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Mössbauer Spectroscopy and Electrical Conductivity of Fe-Doped β-Rhombohedral Boron

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Iron and/or aluminum are doped to β-rhombohedral boron, and the electrical conductivity and ^{57}Fe Mössbauer effect are measured. The temperature dependence of the electrical conductivity is explained as a variable range hopping type. The conductivity increases with an increase in Fe concentration, but it is insensitive to Al concentration. The Mössbauer spectra measured at room temperature are resolved into three kinds of doublets and a sextet due to ferromagnetic FeB. One doublet, γ_0, is attributed to Fe^{3+} ions at A_1 sites, while the others, γ_1 and γ_2, occur from Fe^{2+} ions at *D* sites. When Fe and Al atoms are simultaneously doped into β-boron, the intensity of the γ_0 doublet decreases and, hence, those of the γ_1 and γ_2 doublets relatively increase. The results shows that Fe atoms are moved from A_1 sites to *D* sites by Al atoms. It is proposed that the γ_1 doublet corresponds to $Fe^{2+}(D)$–$Fe^{2+}(D)$ and the γ_2 doublet to $Fe^{2+}(D)$ and that a part of $Fe^{2+}(D)$ is in the magnetic state at 4.2 K.

INTRODUCTION

It is well known that β-rhombohedral boron (β-boron) is an elemental semiconductor with a high melting point and is composed of B_{12} icosahedral clusters. β-boron has peculiar electronic states because of its unique bonding nature and crystalline structure. The rhombohedral unit cell of β-boron consists of 105 B atoms and has three kinds of the main doping sites, A_1, *D*, and *E*, which are large enough to accommodate foreign atoms (1, 2). Structures and bondings of solid solutions of β-boron type crystals were reviewed by Lundström (3). The electronic transport properties of Fe-doped β-boron were reported by Werheit *et al.* (4), Slack *et al.* (5), and Kuhlmann *et al.* (6, 7). We have also reported and discussed the electronic properties of metal-doped β-boron, Li_xB_{105}, Cu_xB_{105}, Ni_xB_{105}, and V_xB_{105} (8–10), and found that the conductivity of 3*d* transition metal-doped β-boron increases with increasing occupancy of the A_1 site as the result of the hybridization between the intrinsic acceptor states (11) of β-boron and the 3*d* states of transition metals.

Knowledge of the position and charge state of transition metals in the β-boron lattice is of primary importance for understanding the transport properties of interstitially doped β-boron. Mössbauer effect measurements are a quite useful method because the information on Fe atoms can be obtained. Some Mössbauer studies were already reported by Kazanin and co-workers (12, 13) and Wäppling *et al.* (14). Kuhlmann *et al.* (7) attempted to obtain a reliable analysis and interpretation successfully to some content, but in this paper we try another way to analyze and interpret the Mössbauer spectra using Fe and Al double doping. Fe and Al atoms are known to occupy only two kinds of sites, A_1 and *D* (15, 16). According to the X-ray structural data for FeB_{49} (15) and AlB_{31} (16), Al atoms preferentially occupy A_1 sites compared with Fe atoms. Then it is thought to be possible to change the occupancy of Fe at A_1 and *D* sites by doping Al together with Fe into β-boron.

In this study, ^{57}Fe Mössbauer spectra of a series of Fe- and/or Al-doped β-boron samples were analyzed in order to understand the charge state of Fe atoms at the doping sites of β-boron structure.

EXPERIMENTAL DETAILS

A series of Fe- and/or Al-doped β-boron samples was prepared by arc-melting cold-pressed pellets of amorphous boron (99.9%), α-iron (99.9%), and/or aluminum (99.9%) powders mixed in appropriate proportions. Excess metals were etched by hydrochloric acid. Bulk samples were sliced for the dc conductivity measurements, and the rest was crushed for X-ray powder diffraction and ^{57}Fe Mössbauer effect measurements.

The dc conductivity was measured by the van der Pauw method in a temperature range of about 30–300 K.

