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Evidence for a ferromagnetic transition in $Yb_{1-x}La_xB_6$ $(0 \leqslant x \leqslant 0.006)$

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Magnetization and muon spin relaxation (μSR) in $Yb_{1-x}La_xB_6$ have been measured to study whether ferromagnetic moments appear as in La-doped CaB_6. Magnetization processes of polycrystalline samples for $0 \leqslant x \leqslant 0.006$ have revealed ferromagnetic hysteresis with a saturation moment of $1 \times 10^{-4} \mu_B$/f.u. On cooling below 150 K, an increase of the internal field up to 0.6 mT has been observed by zero-field μSR measurements on both polycrystals and single crystals. These results indicate a ferromagnetic transition at 150 K in this system.

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It has been reported that $Ca_{1-x}La_xB_6$ ($x \sim 0.005$) is an unusual ferromagnet with a small ferromagnetic moment ($\sim 0.07 \mu_B$/La) but a very high Curie temperature T_c of 600 or 720 K.[1] This report inspired many experimental and theoretical researchers to work on this system and related hexaborides.[2–5] In fact, similar ferromagnetic behavior has been found in SrB_6 and BaB_6.[6,7] However, these observations have left some doubt about an impurity effect because the T_c's are close to those of FeB and Fe_2B, respectively. The possibility of such an impurity effect would be left out for ferromagnetic hexaboride systems with different T_c's. Keeping this in mind, we have searched for another ferromagnet among divalent rare-earth hexaboride systems. It is known that both EuB_6 and YbB_6 are divalent semimetal or semiconductor, and the former is a ferromagnet with $T_c = 16$ K.[8,9] In spite of additional anomalies far below T_c, the ferromagnetism of EuB_6 is likely to originate from the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between $4f$ electrons and conduction carriers. In this compound, a divalent Eu ion has a half-filled f^7 shell that has a large spin magnetic moment of $\frac{7}{2}\mu_B$. Even if EuB_6 would exhibit the $Ca_{1-x}La_xB_6$-type ferromagnetism at temperatures higher than 16 K, it should be difficult to separate such a small ferromagnetic component from the large paramagnetic component due to the f electrons. On the other hand, YbB_6 with a completely filled f^{14} shell is diamagnetic. Band calculations and x-ray photoemission studies[10–13] of YbB_6 indicated that the electronic structure at the Fermi energy is very similar to that of CaB_6. This fact has stimulated us to study the magnetic properties of La-doped YbB_6 system. We have undertaken the complemental experiments by the measurements of bulk magnetization and internal fields with muon-spin-relaxation (μSR) techniques. Since μSR is very sensitive to a small magnetic moment, this technique is powerful as a microscopic probe for the small-moment system with the internal field of ~ 0.1 mT.[14] In this paper, we report on the observation of ferromagnetic behavior in $Yb_{1-x}La_xB_6$ $(0 \leqslant x \leqslant 0.006)$ at temperatures below 150 K.

Polycrystalline samples of $Yb_{1-x}La_xB_6$ were prepared by a borothermal reduction at about 1700 °C,

$$Yb_2O_3 + 15B \rightarrow 2YbB_6 + 3BO\uparrow.$$

For this reaction, we used a radio-frequency induction furnace. Single-crystal samples were grown by a floating-zone method using an image furnace equipped with four xenon lamps.[15] The light was focused in a spot less than 8 mm diam by ellipsoidal glass-mirrors coated with aluminum. Two polycrystalline sintered rods of 6 mm diam were placed respectively from the upper and lower sides. During the crystal growth at 2300 °C, the composition of Yb was easily decreased from the starting one due to its high vapor pressure, leading to the formation of an impurity phase of YbB_{50}. We have found that YbB_{50} crystallizes into the TbB_{50}-type orthorhombic structure.[16] In order to eliminate YbB_{50} from the crystals of YbB_6, a nominal composition of $Yb_{1.08}B_6$ was chosen for sintered polycrystalline rods for the single-crystal growth.

