusion), can be deduced by fitting the two spectra simultaneously. In addition to the conventional μSR measurements, the muon level crossing resonance (μLCR) technique has been employed to probe the electric field gradient (EFG) felt by the boron nuclei.

We show that the muon spin relaxation rate (Δ) in CaB₆ exhibits a clear enhancement below ~130 K, suggesting the emergence of weak magnetic moments at lower temperatures. A similar result was obtained below ~110 K in BaB₆. The absence of coherent muon precession under a zero field, however, indicates that those moments are randomly oriented. On the other hand, the temperature dependence of ν exhibits little correlation with that of Δ, demonstrating that the observed change in Δ is not due to an irrelevant effect such as muon diffusion. Moreover, we have observed the appearance of two resonance fields in the μLCR spectra of CaB₆ below 110 K, indicating that EFG at the boron sites undergoes a significant change at this temperature. These observations strongly suggest that the magnetic anomaly around 110–130 K is intrinsic and common in divalent alkaline earth hexaborides.

2. Experiments

The polycrystalline samples were prepared by the solid-state reaction of high-purity CaCO₃ (99.999%), BaCO₃ (99.999%) and amorphous B (99.995%) powders. The stoichiometric powder mixtures were pressed into pellets and sintered at 1600 °C for 2 h under a reduced atmosphere. The crystal structures of these samples were examined by the conventional powder X-ray diffraction technique. The diffraction signal showed that both CaB₆ and BaB₆ were in the single phase. Magnetic susceptibility measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (MPMSR2, Quantum Design Co., Ltd), from which it was inferred that the present samples do not exhibit any ferromagnetism as a bulk property.

The μSR and μLCR experiments on CaB₆ were performed at the Meson Science Laboratory (KEK-MSL, Japan) and at the Tri-University Meson Facility (TRIUMF, Canada). The μSR measurements on BaB₆ were carried out at the RIKEN-RAL Muon Facility (RIKEN-RAL, UK). The muon spin polarization was measured from the forward-backward asymmetry of the decay positrons using the conventional μSR technique. For the temperature scan, μSR time spectra under a weak longitudinal magnetic field (LF, with B₀≈3 mT) were measured in combination with ZF spectra to extract the parameters in the Kubo–Toyabe (KT) relaxation function, \( G_{\text{KT}}^z(t; \Delta, \nu) \), with `\( \Delta \)` without much ambiguity[9]: When \( \nu \geq \Delta \) is satisfied, the KT function is approximately written in the form

\[ G_{\text{KT}}^z(t; \Delta, \nu) = \exp(\nu t) \]  

with the net relaxation rate \( \lambda \) described as

\[ \lambda(\omega_\mu) = \frac{2\Delta^2 \nu}{\omega^2 + \nu^2} \]  

where \( \omega_\mu = B_0 \gamma_\mu \) is the muon Zeeman splitting with \( \gamma_\mu \) being the muon gyromagnetic ratio (=135.53 MHz/T). Note that \( \Delta \) is determined only by the ratio between \( \Delta \) and \( \nu \) when \( B_0=0 \), which makes it difficult to deduce these two parameters independently from the fitting analysis. The relaxation rate \( \lambda \) exhibits a strong field dependence when \( \omega_\mu \sim \nu \), and thereby one can obtain a reliable estimate of \( \nu \) by additional measurement under a longitudinal field.

The μLCR measurements were performed in the time-integrated mode, where the change in the relaxation rate due to resonance was detected as that in the integrated positron decay asymmetry, \( I(B) \); this allowed the maximal use of incoming muon beam intensity required for the high statistical precision to determine the small change in relaxation rate. In the actual measurements of integrated asymmetry, two sets of data, \( A_{\pm} = I(B \pm \delta B) \), were obtained simultaneously by driving the correction coils for the longitudinal field in the flip-flop mode with the modulation field \( \delta B \approx \pm 0.3 \) mT] to minimize the systematic uncertainty due to the change in beam-delivery conditions throughout the μLCR runs.

