Exchange splitting in $CuGeO_3$ under ultrahigh magnetic fields

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Electron paramagnetic resonance has been observed on $CuGeO_3$ in ultrahigh magnetic fields up to 180 T. The distinct exchange splitting is found between the two inequivalent Cu^{2+} sites along the b axis. Analyzing the data on the basis of a simple two-spin model, we evaluated the interchain exchange coupling J_b as $\sim$0.9 meV. This value is a little smaller than $J_b \sim 1.0$ meV obtained by neutron-scattering experiments. [S0163-1829(98)06917-3]

Since the discovery of the spin-Peierls transition in $CuGeO_3$, a large number of studies have been reported.[1] When compared to several organic spin-Peierls compounds, the one dimensionality is not evident in $CuGeO_3$ whose interchain exchange coupling J_b is large. The ratio of the interchain to the intrachain exchange coupling J_b/J_c is reported to be 0.1 by the neutron inelastic scattering experiment.[2] The role of the interchain coupling is essentially important to analysis of experimental data, such as magnetic susceptibility and the spin-wave dispersion relation. It is one of the key parameters for discussing the field-induced magnetic phase or the coexistence phase in the impurity-doped systems. In spite of its important role in understanding the magnetic properties of $CuGeO_3$, inelastic neutron scattering is the only experiment we are aware of to report the estimation of J_b.

The measurement of the spin-wave dispersion by the inelastic neutron scattering is a useful method to evaluate the exchange coupling in a uniform one-dimensional antiferromagnetic such as $KCuF_3$.[3,4] In the neutron-scattering work on $CuGeO_3$ mentioned above, the values of exchange couplings have been reported to be $J_c = 10.4$ meV, $J_b \sim 1.0$ meV, $J_a \sim 0.01$ meV by assuming the relation of the des Cloizeaux and Pearson formula[5] to the observed spin-wave dispersion in the chain direction and by assuming the relation of the classical spin-wave formula to the dispersion in the a and b axes.[2] Such phenomenological treatments have been successful in the case of a uniform antiferromagnetic chain. However, it is questionable whether the des Cloizeaux–Pearson formula is directly applicable to the case of $CuGeO_3$, where we have to take account of many complex factors such as the alternation of the intrachain exchange coupling or the second-nearest-neighbor exchange interaction in the chain. In fact, the value of J_c estimated from the magnetization saturation[6,7] is considerably larger than that measured by neutron scattering.[2] The reason for this discrepancy is still an interesting open question. As regards the intrachain coupling, it is also important to evaluate J_b by some means other than neutron scattering and to compare the experimental results, but they cannot directly be applied to $CuGeO_3$.

In a previous paper, we reported a direct determination of the intrachain exchange coupling J_c by the measurement of the saturation magnetization curve.[7] In the present work, we used the measurements of the exchange splitting of the electron paramagnetic resonance (EPR) to obtain the interchain coupling J_b as a method completely independent of neutron-scattering measurements. An experiment with the exchange splitting of $CuGeO_3$ was first tried by Ohta *et al.*[8] They observed only a small broadening of the EPR line because their measurement was limited to frequencies below 380 GHz. The exchange-splitting phenomenon can be observed in magnetic materials containing two inequivalent sites of magnetic ions. In low magnetic fields, EPR of these two sites are narrowed to a single peak by a finite exchange coupling between them. In very strong magnetic fields, the exchange splitting is observed when the Zeeman energy difference between these two sites exceeds this exchange coupling. This phenomenon itself it not new and it has been used so far to evaluate the exchange coupling in several materials.[9,10] In the case of the magnetic oxides, however, the superexchange coupling is considerably large. Consequently, we need ultrahigh magnetic fields to observe the exchange splitting. In the present paper, we report the observation of the exchange splitting in $CuGeO_3$ by using a single-turn coil and submillimeter wave lasers.