The high-resolution x-ray diffraction measurements have been performed using synchrotron radiation at SPring-8. The analysis revealed that both polycrystals and single crystals have no impurities of FeB and Fe_2B except for a small amount of paramagnetic YbB_4 ($\leqslant 0.001$ at. %). In the binary phase diagram of Yb-B,[17] the Yb hexaboride has a homogeneity range for $\delta \leqslant 0.08$ as the form of $Yb_{1\pm\delta}B_6$, which incongruently vaporizes above the melting point of 2300 °C. Therefore, one may expect the presence of different amounts of imperfections in the samples, depending on the preparation methods. Nevertheless, the lattice parameter was found to be almost the same irrespective of the starting compositions and of the preparation methods. In fact, lattice parameters of $Yb_{1+\delta}B_6$ single crystals are 4.1479 and 4.1481 Å for starting compositions $\delta = 0$ and 0.08, respectively. For a sintered polycrystal sample of $Yb_{1.00}B_6$, slightly smaller value of 4.1477 Å was obtained. Because the difference between these values is comparable to the resolution of ± 0.0001 Å, it is difficult to estimate the amount of imperfections. On this

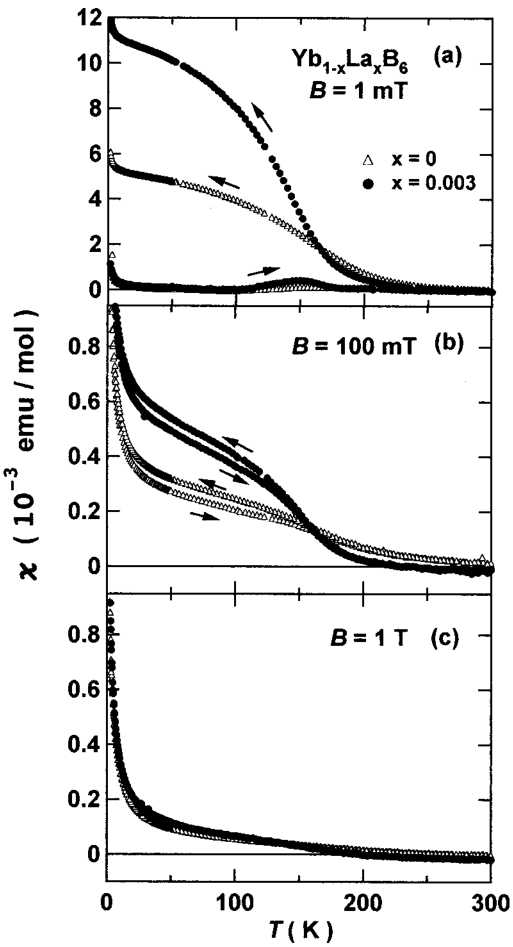

FIG. 1. Temperature dependence of the magnetic susceptibility on polycrystalline $Yb_{1-x}La_xB_6$ with $x=0$ and 0.003 in various magnetic fields $B=1$ mT (a), 100 mT (b), and 1 T (c).

account, an electron-probe microanalysis has been performed in order to check the possible difference in compositions between single-crystal and polycrystal samples. Although evaluation of the absolute composition of boron is difficult by this analysis, the relative resolution is better than 1%. By two-dimensional scans, inhomogeneous distribution of La was observed in single-crystal samples of $Yb_{1-x}La_xB_6$ for $x>0.005$. We examined also the sintered polycrystal samples for $0 \leqslant x \leqslant 0.025$. The spongelike surface prevented us from obtaining reliable values of compositions. Hence, we use hereafter the nominal composition for sintered polycrystals.