3. Results

Fig. 1 shows typical ZF- and LF-μSR time spectra observed in CaB₆ at 2 K (a), 50 K (b), 100 K (c) and 150 K (d) (similar time spectra were observed in BaB₆). Neither of these spectra under a zero field exhibits a spontaneous precession signal expected for the formation of a magnetic long-range order. As mentioned earlier, we employed a fitting procedure to incorporate both ZF and LF time spectra simultaneously, assuming two components with one described solely by the random local fields from boron nuclear moments over the

Fig. 1. ZF- and LF-μSR time spectra in CaB₆ at 2 K (a), 50 K (b), 100 K (c) and 150 K (d). Solid curves are results of fitting obtained using Eq. (3).
These temperatures. As shown in Fig. 2(b), the fractional yield over the temperature region where \( D \) for CaB\(_6\) and BaB\(_6\), respectively, indicating that a can clearly observe the enhancements of function, symbols represent data for CaB\(_6\) and BaB\(_6\), respectively.

For 'magnetic' part of relaxation, and (b) fractional yield. Solid and open change in entire range of temperature, and the other which exhibits a change in \( \Delta \) due to the additional effect of the weak magnetism, both of them being described by the Kubo–Toyabe relaxation function,

\[
P_{\mu}(t) \equiv f G_{\mu}^{KT}(t; \Delta, r_i) + (1-f) G_{d}^{KT}(t; \Delta_{\text{dip}}, r_2)
\]  

(3)

with \( \Delta_{\text{dip}} \approx 0.22(1) \mu s^{-1} \) for CaB\(_6\) and BaB\(_6\), determined from the data above 150 K (which were fixed in the fitting analysis). Note that the convolution of Gaussian random local fields from two independent sources, one from the boron nuclear moments (described by \( \Delta_{\text{dip}} \)) and the other of some electronic origin (\( \Delta_{\text{mag}} \)) gives rise to the Kubo–Toyabe relaxation with \( \Delta^2 = \Delta_{\text{mag}}^2 + \Delta_{\text{dip}}^2 \); there is no need to consider the correlation between those two fields, as it turns out that the moment size in the latter is extremely small (see below) and thereby the associated hyperfine field would be negligible. The \( f \) in Eq. (3) is the fractional yield of the signals between the low temperature phase (convoluted by the nuclear dipolar moment and additional magnetic moment) and high temperature phase (nuclear dipolar moment only).

As shown in Fig. 2(a), the relaxation rate above 140 K (= 0.2 \( \mu s^{-1} \)) could be fully explained by the nuclear dipolar fields from the boron nuclei for CaB\(_6\) as well as a relaxation rate above 120 K for BaB\(_6\), where \( \Delta \) in both cases is in excellent agreement with that of the paramagnetic phase in CeB\(_6\). Thus, the fitting with Eq. (3) has little sensitivity for determining \( f \) over the temperature region where \( \Delta = \Delta_{\text{dip}} \). Meanwhile, one can clearly observe the enhancements of \( \Delta \) below 130 and 110 K for CaB\(_6\) and BaB\(_6\), respectively, indicating that a significant change in the static random local fields sets in at these temperatures. As shown in Fig. 2(b), the fractional yield \( f \) exhibits a gradual increase with decreasing temperature in both specimens over the relevant range of temperature.

