ESR study of Fe-doped $Ca_3Co_2O_6$: Isolated spin state of Fe^{3+} and anomalous *D* parameter caused by exchange interaction

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Impurity spin resonance of Fe^{3+} ions doped in the one-dimensional ferromagnet $Ca_3Co_2O_6$ was investigated in a submillimeter wave region using pulsed magnetic fields at 1.7 K. As expected from the Mössbauer result, the isolated electron state of Fe^{3+} with $g=2.00$ was successfully observed. The *D* values of Fe ions are found to be 0.66 cm^{-1} in a ferrimagnetic region and -0.87 cm^{-1} in a ferromagnetic region which is anomalously large and would be caused by the exchange interaction between a Fe spin and surrounding Co spins. [S0163-1829(98)01742-1]

In the field of Mössbauer spectroscopy, it has been widely believed that an isolated electron spin state of the ^{57}Fe ion is observable only for dilute magnetic materials, such as very dilute solutions of Fe_2O_3 in Al_2O_3, where the relaxation of an individual $^{57}Fe^{3+}$ electron spin is slow compared with the precession time of the nuclear spin.[1–3] On the other hand, in the case of magnetically dense materials, an individual electron spin changes its *z* component at an approximate rate of $J/\hbar$ (*J*: exchange interaction) which is fast enough to make a nuclear spin feel a time averaged effective field.[4]

Recently, we measured the Mössbauer effect of $^{57}Fe^{3+}$ ions doped in a one-dimensional (1D) Ising ferromagnet $Ca_3Co_2O_6$ (Ref. 5) and found that, although this material has a high density of magnetic ions and exhibits a long-range magnetic (ferrimagnetic) ordering at $T_c=25$ K,[6–8] the observed spectra are similar to those in the case of magnetically dilute extreme: the spectra with hyperfine fields corresponding to the exchange-polarized Fe electron spins with $m_z=\pm 5/2$, $\pm 3/2$, and $\pm 1/2$ are first observed below T_c. It is considered that the key lies in the large difference between magnetic characters of the host (Ising) and impurity (Heisenberg) spins. The spin wave band or the spin-cluster excitation energy of the host spin system is much higher than the impurity spin energy so that the impurity spin can be regarded as extremely isolated, and can be treated as an ''isolated paramagnetic moment.''

The above interpretation on the Mössbauer result for $^{57}Fe^{3+}$-doped $Ca_3Co_2O_6$ can be confirmed by ESR experiment since such a localized impurity state of a Heisenberg spin in a host Ising-spin system has already been found by means of ESR. For example, Date *et al.* observed the impurity spin resonance for Mn^{2+} and Fe^{3+} in $FeCl_2$, and Mn^{2+} in $CoCl_2 2H_2O$.[9–11] The present paper reports on the experimental results of ESR for Fe-doped $Ca_3Co_2O_6$, which is discussed from the viewpoint of localized spin resonance, using a simple formula based on the molecular field approximation.

The 1% Fe-doped $Ca_3Co_2O_6$, i.e., $Ca_3(Co_{0.99}Fe_{0.01})_2O_6$, was prepared by a conventional solid state chemical reaction as described in Ref. 7. The powered sample was soaked into an epoxy and then the magnetic field of $H=8$ T was quickly applied to align the sample along the hexagonal *c* axis (parallel to the chain direction). Submillimeter wave ESR has been performed at 1.7 K by using pulsed magnetic fields up to 30 T. The magnetic field is applied parallel to the *c* axis, and the duration time of the pulsed magnetic field is about 4 ms. The optical pumped far-infrared laser (about 40 lines up to 1 THz), backward traveling wave tubes (220 and 370 GHz bands) and Gunn oscillators (95, 110, 135, 190 GHz) have been employed. An InSb hot electron detector has been used.