Temperature variations of magnetic susceptibility $\chi = M/B$ for polycrystal and single-crystal samples of $Yb_{1-x}La_xB_6$ were measured in various fields from 1 mT to 1 T by using a commercial magnetometer (Quantum Design, model MPMS). Polycrystals for $x \geqslant 0.015$ showed Curie-like behavior in the whole temperature range of 2–300 K. By contrast, for samples with $x<0.006$, weak ferromagnetism is manifested by the thermal hysteresis below ~150 K at low fields up to 10 mT, as shown in Fig. 1. This hysteresis vanishes with increasing field above 100 mT, and eventually usual Curie-Weiss behavior is seen at 1 T. This means that the applied field higher than 100 mT saturates a ferromagnetic component to a value smaller than that for a paramagnetic component. To confirm the ferromagnetic state, we measured the magnetization curves for samples with different x values. As an obvious example, isothermal magnetization curves for $x=0.003$ at different temperatures (50 and 200 K) are shown in Fig. 2. The closed circles represent the ferromagnetic component extracted from raw data denoted by open circles. It is assumed that the paramagnetic component increases linearly with the increase of magnetic field up to 500 mT in this temperature region. This assumption, however, becomes inappropriate at lower temperatures, where the magnetization curve of the paramagnetic component should follow the Brillouin function. The ferromagnetic components at 50 and 100 K saturate with increasing fields to about 100 and 50 mT, respectively. It is noteworthy that the spontaneous moment per the formula unit is only $7\times10^{-5}\mu_B$ at 50 K. This small spontaneous moment vanishes on heating up to 200 K, as shown in Fig. 2(b). These results indicate the presence of ferromagnetic component with $T_C \approx 150$ K. Since the value of T_C is far below that of FeB or Fe_2B, we exclude the impurity effect of such iron compounds.

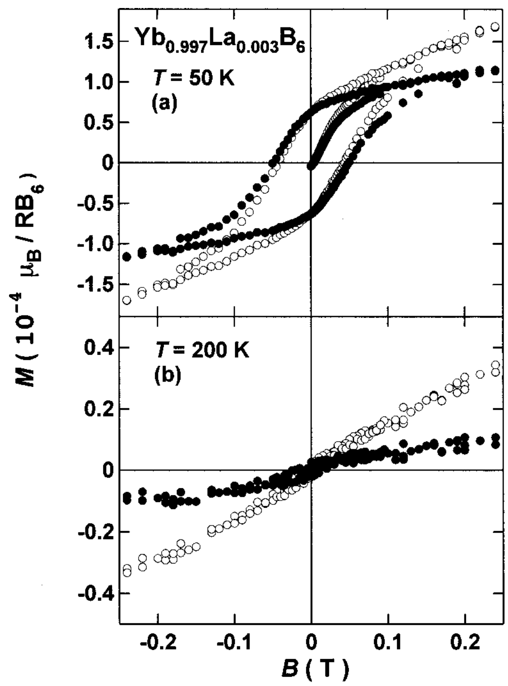

FIG. 2. Magnetization curves of polycrystalline $Yb_{0.997}La_{0.003}B_6$ at $T=50$ K (a) and 200 K (b).

Figure 3 displays the x dependence of the magnetization measured at 2 K under 5 T for polycrystalline samples $Yb_{1-x}La_xB_6$, $0 \leqslant x \leqslant 0.025$. Under this condition, both the ferromagnetic component and the paramagnetic component are almost saturated. The magnetization vs x exhibits a remarkable peak at around $x=0.006-0.008$, while in the range $x>0.01$ the value of magnetization remains unchanged. On the other hand, the saturation moment M_S of the ferromagnetic component was estimated by the linear extrapolation of the M-B curve from $B=0.1-0.2$ T to $B=0$ T. The x dependence of M_S and M in Fig. 3 suggests that the vanishing of the ferromagnetic component at $x \sim 0.0065$ is followed by