Since, both time spectra are well described by the Kubo–Toyabe relaxation function in which the Gaussian field distribution is adopted, the additional local fields below 130 and 110 K are probably due to newly appeared magnetic moments which are small, randomly oriented, and closely situated to muons similar to the boron nuclei. It must be stressed that such a Gaussian distribution of local fields is not explained by dilute paramagnetic impurities; it would give rise to the Lorentzian-type broad distribution, leading to the exponential decay of the muon polarization. Assuming a unique size for the speculative electronic moment associated with boron atoms, we can estimate the moment size by evaluating the relation \( \Delta_{\text{mag}} = \sqrt{\Delta^2 - \Delta_{\text{dip}}^2} \approx \sqrt{2}\delta_{\text{VV}} \approx 0.5 \mu s^{-1} \), where \( \delta_{\text{VV}} \) is the polycrystalline average of the classical Van Vleck second moment given as

\[
\delta_{\text{VV}}^2 = \frac{4}{15} \gamma^2 \sum_i \frac{\mu_i^2}{r_i^6},
\]

(4)

with \( \mu_i \) being the electronic magnetic moment associated with the \( i \)th boron site located at a distance \( r_i \) from the muon site [9]. Since, muons can be assumed to occupy the (1/2,0,0) site in the cubic unit cell with a boron octahedron at the body center [10], our estimation using Eq. (4) yields \( \sqrt{\mu_i^2} = 3.2 \times 10^{-3} \mu_B \). It is readily understood that such a small moment is not detected by any other experimental techniques.

One might suspect that the increase in \( \Delta \) at low temperatures may originate from the slowing down of the muon hopping motion. The present ZF/LF-\( \mu \)SR data allow us to examine this possibility by investigating the temperature dependence of the fluctuation rate, \( \nu \), which is well separated from the dipolar width \( \Delta \). Fig. 3(a) shows the temperature dependence of \( \nu_1 \), where a small hump is observed at approximately 100 K in CaB\(_6\) and 80 K in BaB\(_6\). On the other hand in Fig. 3(b) (and inset), \( \nu_2 \) exhibits a monotonic increase at temperatures above \( \sim 130 \) K in CaB\(_6\) and \( \sim 110 \) K in BaB\(_6\). The former, \( \nu_1 \), which might be dominated by the fluctuation of \( \Delta \), coincides with the temperature where \( \Delta \) levels off, while the latter, \( \nu_2 \), has little correlation with the behavior of \( \Delta \). The increase in \( \nu_2 \) for a high-temperature region is readily understood by considering thermally activated muon diffusion, whereas the small hump may be due to the spin dynamics of additional moments. The large difference in muon hopping rate (\( \nu_2 \)) between CeB\(_6\)/BaB\(_6\) and CeB\(_6\) is probably because the \( \mu^+ \) hopping rate is predominantly determined by the tunneling matrix element which is extremely sensitive to the distance between the nearest neighboring sites; it is well established that muon diffusion in solids at ambient temperature is controlled by phonon-assisted tunneling. However, there remains a possibility at this stage that the ‘motional narrowing’ effect may contribute to the change in \( \Delta \) over the intermediate-temperature region.

The presence of a magnetic anomaly, which is attributed to the contribution of newly appeared small magnetic moments, is

![Fig. 2. Temperature dependence of (a) dipolar width in Kubo–Toyabe function for ‘magnetic’ part of relaxation, and (b) fractional yield. Solid and open symbols represent data for CaB\(_6\) and BaB\(_6\), respectively.](image)
further supported by the result of the \( \mu \)LCR experiment. The time-integrated and field-differentiated \( \mu \)LCR spectra \( \delta A \) at several temperatures are shown in Fig. 4, where the resonance is observed at the field of ‘zero-crossing’.

In the case of \( ^{11}\text{B} \) (\( I = \frac{3}{2} \)), single resonance is expected to occur at the field

\[
B_{\text{res}} \approx \frac{3e^2qQ}{4\hbar^2\gamma_\mu},
\]

where \( q \) is the EFG at the boron sites and \( Q \) is the nuclear electric quadrupolar moment of boron nuclei [11]. At higher temperatures above \( T_q \approx 110 \text{ K} \), one can observe a resonance near 4 mT which is overlapped with the gross change associated with a ‘zero-field’ crossing. On the other hand, the resonance field is shifted to \( \approx 7 \text{ mT} \) below \( T_q \). More surprisingly, two resonances are clearly observed at low temperatures. These \( \mu \)LCR spectra can be reproduced by the form