Before presenting the ESR results, we will give a brief review of the structural and magnetic properties of the host material. The structure of $Ca_3Co_2O_6$ (K_4CdCl_6 type; $R3c$) is characterized by 1D chains consisting of alternating face-sharing CoO_6 octahedra and CoO_6 trigonal prisms along the *c* axis.[12] These chains are widely separated from each other by Ca ions. Another point of the structure is that the chains form a triangular lattice in the *c* plane. It should be noted here that the phase of each chain differs from that of three nearest-neighbor chains by 1/6 along the c axis and from that of other three chains by 2/6 along the same axis.[7] Concerning its magnetism, $Ca_3Co_2O_6$ is known as one of the typical Ising spin systems due to a strong anisotropy of the *g* tensor.[7,8] The intrachain interaction is ferromagnetic, whereas the interchain one is antiferromagnetic, which induces a ferrimagnetic ordering of the ferromagnetic chains below 25 K ($=T_c$). Some anomalies have been observed at lower temperatures: the 1/3 plateau in magnetization curves disappears below 10 K.[8] The temperature dependence of the neutron diffraction intensity of the magnetic (100) reflection does not obey the Brillouin function.[6] This implies the existence of successive magnetic phase transitions. However, the results of our neutron diffraction experiment[13] and the specific heat measurement by Michor and Hilscher[14] show no evidence of successive phase transition. Therefore, we will discuss the following ESR result by assuming that the lower field phase at 1.7 K is a ferrimagnetic state, though further study is needed to confirm this assumption.

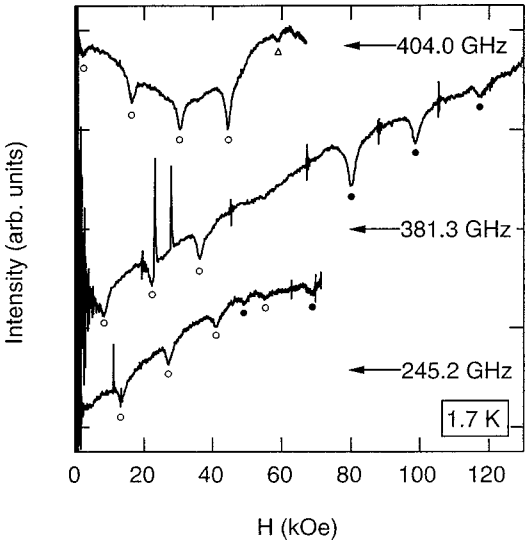

FIG. 1. Typical absorption lines observed at 1.7 K. The solid circles, open circles, and triangles denote absorptions from branches *A*, *B*, and *C*, respectively (see Fig. 2).

Many resonance lines having systematic frequency dependence were observed at 1.7 K in the frequency range 190 and 717 GHz. Typical examples of the resonance are shown in Fig. 1, where only the process under an increasing magnetic field is displayed. Figure 2 shows the frequency-field diagram of the resonance points. These resonance points can be classified into three branches, that is, *A*, *B*, and *C*, in the ferrimagnetic state, the ferromagnetic state, and near the boundary of the two states, respectively. The linewidth for branches *A* and *B* is about 1~2 kOe. However, the linewidth of branch *C* is unclear because of the very weak absorption intensity, and the origin of the resonance has not been identified at the present stage.

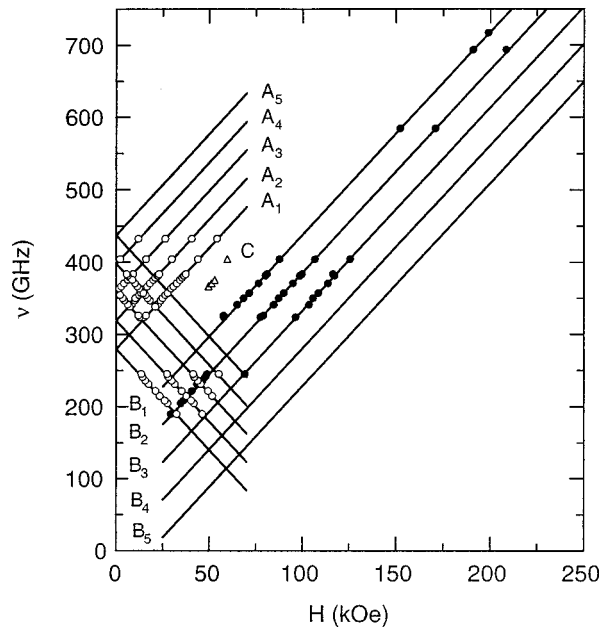

FIG. 2. Frequency-field diagram of the Fe^{3+} impurity resonance in $Ca_3Co_2O_6$ observed at 1.7 K ($H_0 \| c$ axis). The solid circles, open circles, and triangles denote absorptions from branches *A*, *B*, and *C*, respectively. Full lines represent the theoretical ones.

