Observation of antiferromagnetic resonance affected by hyperfine interaction in GdBi

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Electron spin resonance (ESR) measurements on a single crystal of GdBi have been performed in the temperature range from 50 to 1.7 K at the frequency range between 58 and 107 GHz to obtain the microscopic information about the magnetic properties. The absorption line of ESR corresponding to $g=2$ of the Gd^{3+} ion is observed at temperatures between 50 and 10 K. With decreasing temperature from 7 K, the absorption line shifts to lower field side. The results obtained indicate that the shift in resonance field is due to a temperature-dependent anisotropy field arising from hyperfine interaction of Gd spin with the Bi nuclear moments. The estimated values of the anisotropy field and the hyperfine anisotropy field are $B_a=5.6\times10^{-4}$ T and $B_n=7.9\times10^{-3}$ T, respectively, at 4.2 K.

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I. INTRODUCTION

Gd monopnictides GdX (X=N, P, As, Sb, and Bi) with the NaCl-type crystal structure are typical materials of low carrier density. The carrier concentration is 0.016/Gd for GdP and systematically increases with increasing number of electrons in the series to GdBi.[1,2] Because Gd^{3+} with $S=\frac{7}{2}$ has no orbital momentum, the crystalline electric field effect is expected to be fairy weak in GdX.[3] The anisotropic exchange interaction is negligibly small. Since $4f$ level in GdX is sufficiently below the Fermi level, furthermore, the *d-f* or *p-f* mixing can also be negligible. Therefore, it has been supposed that the magnetic properties are determined mainly by the indirect exchange and the dipole interactions.

GdP, GdAs, GdSb, and GdBi are antiferromagnets with the Néel temperatures T_N of 15.9, 18.7, 23.4, and 25.8 K, respectively, while only GdN is a ferromagnet with the Curie temperature of 58 K.[1,2,4] The saturation fields B_s from the antiferromagnetic to the forced ferromagnetic states at 4.2 K are 9.5, 17.5, 34, and 42 T for GdP, GdAs, GdSb, and GdBi, respectively.[2,5] However, the magnetic anisotropy of these compounds had not been studied clearly from magnetization measurements, because Gd^{3+} has no orbital momentum. From neutron diffraction studies of GdSb and GdBi powder, McGuire *et al.* suggested that they have a type-II antiferromagnetic structure below the Néel temperature and the magnetic moments lie in the (111) plane in zero magnetic field.[3,6,7] In general, it is difficult to determine the magnetic structure using the conventional neutron diffraction experiments, because the absorption cross-section of neutron is very large for Gd.

On the other hand, electron spin resonance (ESR) measurement is also a useful method to obtain the microscopic information on the magnetic properties such as the spin structure. However, no ESR studies have been reported for GdX compounds in the ordered state so far, except for our previous measurements on GdP and GdAs.[8,9] The main reason is the difficulty of clear detection of the ESR signal for compounds with high conductivity. GdX are semimetals except for GdN that is a semiconductor, and the skin effect prevents from the penetration of microwave into the specimen. In addition, the magnetization curves of the antiferromagnets GdX showed that the spin-flop field is negligibly small and B_s is over 9 T.[2,3] That is, we need high sensitivity ESR measurements at high frequency and high magnetic field to obtain the microscopic information on GdX.

In previous work, we observed successfully the antiferromagnetic resonance (AFMR) of both GdP and GdAs single crystal, and the spin structure was determined.[8,9] The results indicate that these compounds are ''easy-plane'' antiferromagnets with the magnetic moment lying in the (111) plane below the Néel temperature, which consistent with the results of neutron diffraction studies for GdSb and GdBi. In this paper, we present the experimental results on ESR measurements for a single crystal of GdBi.

II. EXPERIMENTAL

The high-quality single crystals of GdBi were grown by Bridgman method in tungsten crucible.[1,2] The values of residual resistivity and RRR for the crystal are 0.6 $\mu\Omega$ cm and 53.3.[1,2] The single crystal was cut into a small plate with a size of $1.5\times1.5\times0.2$ mm along the (100) plane. ESR measurements have been preformed using a vector network analyzer (*AB* Millimétre Co. Ltd.) in the frequency range between 57 and 107 GHz, in the temperature range from 50 to 1.7 K and in magnetic fields up to 14 T by a superconducting magnet. To obtain high sensitivity, we used a cylindrical resonant cavity in which the resonant frequency for TE_{011} mode is about 58 GHz. The sample is placed on the cavity-endplate where rf magnetic field for TE_{011} and TE_{012} ($\sim$68 GHz) modes is strongest. This is the conventional geometry in a cylindrical cavity to observe ESR.[10,11] In addition, we also performed ESR measurements using other TE and TM modes at the same sample position, because the sample couples the component of the rf magnetic field due to the finite size of the sample. In the measurement, Q factor of the cavity varies from 6×10^3 to 1×10^4 depending on the temperature, the sample angle, the sample shape and the resonance mode.

