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Itinerant-electron metamagnetic transition in $LaFe_{12}B_6$

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ABSTRACT

$LaFe_{12}B_6$ ($SrNi_{12}B_6$-type) is an antiferromagnet with a low moment of 0.36 μ_B/Fe-atom in the ground state. The field-induced first-order transition takes place in a wide range of temperature including below and above the Néel temperature of 35 K. This transition results in a high moment of 1.6 μ_B/Fe-atom, being characteristics of the itinerant-electron metamagnetic transition. The critical magnetic field of the metamagnetic transition B_C increases with increasing temperature except for low temperature ranges, in which the kinetic arrest occurs. Above the arrested temperature, the sign of the temperature dependence of dB_C/dT is positive. The metamagnetic transition brings about large magnetocaloric effects, that is, a large negative value of the isothermal magnetic entropy change, ΔS_m, and a large positive value of the adiabatic temperature change, ΔT_{ad}.

1. Introduction

In Fe-based compounds, only $LaFe_{12}B_6$ is stable in the $REFe_{12}B_6$ (RE: rear earth element) systems, although Co-based compounds $RECo_{12}B_6$ exist for the entire rare earth series. $LaFe_{12}B_6$ crystallizes in a rhombohedral $SrNi_{12}B_6$-type structure with the space group $R\bar{3}m$ [1]. The La atoms occupy the 3*a* crystallographic site, the Fe atoms the 18*g* and 18*h* sites. Rosenberg et al. investigated $REFe_{12-x}Co_xB_6$ series and showed that the thermomagnetization curve of $LaFe_{12}B_6$ in 1.75 T exhibits a broad cusp around 40 K [2]. Furthermore, the average hyperfine field at 4.2 K was evaluated to be about 6 T from the Mössbauer effect data, and hence the average magnetic moment was derived to be about 0.35μ_B/Fe-atom [2]. From these results, the magnetic state of $LaFe_{12}B_6$ below 40 K has been considered to be in an antiferromagnetic or a spin-glass type state [2]. These results strongly suggest that $LaFe_{12}B_6$ is a compound in which the iron sublattice moment is close to collapsing.

The possibility of itinerant-electron metamagnetic transition from the paramagnetic to ferromagnetic state was first proposed by Wohlfarth and Rhodes [3]. Later, their work has been extended by Shimizu [4] who considered two types of metamagnetic transition: (1) paramagnetic (PM) → ferromagnetic (FM) and (2) low moment FM (LMFM) → high moment FM (HMFM) states. Nowadays, itinerant-electron metamagnetic transitions including the antiferromagnetic (AFM) → ferromagnetic (FM) are well known [5,6]. Li et al. reported that a magnetization curve of $LaFe_{12}B_6$ shows a sudden jump at an applied field of about 8.6 T, at which the magnetic moment of Fe increases drastically up to 1.67 μ_B/Fe-atom [7]. The transition from the low moment to high moment state can also be driven by adding a magnetic rare earth such as Gd [7].

According to the fixed spin moment (FSM) calculations, it has also been pointed out that $LaFe_{12}B_6$ has a metastable state with the magnetic moment of 0.39 μ_B/Fe-atom in addition to a stable state with the magnetic moment of 1.28 μ_B/Fe-atom [8]. Recent tight binding FSM calculations have confirmed this moment instability, and have further pointed out that the magnetic moment of Fe on the 18*h* site is more sensitive to its environment [9]. We draw an inference from the experimental and theoretical results described above that $LaFe_{12}B_6$ exhibits a metamagnetic transition, namely, a field-induced first-order transition from a low moment AFM (LMAFM) to HMFM state.

The objective of the present study is to shed light on the type of metamagnetic transition of the $LaFe_{12}B_6$ compound and to clarify its temperature and magnetic field dependences. In association with the metamagnetic transition, we make relation to the large magnetocaloric effects induced by applying magnetic fields.