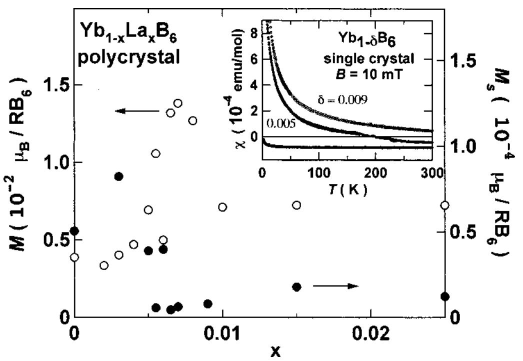

FIG. 3. Total magnetization M and ferromagnetic saturation moment M_S of polycrystalline $Yb_{1-x}La_xB_6$ as a function of x for $0 \leqslant x \leqslant 0.025$. The value of M was obtained at $T=2$ K and $B=5$ T, where the magnetization was almost saturated. The value of M_S was obtained by the linear extrapolation of the M-B curve from $B=0.1$ to 0 T. The inset shows the temperature dependence of magnetic susceptibility of a single-crystal $Yb_{1-x}B_6$ that was heat treated in a vacuum at 1700 °C for different periods (see text).

the development of total magnetization. Therefore, the peak in M vs x is attributed to the enhancement of the paramagnetic component.

We have measured magnetic susceptibility for single-crystalline $Yb_{1-x}La_xB_6$ under same field conditions as for polycrystals. Interestingly, diamagnetic behavior was observed for $x \leqslant 0.003$, as was reported for the nondoped YbB_6.[18] For $x=0.005$, however, paramagnetic behavior was manifested without ferromagnetic hysteresis. As for this distinctly different behavior between single crystals and polycrystals, we conjecture that some sort of defects in polycrystals play an important role in the formation of ferromagnetic component. A similar model was proposed to explain the ferromagnetism in nondoped CaB_6 samples.[4] It was reported that Ca-deficient samples were ferromagnetic while stoichiometric ones were diamagnetic, although the content of the Ca defect was not evaluated. To produce Yb defects in a single-crystal $Yb_{1.08}B_6$, we have heat treated the crystal in a vacuum at 1700 °C for a few hours step by step. The treatment for 1.5 and 3 h resulted in the weight loss corresponding to the Yb deficiency δ of 0.005 and 0.009, respectively, in $Yb_{1-\delta}B_6$, if the weight loss is attributed to the loss of Yb solely. The results of magnetic-susceptibility measurements under a field of 10 mT are shown in the inset of Fig. 3. The diamagnetic behavior in the as-grown crystal changes to the Curie-Weiss behavior with the increase of the deficiency of Yb. It is noteworthy that the absolute value of the paramagnetic Curie temperature of ~150 K for $\delta=0.005$ and 0.009 is close to the Curie temperature of the polycrystalline samples of $Yb_{1-x}La_xB_6$. However, the magnetization curve of the Yb-deficient single crystals did not show the ferromagnetic hysteresis.

To further examine the anomalous magnetism in $Yb_{1-x}La_xB_6$, we have performed μSR measurements on both polycrystal and single-crystal samples for $x=0.005$ using π- and μ ports at the Meson Science Laboratory Facility, High Energy Accelerator Research Organization. The relaxation spectra were recorded at temperatures from 300 to 5 K

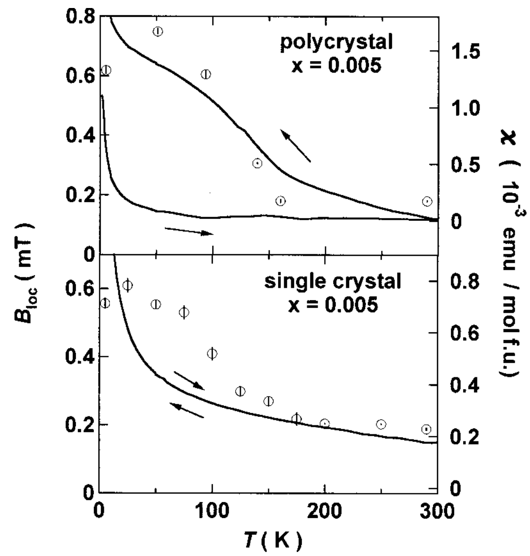

FIG. 4. Temperature dependence of internal fields (open circles) and magnetic susceptibility (solid lines) in single-crystal and polycrystal samples of $Yb_{0.995}La_{0.005}B_6$. The internal fields were estimated from time-dependent spectra of muon relaxation in zero field.