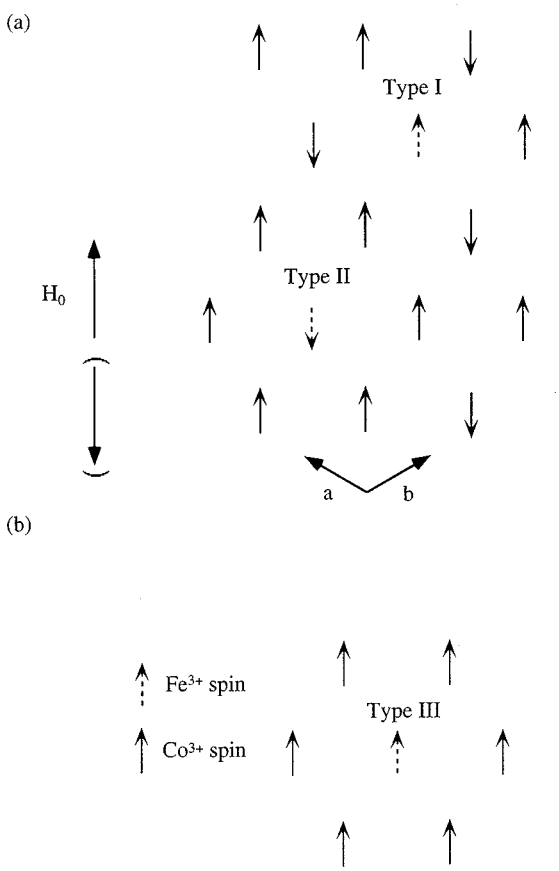

FIG. 3. Models of the impurity Fe^{3+} spin site in the hexagonal *ab* plane. Note that there are two sites denoted by I, II in the ferrimagnetic region.

What is important is that both branches *A* and *B* have a linear field dependence of the resonance frequency with an effective *g* valve of 2.00. It is clear that these come from the isolated impurity Fe^{3+} spins in $Ca_3Co_2O_6$ in accordance with the expectation from the Mössbauer experiment.[5] Each branch consists of several resonance lines equally separated, which is attributed to the uniaxial anisotropy *D* acting on the Fe^{3+} spin. The same kind of line separation is seen in the case of Mn^{2+}-doped $CoCl_2 2H_2O$.[11]

The effective spin Hamiltonian of the Fe^{3+} spins *S* under an external magnetic field H_0 is expressed as

$$\mathcal{H}=g\mu_B(H_0+H_E)S+DS_z^2, \tag{1}$$

where μ_B is the Bohr magneton, H_0 is an external magnetic field, and H_E is the resultant effective field coming from the exchange and dipolar interactions between the Fe and the surrounding Co spins. In this case, the dipole field is negligible because it is much smaller than the exchange field. The last term represents the uniaxial anisotropy. Considering that the Fe^{3+} spin is $S=5/2$, each branch should consist of five resonance lines, though in reality the positions of the branches *A* and *B* have four (A_1,A_2,A_3,A_4) and three lines (B_1,B_2,B_3), respectively. The remaining unobserved lines (A_5,B_4,B_5) as drawn in Fig. 2 were determined by comparing the relative absorption intensities: Since the $m_z=-5/2$ state, where m_z represents the expectation value of S_z, is by far most populated at low temperature 1.7 K, the lines

A_1 and B_1 having the highest relative intensity in each branch (see Fig. 1) should correspond to the transition from $|m_z| = 5/2$ to $3/2$.