2. Experimental

The $LaFe_{12}B_6$ compound was prepared by arc-melting in an argon gas atmosphere and the subsequent heat-treatment in a vacuum quartz tube. The annealing temperature and duration were 1173 K and 10 days, respectively. The powder X-ray diffraction patterns at room temperature were measured using a Rigaku

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diffractometer with CuKα radiation. Several kinds of magnetic data were obtained with a SQUID magnetometer (QUANTUM Design). The specific heat measurements were carried out by a relaxation method using a PPMS (QUANTUM Design). The Mössbauer effect spectra were measured using a Wissel electromechanical spectrometer (Wissenschaftliche Elektronik GmbH) with ^{57}Co γ-ray.

3. Results and discussion

Fig. 1 shows room temperature X-ray diffraction patterns for four kinds of the specimens. Each specimen has the following nominal composition; (a) La–Fe_{12}–B_6, (b) $La_{1.015}$–Fe_{12}–B_6, (c) $La_{1.02}$–Fe_{12}–B_6 and (d) $La_{1.03}$–Fe_{12}–B_6. The specimen (a) exhibits extra peaks associated with the ferromagnetic Fe_2B phase. Because available commercial boron (99.4%) used as starting material contains a high level of oxygen atoms, the impurity phase of La_2O_3 is formed readily during the alloying process, resulting in the formation of Fe_2B due to a deficit of La in the $LaFe_{12}B_6$. As seen from the data on the specimens (b) and (c) in Fig. 1, the diffraction peaks of the Fe_2B phase are reduced by increasing La content. Therefore, it is necessary to increase the La content in order to make a stoichiometric $LaFe_{12}B_6$. Any other second phase except for La_2O_3 is ensured by X-ray diffraction measurement for the specimen (d) presented in Fig. 1. Accordingly, a stoichiometric $LaFe_{12}B_6$ is obtainable from the relevant nominal composition of $La_{1.03}$–Fe_{12}–B_6. Hereafter, in the present study, we describe the specimen (d) with the nominal composition of $La_{1.03}$–Fe_{12}–B_6 as the stoichiometric $LaFe_{12}B_6$. It should be noted that no ferromagnetic phase behavior is affirmed in the magnetization curves of the stoichiometric $LaFe_{12}B_6$ as described in connection with Figs. 4 and 5 in latter part.

Temperature dependence of magnetic susceptibility measured in various magnetic fields for the stoichiometric $LaFe_{12}B_6$ is plotted

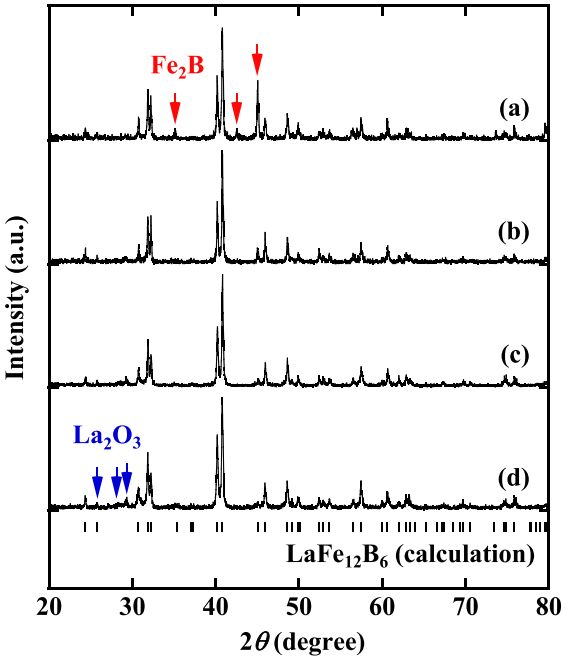

Fig. 1. X-ray diffraction patterns at room temperature for four kinds of the specimens. Each specimen has the following nominal composition denoted as (a) La–Fe_{12}–B_6, (b) $La_{1.015}$–Fe_{12}–B_6, (c) $La_{1.02}$–Fe_{12}–B_6 and (d) $La_{1.03}$–Fe_{12}–B_6. The red and blue arrows indicate the diffraction peaks of Fe_2B and La_2O_3 phases, respectively. The short bars below diffraction patterns show the calculated Bragg diffraction peaks of $LaFe_{12}B_6$ compound with the $SrNi_{12}B_6$-type structure.