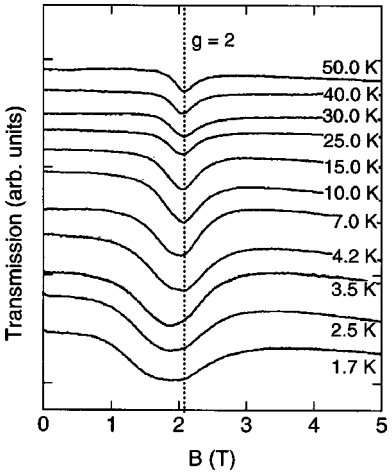

FIG. 1. ESR spectra for magnetic field B parallel to the [110] direction at various temperatures from 50 to 1.7 K at 57.7 GHz. The broken line indicates the position that corresponds to a g value of 2.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the ESR spectra for magnetic field B parallel to the [110] direction at various temperatures from 50 to 1.7 K at 57.7 GHz. In this figure, the broken line indicates the position that corresponds to $g=2.00$. At 50 K in paramagnetic region, the absorption of the electron paramagnetic resonance is observed at $B_0=2.05$ T and is well on the broken line. This is in good agreement with the expected value for an S state of the Gd^{3+} ion. Since the Néel temperature T_N for the GdBi single crystal is 25.8 K,[1] the ESR spectra are due to the antiferromagnetic resonance (AFMR) below 25 K. In the temperature range below 25 K down to 10 K, B_0 of AFMR for $B\|[110]$ is at the position of $g=2.0$. It is shown, however, that B_0 shifts to the lower field side with decreasing temperature below 7 K, and the linewidth increases up to about 1 T at 1.7 K. No other absorption line has been observed below T_N in our experimental condition.

Figure 2 shows the ESR spectra for $B\|[111]$ at 57.5 GHz

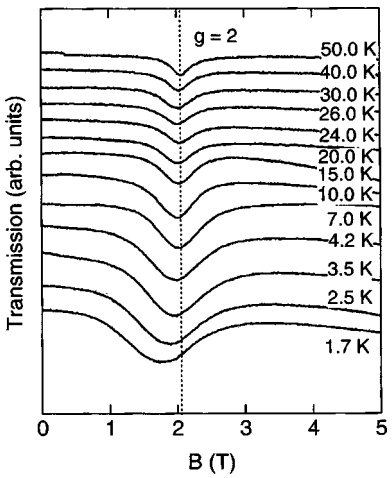

FIG. 2. ESR spectra for magnetic field B parallel to the [111] direction at various temperatures from 50 to 1.7 K at 57.5 GHz. The broken line indicates the position that corresponds to a g value of 2.

and at various temperatures between 50 and 1.7 K. The broken line in the figure is the field corresponding to the $g=2.00$. This suggests that the magnetic anisotropy field is negligibly small compared with the exchange field in GdBi. We have also observed that B_0 shifts to the lower field side from the position of $g=2$ with decreasing temperature below 7.0 K. The similar behavior is observed in any magnetic field direction of the single crystal, while no such shift of B_0 was observed in the cases of GdP, GdAs, and GdSb.[8,9,12] This shift to the lower field side in B_0 is the characteristic feature only for GdBi, and this behavior cannot be explained as the simple AFMR mode.

It was found by Heeger *et al.* that similar shift occurred in the AFMR mode of $KMnF_3$ at low temperature.[13] They showed that the hyperfine field arising from the nuclear moments of Mn^{2+} causes the shift of B_0 at lower temperature. As mentioned in the Introduction, the results of neutron diffraction and ESR measurements for GdX indicate that GdBi is an ''easy-plane'' antiferromagnet with the magnetic moment lying in the (111) plane. Assuming that the AFMR mode in GdBi is affected by the hyperfine interaction due to the nuclear moments under the condition of B_E (exchange field) $\gg B_A$ (out-of-plane anisotropy field), B_a (in-plane anisotropy field), and B_f (spin-flop field), and using a mean-field approximation,[13–15] B_0 for GdBi can be expressed as follows: for B in the (111) easy plane ($B\|[110]$)

$$B_0=\sqrt{(\omega_1/\gamma)^2-2B_EB_n} \tag{1}$$

and for B perpendicular to the (111) easy plane ($B\|[111]$)