Each crushed sample was mixed with Si powder as the internal calibration standard, and then X-ray powder diffraction was measured. The lattice parameters were determined by a least squares method.

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Successively Fe-doped boron powder samples were mixed with starch as binder and pressed into pellets with the thickness of about 10 mg $^{57}Fe/cm^2$. ^{57}Fe Mössbauer absorption spectra were measured at 290, 77, and 4.2 K. The Doppler velocity was calibrated by the isomer shift and the hyperfine splitting of an α-Fe foil. The Mössbauer spectra were decomposed by a least square fitting program assuming a superposition of discrete Lorentzians.

RESULTS AND DISCUSSION

The compositions of the samples are given by $Fe_xAl_yB_{105}$ ($x = 0$–4, $y = 0$–4), where x and y stand for the number of Fe and Al atoms in the unit cell of β-boron, respectively. From the results of the X-ray measurements, it is found that the samples within the range $x + y < 2$ have only one phase, i.e., doped β-rhombohedral boron, but samples in the range $x + y \geq 2$ have two phases, doped β-boron and FeB. Samples with a composition close to FeB_{29} (3.3 at.% Fe) which was reported previously by Kuhlmann *et al.* (7) and has the maximum solubility of Fe to β-boron for now, could not be obtained without annealing. The unit cell volume of each doped β-boron samples exceeds that of pure β-boron (1) and is nearly proportional to the nominal concentrations. The maximum volume among the samples is nearly in accordance with FeB_{49} (2.0 at.% Fe) (17). Therefore, metals are expected to occupy the interstitial sites in the β-boron structure. As FeB makes the actual Fe concentration in β-boron largely uncertain at higher Fe concentration and the precise concentrations, especially in the cases of Fe and Al double doping, are not yet determined, nominal concentrations are used in the following discussion.

As shown in Fig. 1, the temperature dependence of electrical conductivity of each sample shows a typical temperature dependence for the case of variable range hopping type conduction according to Mott's law like the cases of other metal doping of β-boron (8–10),

$$\sigma = \sigma_0 \exp\{-(T_0/T)^{1/4}\},$$

$$T_0 = 60\alpha^3/\pi N(E_F) k_B,$$

where α^{-1} is the localization length of the wave function of the carriers and $N(E_F)$ is the density of states at the Fermi energy. The conductivity at each temperature increases with an increase in the nominal Fe concentration, which shows the same order as other results for Fe-doped β-boron (4, 5). The existence of the metallic FeB phase for the samples with concentration of $x + y \geq 2$ may affect the data at low temperatures. On the other hand, it is shown that the conductivity is insensitive to the Al concentration.

The Mössbauer spectra were decomposed as follows: Fe atoms are known to occupy only two kinds of the interstitial

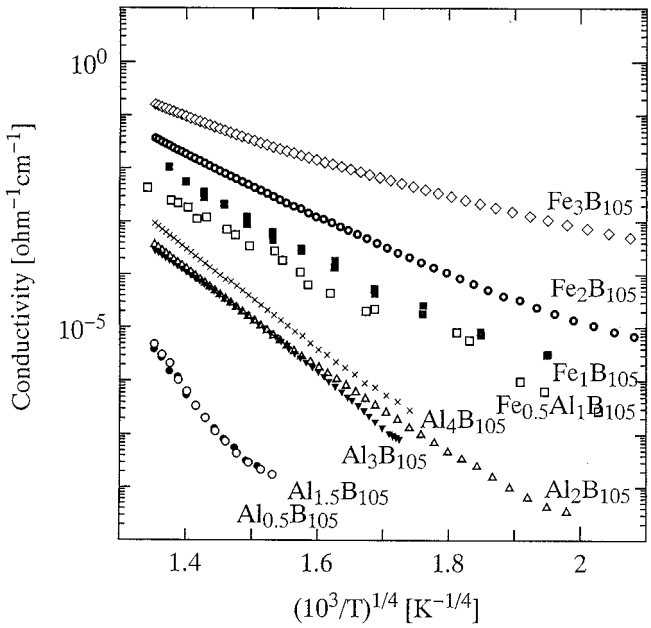

FIG. 1. Temperature dependence of dc electrical conductivity of $Fe_xAl_yB_{105}$ plotted according to Mott's law. The linear relationship is explained as the variable range hopping type.