by a step of 25 or 50 K under both zero-field and a transverse magnetic field of 3 mT. The ZF-μSR spectra do not show a spontaneous precession pattern as expected for a uniform internal field in a magnetically ordered state. However, we observed a strong increase in the relaxation in zero-field spectra on cooling below 150 K. The internal field was evaluated from the relaxation time by assuming that Kubo-Toyabe function describes the acquired muon relaxation spectra. This assumption is allowed when the spontaneous field is weak or the local field is widely distributed.[14] The local fields thus obtained are shown in Fig. 4 as a function of temperature for single-crystal and sintered polycrystal samples, respectively. For both samples, internal fields are 0.2 mT at room temperature, and do not change down to 150 K. On cooling further, the internal field increases strongly and reaches a value of 0.6 mT at 10 K. This temperature dependence is very similar to that of the magnetic susceptibility of polycrystalline sample for $x=0.005$, as shown in Fig. 4(a). This coincidence between the magnetic susceptibility and the internal field provides an evidence of the intrinsic magnetic order in $Yb_{1-x}La_xB_6$ at temperatures below 150 K. However, it should be noted that the magnetic susceptibility of the single crystal with $x=0.005$ did not show any ferromagnetic behavior.

Here, we suppose that positive muons stop at the site (0.5 0 0) as similar in the iso-structural[19] CeB_6 and then the muon spin relaxes in a magnetic dipole field. This field is assumed to originate from ferromagnetically aligned magnetic moments at every boron-octahedron site. Under these hypotheses, the value of the magnetic moment is estimated to be $10^{-3}\mu_B$/f.u., which is one order of magnitude larger than the saturated ferromagnetic moment as shown in Fig. 2. This discrepancy indicates the inhomogeneity in the magnetically ordered state. Some sort of inhomogeneous state is also inferred from the absence of the spontaneous magnetization in the single crystal with $x=0.005$. As for the small ferromagnetic moment in $Ca_{1-x}La_xB_6$, Kunii *et al.* proposed that the ferromagnetism originates from a surface state.[2] The proposal is consistent with our observation that ferromagnetic moments in $Yb_{1-x}La_xB_6$ appear only in polycrystal samples with the large surface-to-volume ratio. In any event, the T_c of 150 K for $Yb_{1-x}La_xB_6$ is much higher than those of trivalent rare-earth hexaborides, where the RKKY-type interaction governs the magnetism.

In summary, we have found that $Yb_{1-x}La_xB_6$ ($0 \leqslant x \leqslant 0.006$) has a weak ferromagnetic moment ($\sim 10^{-4} \mu_B$/f.u. at 2 K) and Curie temperature $T_c \approx 150$ K. This ferromagnetism coexists with the paramagnetic component that has the sharp maximum in the magnetization as a function of the La-doping concentration at $x=0.007$. The development of paramagnetic component was also found in single-crystalline samples of $Yb_{1-\delta}B_6$ with increasing δ up to 0.009, whereas no spontaneous magnetization was observed. The μSR experiments revealed that internal fields increase on cooling below 150 K in both *ferromagnetic* polycrystalline and *paramagnetic* single-crystalline samples. This temperature dependence is very similar to that of the magnetic susceptibility for polycrystalline samples. The value of T_c (150 K) and magnetic moment ($\sim 10^{-4} \mu_B$/f.u.) are one third and one tenth, respectively, of those reported for $Ca_{1-x}La_xB_6$. From the similar electronic structure between YbB_6 and CaB_6, we speculate that the ferromagnetism should arise from a similar mechanism.

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