$$B_0=\sqrt{(\omega_2/\gamma)^2-2B_E(B_A+B_n)}. \tag{2}$$

Here, B_n is the hyperfine anisotropy field and small B_a and B_f are neglected. From the Curie law for the nuclear magnetic moment, the relation $B_n \propto Am_N \propto 1/T$ is given, where A is the hyperfine coupling constant and m_N the nuclear moment.[13] Figures 3(a) and 3(b) show the temperature dependence of B_0 below 15.0 K for $B\|[110]$ at 57.7 GHz and for $B\|[111]$ at 57.5 GHz, respectively. The solid lines in Figs. 3(a) and 3(b) are the result calculated using Eqs. (1) and (2). The agreement between the experimental data and the calculated results is quite good. Using $B_E=21$ T estimated from the relation of $B_c=2B_E$, the anisotropy field and hyperfine anisotropy field are determined to be $B_A=5.6\times10^{-4}$ T, $B_n=3.3\times10^{-2}/T$ T, respectively.

We have measured the frequency dependence of the AFMR spectra for B parallel to several directions at 4.2 and 1.7 K. In Figs. 4(a) and 4(b), for example, we show the AFMR spectra at various frequencies for $B\|[110]$ at 4.2 and 1.7 K, respectively. Figures 5(a)and 5(b) show the frequency-field diagram of the AFMR mode at 4.2 and 1.7 K for $B\|[110]$ and [111], respectively. We can see that the deference in B_0 between two temperatures (open and solid circles in Fig. 5) is small with increasing the frequency. Using the Eqs. (1) and (2) with the determined parameters B_A and B_n, we calculate the AFMR modes that are shown as the broken (4.2 K) and solid (1.7 K) lines in the figures. The calculated modes also represent well the experimental data at 4.2 and 1.7 K in the frequency-field diagram.

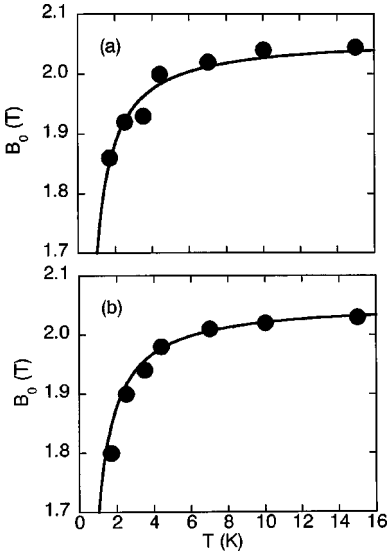

FIG. 3. Temperature dependence of the resonance field B_0 in magnetic field parallel to the (a) [110] and (b) [111] directions. Solid lines represent the calculated result of AFMR considered by hyperfine interaction.

Next question is which nuclear moment of Gd or Bi is responsible to this hyperfine field shift. Unfortunately, there has been no report on the NMR frequencies or the corresponding hyperfine fields for Gd and Bi nuclei in GdBi so far. In this paper, therefore, we briefly discuss the origin of B_n and estimate the hyperfine effective field $B_{S\,\mathrm{eff}}$ in both cases of Gd nuclear moments and the Bi nuclear moments using the NMR data for Gd nuclear in GdN (Ref. 16) and for Bi nuclear in Gd(Zn,Bi),[17,18] respectively.

The hyperfine effective field $B_{S\,\mathrm{eff}}$ acting on the electron spin system from the nuclear spin system and the effective

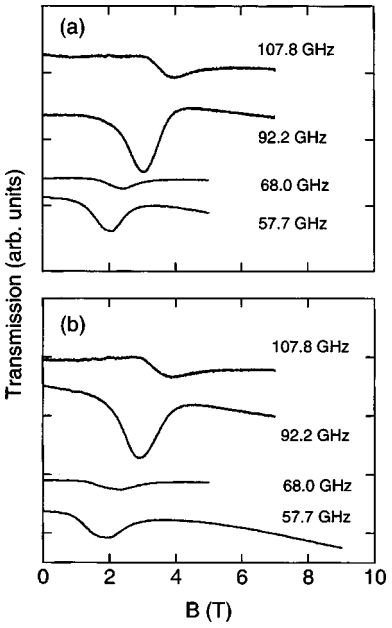

FIG. 4. ESR spectra for various frequencies at (a) 4.2 K and (b) 1.7 K in magnetic field parallel to the [110] direction.