sites in the β-boron structure, A_1 and D. All spectral components except that of ferromagnetic FeB should be doublets because neither A_1 nor D site has cubic symmetry. The combination of components should be found under the condition that both isomer shift and quadrupole splitting remain almost unchanged irrespective of the dopant concentration. Mössbauer spectra measured at room temperature, as shown in Fig. 2, were decomposed into three doublets, named γ_0, γ_1, and γ_2, together with a sextet due to FeB at higher Fe concentrations. The parameters of the sextet of FeB are nearly in accordance with those reported previously (18). Figure 3 shows the Fe concentration dependence of the fractional intensity of each component for the Fe- and Al-doped β-boron samples. The values of the isomer shift and the quadrupole splitting are listed in Table 1. The parameters remain almost unchanged in the various Fe and/or Al concentrations. The spectra measured at 77 and 4.2 K for Fe_1B_{105} are decomposed into the same doublets as those measured at room temperature. The broad background is assumed to be a sextet with a large linewidth, and the spectra measured at 4.2 K are decomposed as shown in Fig. 4. The temperature dependence of the fractional intensities of the subspectra is shown in Fig. 5.

The quadrupole splitting Δ represents the gradient of the electric field at the Fe nucleus. When the Fe atoms are surrounded by the same kind of atoms with cubic symmetry, the gradient of the electric field is zero, and hence a single line is obtained. Two A_1 sites in the rhombohedral unit cell

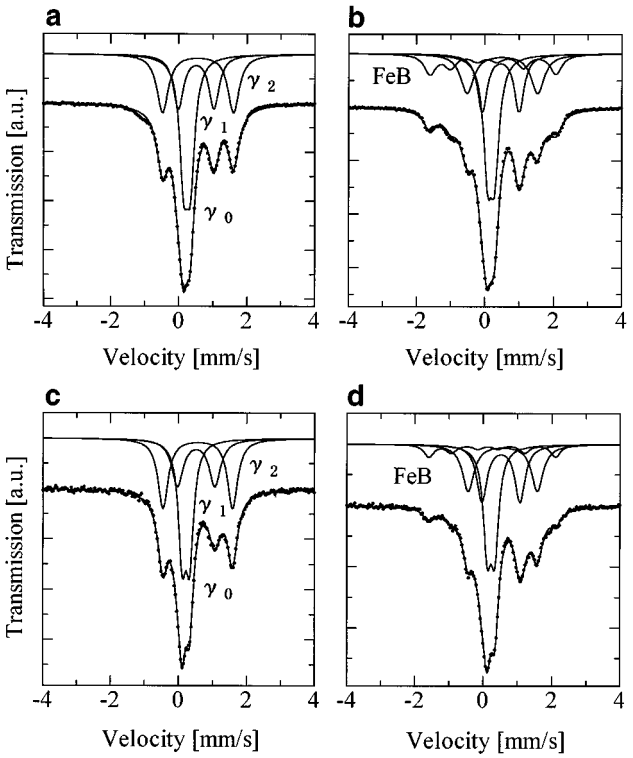

FIG. 2. Mössbauer spectra measured at room temperature together with the decomposed components for four different samples, (a) Fe_1B_{105}, (b) Fe_2B_{105}, (c) $Fe_{0.5}B_{105}$, and (d) $Fe_1Al_1B_{105}$.

are distorted tetrahedral sites surrounded by four B_{12} icosahedra. Six *D* sites surrounding a single B atom are located in a plane which is oriented perpendicular to the longer body-diagonal of the unit cell. Therefore, A_1 sites have a higher symmetry than *D* sites. Because the quadrupole splitting of