Several different submillimeter wave radiations up to $\nu = 4.25$ THz ($\lambda = 70.5$ μm) have been used in the present experiments. An optically pumped far-infrared laser has been employed as the light source. Magnetic fields as high as 180 T have been obtained by using the single-turn coil system.[11] Usually, the accuracy of the field measurement by the calibrated pickup probes for the single-turn coil system is better than 3%. In the present experiment, the EPR of ruby in the identical setup was used for the field calibration. The error of the field calibration in this case is estimated to be less than 2%. For tilted magnetic fields, the error arising from the field inhomogeneously is about 5%, which is caused by the small

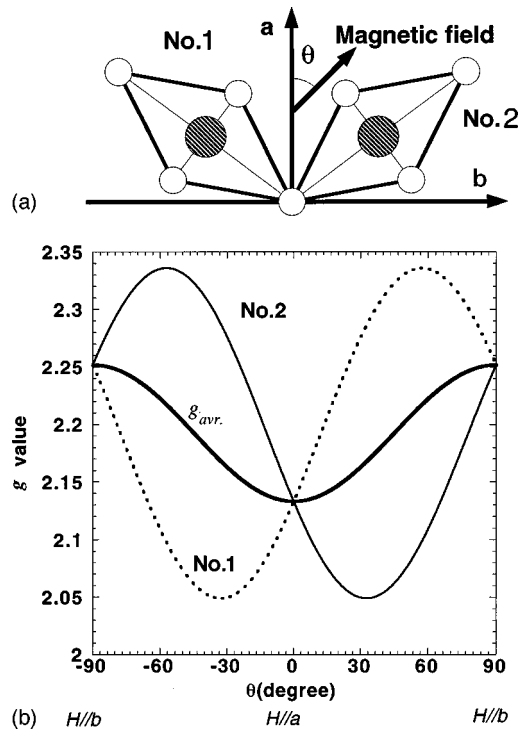

FIG. 1. (a) Schematic view of the two octahedrons in the ab plane. Open circles denote oxygen and the shadowed circles Cu^{2+}. θ is the angle between the magnetic field and the a axis in the ab plane. Two Cu^{2+} ions are coupled by the interchain exchange coupling J_b. (b) The angular dependence of the g value in the ab plane for sites No. 1 and No. 2 taken from Ref. 12. $g_{\text{avr.}}$ is the averaged g value between those for No. 1 and No. 2.

size of the coils. However, from the scattering of the data among many shots, the overall uncertainty involved in the measurement is less than 5% in the case of tilted-field measurements. This has been proven by many previous experiments such as cyclotron resonance at the Megagauss Laboratory. Single-crystal samples have been used that were grown by the floating-zone method.

Figure 1(a) shows the schematic crystal structure of $CuGeO_3$ in the ab plane. There are two different CuO_6 octahedron cells, i.e., No. 1 and No. 2 as shown in Fig. 1. The angle between the principal axes of these two types of octahedrons is about 114° in the ab plane. The angular dependence of the g values for sites No. 1 and No. 2. calculated by Yamamoto *et al.* is also shown in Fig. 1(b).[12] This calculation was made by using a charge-point model and by adjusting the spin-orbit coupling λ to fit the experimentally observed angular dependence of the averaged g values in an exchange-narrowed regime. Were it not for exchange coupling between Cu^{2+} ions in these two sites, two independent EPR absorptions could be observed for two different g values. In reality, however, there is an interchain exchange coupling J_b between these two Cu^{2+} ions, so that two resonances in No. 1 and No. 2 are unified to a single peak by the exchange narrowing. The exchange splitting of the EPR line is expected when the difference of the Zeeman energy between sites No. 1 and No. 2 exceeds the exchange coupling J_b under ultrahigh magnetic field. The threshold field H for this splitting is given by

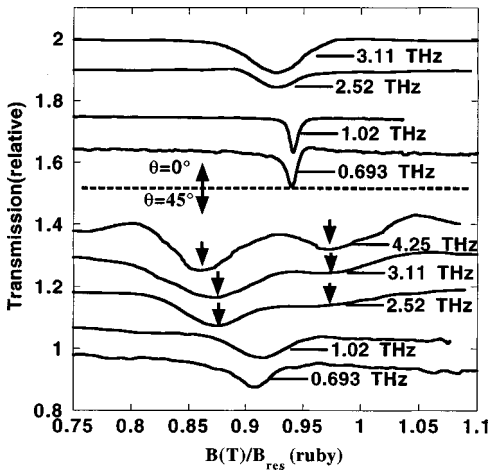

FIG. 2. Frequency dependence of EPR line shape in two different magnetic-field orientations θ=0° and 45°. The horizontal axis is divided by the resonance field of ruby whose g value is 1.98.