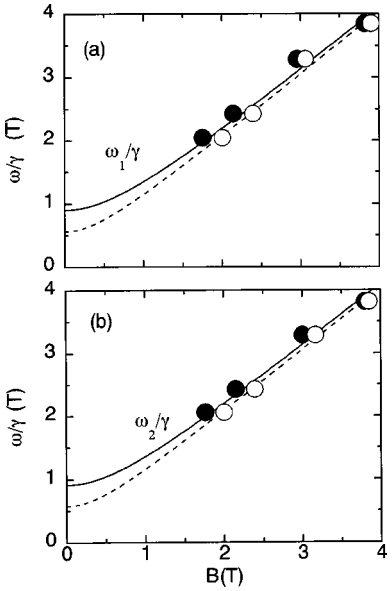

FIG. 5. Frequency-field diagram for magnetic field parallel to the (a) [110] and (b) [111] directions. The open and solid circles show data at 4.2 and 1.7 K, respectively. Broken and solid lines represent the calculated results AFMR mode considered by hyperfine interaction at 4.2 and 1.7 K, respectively.

field $B_{I\,\mathrm{eff}}$ acting on the nuclear spin system from the electron spin system are given by

$$B_{S\,\mathrm{eff}}=\frac{1}{g\mu_B}\sum_j A_j\alpha_j\gamma_{N,j}\hbar\frac{I_j(I_j+1)}{3k_BT}B_{I\,\mathrm{eff},j}, \qquad (3)$$

and

$$B_{I\,\mathrm{eff},j}=\frac{A_j}{\gamma_{N,j}\hbar}S, \qquad (4)$$

respectively. Here α_j is the natural abundance of the isotope, S the spin angular momentum, I_j the nuclear spin angular momentum, and $\gamma_{N,j}$ the gyromagnetic ratio for I_j. For ^{155}Gd ($\alpha_1=0.151$) and ^{157}Gd ($\alpha_2=0.156$), the NMR frequencies are 44.2 and 58.7 MHz at 4.2 K,[16] which correspond to $B_{I\,\mathrm{eff},1}=33$ T and $B_{I\,\mathrm{eff},2}=34$ T, respectively. Using these values, $B_{S\,\mathrm{eff}}$ is estimated to be 1.3×10^{-7} T at 4.2 K. This value is much smaller than B_n ($=7.9\times10^{-3}$ at 4.2 K) determined by our ESR measurement. The hyperfine interaction between the $4f$ spins and the nuclear spins in the Gd ion is considered to be in the same order in any Gd compounds. Therefore, the low field shift of B_0 in GdBi may not be mainly due to hyperfine interaction from nuclear moments of the Gd ion.

On the other hand, it has been reported that $B_{I\,\mathrm{eff}}$ at ^{209}Bi ($\alpha=1$) is 65.9 T in a Gd(Zn,Bi) compound at 4.2 K.[17,18] Since Zn and Bi are nonmagnetic ions, $B_{I\,\mathrm{eff}}$ at the Bi nucleus is mainly due to the $4f$-spin moments of the Gd ion. Using this value, $B_{S\,\mathrm{eff}}$ is estimated to be 2.1×10^{-4} T at 4.2 K, which is in good agreement with B_n ($=7.9\times10^{-3}$ T) obtained by our experiment at 4.2 K. Therefore, the hyperfine anisotropy field B_n acting on the $4f$-spin system is con-

sidered to be due to the nuclear spin moment of Bi and this strong effect may come through the spin polarization of *s*-like conduction electrons.

Next we consider why this effect is not observable in other cases. According to the NMR data of MnX (X=P, As, Sb, and Bi),[19] the hyperfine interaction of the Bi nucleus case is much larger than that of other nuclei cases. The estimated hyperfine coupling constant A of the Bi nucleus is about two times larger than that of other nuclei in MnX. Since $B_{S\,\mathrm{eff}}$ is proportional to A^2, the contribution of the hyperfine interaction to the spin moment is negligibly small for GdX with X =P, As, and Sb. It should be mentioned that B_n is also very small ($\sim 10^{-3}$ T) compared with B_0 ($\sim 10^{0}$ T) in GdBi, but the large exchange field ($B_E \sim 2\times 10^{1}$ T) amplified the AFMR frequency, as given by $2B_E B_n$ in Eqs. (1) and (2). Consequently, slight changes of temperature or slight change of nuclear magnetization can produce very large shift of the AFMR modes in the case of GdBi.

IV. CONCLUSION

We have performed the ESR measurements on single crystals of GdBi in the temperature range between 50 and 1.7 K and in the frequency range from 57 to 107 GHz. The resonance field shifts to lower field side with decreasing temperature from 7.0 K. The obtained results indicate that the hyperfine field arising from the nuclear moments of Bi affects the AFMR modes of GdBi. The estimated values of the anisotropy field and the hyperfine anisotropy field are $B_A = 5.6\times 10^{-4}$ T and $B_n = 7.9\times 10^{-3}$ T, respectively, at 4.2 K.

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