TABLE 1

Isomer Shifts (δ) and Quadrupole Splittings (Δ) of Three Components at Room Temperature for Fe_xB_{105} and Their Changes in the Fractional Intensities after the Addition of Al($I' - I$)

Component	δ (mm s^{-1})	Δ (mm s^{-1})	$I' - I$	Charge state	Site
γ_0	+ 0.25	0.2	−	Fe^{3+}	A_1
γ_1	+ 0.54	1.1	+	Fe^{2+}	*D*
γ_2	+ 0.60	2.0	+	Fe^{2+}	*D*

Note. I.S. and Q.S. are almost independent of the concentration of Fe and Al. The fractional intensity of the each component are shown in Fig. 3.

the γ_0 doublet, $\Delta(\gamma_0)$, is very small, this doublet is attributed to A_1 sites. Because $\Delta(\gamma_1)$ is about half as large as $\Delta(\gamma_2)$ and much larger than $\Delta(\gamma_0)$, both γ_1 and γ_2 doublets are attributed to *D* sites. The difference between $\Delta(\gamma_1)$ and $\Delta(\gamma_2)$ is considered to be due to an interaction between doped Fe atoms described later in detail.

Both the spectra with and without six peaks of FeB in this study are nearly the same as those obtained by Kuhlmann *et al.* (7), respectively, but there is a difference in the decomposition of the spectra. The position of the left-hand side peak of the doublet with the smallest value of the quadrupole splitting and that of the doublet with the second smallest value are fit to be in reverse. The lattice parameters and the temperature dependence of the electrical conductivity for $Fe_xAl_yB_{105}$ samples are thought to assure random distribution of Fe atoms to some extent, but details in the sample preparation, especially heat treatment, may cause the difference. The result of the way of decomposition in this paper has two features. First, the Mössbauer spectra obtained in

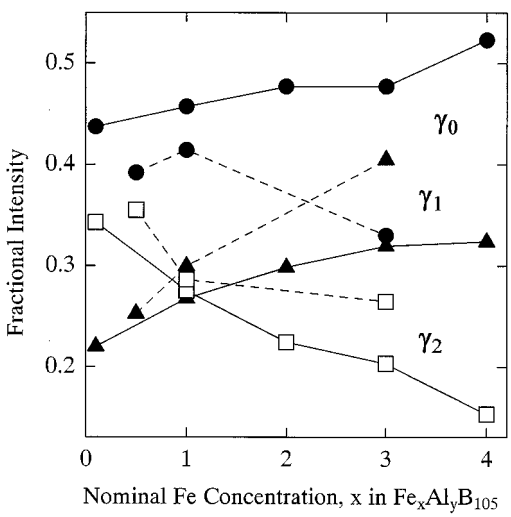

FIG. 3. Fractional intensity of each component as a function of Fe concentration. Solid lines stand for $y = 0$ and dotted lines for $y = 1$ in $Fe_xAl_yB_{105}$.

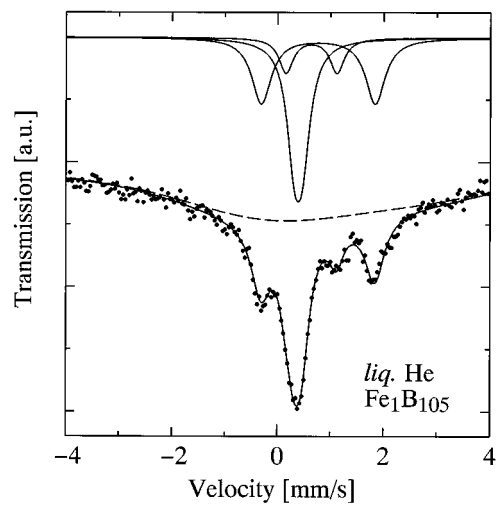

FIG. 4. Mössbauer spectrum of Fe_1B_{105} measured at 4.2 K, together with decomposed three components after subtraction of broad background shown by a dashed line. The broad background is tentatively assumed to be a broad sextet.