One can calculate the resonance conditions in the manner used in the impurity Mn^{2+} spin resonance in $CoCl_2 2H_2O$.[11] For simplicity, we assume that the Fe^{3+} ion is surrounded by six Co^{3+} ions in the c plane, that is to say, the phase difference between the chains as mentioned above is neglected here. One can thus introduce the effective exchange fields, H_1 and H_2, corresponding to the intrachain and interchain exchange interactions between Fe^{3+} and Co^{3+} spins, respectively. Consider the Fe^{3+} impurity spins in the c plane as illustrated in Fig. 3. We assume that the intrachain exchange interaction between Fe^{3+} and Co^{3+} spins is ferromagnetic and the interchain one is antiferromagnetic. When H_0 is applied along the c axis, the resonance conditions of Fe^{3+} spins are expressed as follows.

(a) Ferrimagnetic state $0 < H_0 < H_c$ (H_c: the metamagnetic critical field). Although only one branch has been observed experimentally, two inequivalent impurity sites are considered theoretically as shown in Fig. 3(a),

$$\omega/\gamma = 2H_1 \pm H_0 \quad \text{for type I,} \tag{2}$$

$$\omega/\gamma = 2H_1 + 6H_2 \pm H_0 \quad \text{for type II,} \tag{3}$$

where the D term is omitted or, in other words, only the transition between $m_z = 1/2$ and $-1/2$ of the Fe^{3+} ion is considered.

(b) Ferromagnetic state $H_c < H_0$. As shown in Fig. 3(b), all impurity spins in this region are equivalent so that we have only one resonance formula given by

$$\omega/\gamma = 2H_1 - 6H_2 + H_0 \quad \text{for type III.} \tag{4}$$

Let us compare Eqs. (2), (3), and (4) with the experimental data. Extrapolating the lines A_3 and B_3 in Fig. 2 to the zero field, i.e., to the ordinate, the resonance frequencies in the absence of the external magnetic field are given as 358.5 GHz (=128.0 kOe) and 53.2 GHz (=19.0 kOe), respectively. In the ferromagnetic state, one obtains $H_E = 2H_1 - 6H_2 = 53.2$ kOe by comparing with Eq. (4). In the ferrimagnetic state, the value of 128.0 kOe is comparable to 100 kOe obtained by the Mössbauer effect measured at zero magnetic field.[5] Note that in the analysis of the Mössbauer result only one branch was assumed. One cannot, however, determine whether the observed resonance corresponds to the Fe^{3+} spin at a type-I or type-II site. If branch A comes from a type-I site, the two exchange fields are calculated as $H_1 = 64.0$ kOe and $H_2 = 18.2$ kOe, or $H_1 = 36.8$ kOe and $H_2 = 9.1$ kOe if A comes from a type-II site. Since the low-field phase below 10 K is still not clear as mentioned above, the fact that only one branch is observed implies the low-temperature phase is not a ferrimagnetic phase but an antiferromagnetic phase.

Finally, we discuss the fine structure splitting observed in branches A and B. The D values of Fe^{3+} are found to be 0.66 cm^{-1} for branch B. Here, the magnitude of D is determined by the line separation, and its sign is specified by the absorption intensity ratio of each line. The point we wish to stress is that the magnitude of the D values is unusually large. So far the largest D value was obtained for the Mn^{2+} ion in $CoCl_2 2H_2O$ ($D = -0.13\ cm^{-1}$). In addition, the sign of the D values changes between the branches A and B. Obviously, the crystalline field contribution alone does not account for the results. As proposed in the case of Mn^{2+}-doped $CoCl_2 2H_2O$, the main reason should be the antisymmetric exchange interaction of the form $d \cdot [S_1 \times S_2]$ (Dzyaloshinski-Moriya type).[11,15] Since the present material is an oxide, the superexchange interaction through the oxygen ion would play an important role in giving rise to the anomalously large D value.

In conclusion, as expected from the previous Mössbauer experiment, the impurity spin resonance of Fe^{3+} in $Ca_3Co_2O_6$ has been successfully observed. The exchange fields are evaluated to be 128.0 and 19.0 kOe for branches A and B, respectively. The D values of 0.66 cm^{-1} for branch A and -0.87 cm^{-1} for branch B are unusually large and the sign changes between these states, which would arise from the exchange interaction between Fe and Co spins.

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