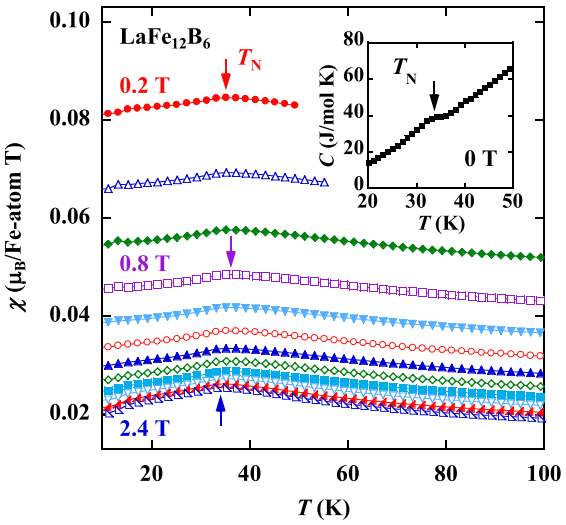

Fig. 2. Temperature dependence of magnetic susceptibility measured in the magnetic field range between 0.2 and 2.4T at an interval of 0.2T for the stoichiometric $LaFe_{12}B_6$. The arrows indicate the Néel temperature T_N under magnetic files of 0.2, 0.8 and 2.4T. The inset shows the specific heat C under zero magnetic field in the vicinity of T_N indicated by the arrow.

in Fig. 2. The measurement was carried out after zero field cooling from room temperature. The curve in 0.2T exhibits a clear sharp peak which is distinctive in antiferromagnets and thus the peak position is denoted as the Néel temperature T_N. The Fe 3d bandwidth of $LaFe_{12}B_6$ is enough wide [8,9] to classify into itinerant-electron systems. Thus, a Curie–Weiss like curve in Fig. 2 is explained by the self-consistent renormalization (SCR) theory of spin fluctuations [10]. Temperature dependence of the specific heat measured in zero magnetic field also exhibits a small peak at T_N as seen from the inset of Fig. 2. These behaviors tell us that $LaFe_{12}B_6$ is an itinerant-electron antiferromagnet. It is notable that the above-mentioned behaviors are similar to those of a typical itinerant-electron antiferromagnet Cr [11]. The value of T_N is slightly affected by applying magnetic fields as seen from Fig. 2.

From the room temperature X-ray diffraction data, the lattice constants of a and c axes of the stoichiometric $LaFe_{12}B_6$ were calculated to be about 9.618 and 7.607 Å, respectively. Almost same values of lattice constants were confirmed in the specimens (a)–(c) in Fig. 1. In addition, the nearest neighbor Fe–Fe distance d of the stoichiometric $LaFe_{12}B_6$ was deduced to be 2.52 Å, which is larger than that of 2.38–2.40 Å for 2:17 antiferromagnetic compounds such as Y_2Fe_{17}, Sm_2Fe_{17} and Lu_2Fe_{17} [12]. It is striking that the sign of exchange interactions in the these 2:17 compounds changes from negative to positive around 2.45 Å [12], being shorter than the d value of the stoichiometric $LaFe_{12}B_6$. In association with such a situation, the data for $LuFe_4Ge_2$ (T_N=32 K, d=2.50 Å) [13], $ScFe_4Al_8$ (T_N=100 K, d=2.51 Å) [14,15] and YFe_4Al_8 (T_N=195 K, d=2.52 Å) [14] are noticeable. The Fe–Fe distance (d value) of the stoichiometric $LaFe_{12}B_6$ is classified into the latter case.

Shown in Fig. 3 are the Mössbauer spectra at 5, 50 and 295K for the stoichiometric $LaFe_{12}B_6$. The doublet in the spectra at 50 and 295K is associated with the paramagnetic state. The broad spectrum at 5K proves that the magnetic order is present in the stoichiometric $LaFe_{12}B_6$. The average hyperfine field is estimated to be about 5.4T. By using the hyperfine coupling constant 14.8T/μ_B of Fe, the average magnetic moment is estimated to be about 0.36 μ_B/Fe-atom, in consistent with the reported data [2]. This result reflects the small peaks in Fig. 2.

Fig. 4 presents the magnetization curves at 19K and below for the stoichiometric $LaFe_{12}B_6$ after zero field cooling from room