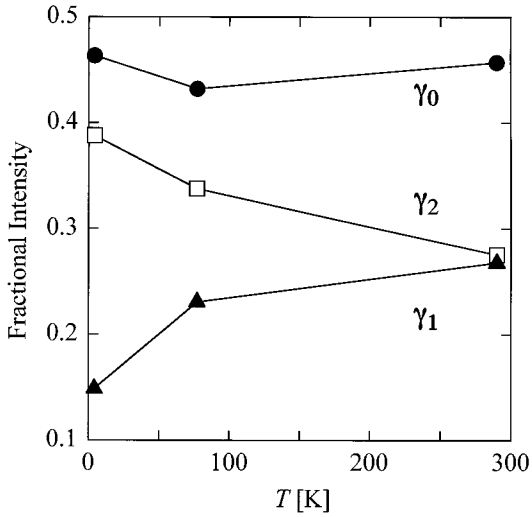

FIG. 5. Temperature dependence of the fractional intensities of the Mössbauer spectral components for Fe_1B_{105}.

this study are decomposed into the three doublets, and the value of quadrupole splitting of each doublet is independent of the dopant concentration, the existence of the FeB phase, and the measured temperature. The other is that the changes in the fractional intensities for Fe- and Al-double-doped boron samples have a systematic trend on the amount of Al addition as shown in Fig. 3. The fractional intensity of γ_0 doublet for Fe- and Al-double-doped boron, $I'(\gamma_0)$, is small, and both $I'(\gamma_1)$ and $I'(\gamma_2)$ are large compared with those of Fe-single-doped boron. It is considered that the occupancy of Fe atoms at the A_1 site is decreased and then the ratio of the number of Fe atoms at the A_1 sites to that at the D sites, $N(A_1)/N(D)$, is reduced, when Fe and Al are doped simultaneously in β-boron. Therefore, Al has a tendency to occupy preferentially the A_1 site compared with Fe. It is proved to be possible to alter the fraction of the occupancy of Fe at A_1 and D sites by the Fe and Al double doping.

The chemical isomer shift δ is related to the density of s electrons at the nucleus of Fe atom. The $3d$ orbit has a node at the nucleus but the s orbits imply a nonzero electron charge density within the nuclear volume. In the case of Fe atoms, with an increasing number of $3d$ electrons, the isomer shift becomes more positive, because $3d$ electrons shield the $4s$ electrons off and make the s electron charge density at the nucleus smaller.

From the values of isomer shifts and quadrupole splittings for the three components, the authors conclude that the γ_0 doublet is attributed to Fe^{3+} and both γ_1 and γ_2 to Fe^{2+}. There are three reasons for the decision. First, it is usually accepted in various kinds of iron compounds that the isomer shift for the iron trivalent ion is in the range -0.2–$0.6\,mm\,s^{-1}$, that for iron divalent ion is between -0.2 and $1.5\,mm\,s^{-1}$, and that isomer shift for Fe^{3+} is more negative than that for Fe^{2+} in the similar types of compounds. Second, Fe atoms in the β-boron are thought to be in the high spin states because Fe atoms are accommodated in the covalent crystal of β-boron. The value of the isomer shift attributed to Fe ions in the high spin state is usually smaller than those in the low spin state even if the numbers of the valences are the same. Third, it is considered that the quadrupole splitting for Fe^{3+} is much smaller than that for Fe^{2+} in the high spin state in various kinds of iron compounds (19, 20).