\[
\delta A \propto -\sum_{n=0}^{m} c_n(B - B_{\text{res}}^n) \exp[-\gamma_\mu^2(B - B_{\text{res}}^n)^2/L^2],
\]

where the term with \( n = 0 \) is for the zero-field crossing \( (B_{\text{res}}^0 = 0) \), \( c_n \) is the amplitude of reduction determined by the relaxation rate at each level-crossing field, and \( L \) is the resonance width determined by \( \Delta \). The solid curves in Fig. 4 are fitting results obtained using Eq. (6), with which we obtain the resonance fields as displayed in Fig. 5.

The resonance field above \( T_q (B_{\text{res}} \approx 4 \text{ mT}) \) is in perfect agreement with that in the paramagnetic phase of CeB\(_6\) obtained by \( \mu \)LCR (\( = 3.89(4) \text{ mT} \)) [10] and \( ^{11}\text{B} \) NQR (\( = 3.95(4) \text{ mT} \)) [12], thereby indicating that there is no muon-induced effect; the EFG at the boron site is predominantly determined by the crystal field and the additional charge brought by muons has little influence. On the other hand, we clearly observed two resonance fields below \( T_q \), both being larger than that above \( T_q \). This is not explained by the change of muon site, because there is no such site to increase \( q \) for all the neighboring boron nuclei in this simple crystal structure; muons are situated at the center of the boron octangle, where any shift of the muon toward one boron atom (to obtain a larger

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Fig. 3. Temperature dependence of (a) fluctuation rate \( \nu_1 \) for internal field \( \Delta \), and (b) \( \nu_2 \) for \( \Delta_{\text{dip}} \) in CaB\(_6\) (solid symbols) and BaB\(_6\) (open symbols), respectively. The inset shows a magnified view of \( \nu_2 \) for 65–165 K.

Fig. 4. Time-integrated \( \mu \)LCR spectra of CaB\(_6\) at several temperatures, where arrows indicate position of resonance field. Solid curves are results of fitting obtained using Eq. (6).

Fig. 5. Temperature dependence of resonance field in CaB\(_6\) obtained by fitting the \( \mu \)LCR spectra in Fig. 4.
q by the positive muon charge) would lead to a shift away from another boron atom (smaller q). Since, the change in the crystal structure of CaB$_6$ is not observed at around $T_q$ by Raman scattering, [13] the increase in q may be attributed to a slight change in the electronic state around boron atoms without crystal structure change. Meanwhile, the quadrupolar splitting of $^{11}$B NMR in CaB$_6$ under a field of 5.2 T is reported to be approximately 4 mT and remains unchanged in passing through $T_q$ [14], suggesting that the change observed by μLCR occurs only at lower magnetic fields. The fact that $T_q$ nearly coincides with the temperature where $\Delta$ levels off suggests a close link between the change in EFG and the emergence of a weak magnetism in CaB$_6$. In any case, these characteristic temperatures seem to have little correlation with the high Curie temperature found in the previous study [1].

4. Conclusion

In conclusion, we have performed extensive μSR experiments on polycrystalline samples of alkaline earth hexaborides MB$_6$ (M = Ca, Ba) and additional μLCR experiments on CaB$_6$ to elucidate the microscopic origin of the magnetic anomaly in these compounds. In both CaB$_6$ and BaB$_6$, we clearly observed enhancements of relaxation rate below 130 and 110 K, respectively, which are attributed to the contribution of newly appeared small magnetic moments ($\sim 3.2 \times 10^{-3} \mu_B$) without a long-range order. Furthermore, it was revealed by μLCR that a change in the EFG at the boron site occurs in CaB$_6$ at a well-defined temperature, $T_q \approx 110$ K. These results strongly suggest that alkaline earth hexaborides undergo a subtle change in electronic state at a low temperature around $T_q$, while seems hardly relevant to the previously reported ferromagnetic behavior in Ca$_1-x$La$_x$B$_6$.

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