It is considered that the γ_0 doublet is attributed to Fe^{3+} ions at the A_1 sites, $Fe^{3+}(A_1)$, while both γ_1 and γ_2 doublets are attributed to Fe^{2+} ions at the D sites, $Fe^{2+}(D)$. The ratio of the fractional intensity of the γ_0 doublet at room temperature for Fe-single-doped β-boron to the γ_1 and γ_2 doublets, $I(\gamma_0)/(I(\gamma_1)+I(\gamma_2))$ is estimated to be among 0.78 ($Fe_{0.1}B_{105}$) and 1.1 (Fe_4B_{105}) from the values shown in Fig. 3, which is consistent with the ratio of the number of dopants at the A_1 and D sites, $N(A_1)/N(D) = 0.914$ obtained from the X-ray structural data (15) for FeB_{49}. The reason two components, γ_1 and γ_2, exist for $Fe^{2+}(D)$ is not clear, but it is speculated as follows: The effect of the $Fe^{2+}(D)$–$Fe^{2+}(D)$ interaction is considered to increase with increasing Fe concentration. As shown in Fig. 3, the fractional intensities of the γ_0 and γ_1 doublets, $I(\gamma_0)$ and $I(\gamma_1)$, increase with an increase in Fe concentration, but $I(\gamma_2)$ shows an opposite tendency. Moreover, the ratio $I(\gamma_1)/I(\gamma_2)$ becomes large with an increase in Fe concentration. Hence, it is considered that the γ_1 doublet is attributed to $Fe^{2+}(D)$–$Fe^{2+}(D)$ and the γ_2 doublet to $Fe^{2+}(D)$ monomers. We interpret that $Fe^{2+}(D)$ ions are interacting in each other.

Furthermore, a broad background which seems to be due to a magnetic hyperfine splitting appears in the spectrum at 4.2 K shown in Fig. 4, and the fractional intensity of the γ_1 doublet measured at 4.2 K, $I_H(\gamma_1)$, remarkably decreases compared to $I(\gamma_1)$ at room temperature as shown in Fig. 5. The fact indicates that parts of $Fe^{2+}(D)$ are magnetically interacting with each other at 4.2 K. The γ_1 doublet is considered to be attributed to $Fe^{2+}(D)$ which interact with each other as mentioned above. Some of them possibly form clusters or regions with high occupational density of ion. Such ions at $Fe^{2+}(D)$ can be magnetic at the low temperature. To clarify the situation, further Mössbauer effect studies such as field dependent measurements will be necessary.

By the Mössbauer effect measurement at 4.2 K, the possibility that $Fe^{2+}(D)$ strictly separates three sites, Fe(2–1), Fe(2–2), and Fe(2–3) like the case of $Cu_{4.2}B_{105}$ (16), is denied because the ratio of the fractional intensities of the three doublets changes.

CONCLUSION

The electrical conductivity of $Fe_xAl_yB_{105}$, which is in agreement with that reported in earlier papers (8–11), is

explained as a variable range hopping type. The conductivity increases with increasing Fe concentration and is insensitive to the Al concentration.

The Mössbauer spectra are decomposed into three doublets named γ_0, γ_1, and γ_2 and a sextet due to FeB. From the consideration of the values of isomer shift and quadrupole splitting, the γ_0 doublet is identified to be attributed to Fe^{3+} ions at A_1 sites and both the γ_1 and γ_2 doublets to Fe^{2+} ions at D sites. The intensity of the γ_0 doublet decreases, and hence, those of the γ_1 and γ_2 doublets increase relatively when Fe and Al atoms are simultaneously doped into β-boron. It is considered that Fe atoms are moved from A_1 sites to D sites by Al atoms since Al atoms preferentially occupy A_1 sites compared with Fe atoms.

The reason two doublets, γ_1 and γ_2, exist for the same $Fe^{2+}(D)$ is speculated as follows. From the Fe concentration dependence of the intensity ratio of three doublets, it is considered that the γ_1 doublet corresponds to $Fe^{2+}(D)$–$Fe^{2+}(D)$ and the γ_2 doublet to $Fe^{2+}(D)$ monomers. Since a broad magnetic hyperfine component appears in the spectrum at 4.2 K at the expense of the γ_1 doublet, a part of $Fe^{2+}(D)$ is considered to be in the magnetic state at that temperature.

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