$$\sqrt{2}J_b \approx \Delta g \mu_B H \tag{1}$$

using the theory of exchange narrowing by Anderson,[13] where $\Delta g = |g_1 - g_2|$ and g_1 and g_2 are the g values of sites No. 1 and No. 2, respectively. The factor of $\sqrt{2}$ in Eq. (1) comes from the parameter ω_e/ω_0 in Fig. 2 of Ref. 13. However, this theory is treating the isolated two-spin systems. In the case of the $CuGeO_3$, J_c is much larger than J_b and we have to consider the correlation by the internal field caused by J_c to evaluate J_b accurately. Such treatment has been performed by using a mean-field random-phase approximation and J_b has been estimated to be 15% less than the present results.[14] In this paper, we report the observation of the distinct exchange splitting in $CuGeO_3$ and the preliminary evaluation of J_b using the simplified equation (1). The complete quantitative analysis will be given in a separate paper. We define the Hamiltonian of the system as

$$H = J_c \sum_{\text{intrachain}} S_i S_j + J_b \sum_{\text{interchain}} S_k S_l . \tag{2}$$

With this definition, we can directly compare the values of J_b with those in other papers.[2,7] Since Δg is about 10% of the average g value as shown in Fig. 1(b), the EPR measurement should be made with ten times as large a frequency as J_b to satisfy Eq. (1). Recently, rotation of the octahedron along the c axis and the existence of the four nonequivalent sites along the c axis have been reported in an x-ray study of $CuGeO_3$.[15] This is not effective in the present results because the resonance of Cu^{2+} ions in the chain are strongly exchange narrowed by the large J_c.

The EPR spectra in two different magnetic-field orientations θ=0° and 45° are shown in Fig. 2 at different frequencies. The angle θ is defined in Fig. 1(a). The horizontal axis is the magnetic field divided by the resonance field of ruby whose g value is 1.98. In all frequencies, the linewidth is broader at θ=45° than at θ=0°. This is because Δg is the largest around θ=45° and is zero at θ=0° as shown in Fig. 1(b). At 2.52, 3.11, and 4.25 THz, the EPR lines split into two distinct peaks as indicated by arrows for θ=45°. The

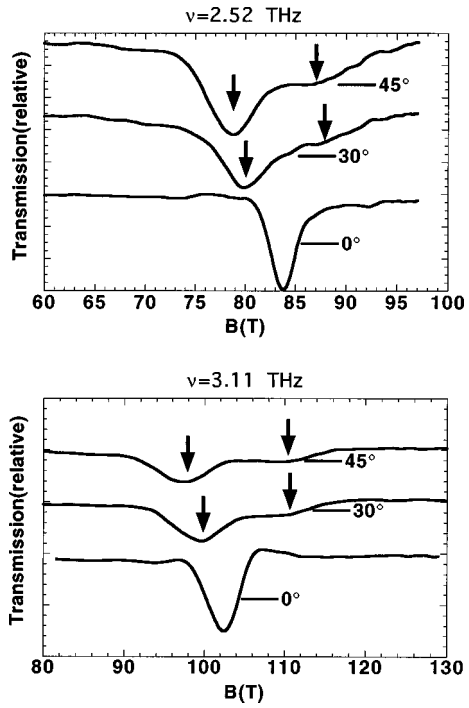

FIG. 3. Angular dependence of the EPR line shape at 2.52 and 3.11 THz. Arrows indicate that the two peaks appear as a result of the exchange splitting.

broadening of the EPR line observed at $\theta=0°$ for 2.52 and 3.11 THz is caused by the limited field homogeneity of the single-turn coil.

The angular dependence of the EPR lines for 2.52 and 3.11 THz is shown in Fig. 3. The single peak observed at $\theta=0°$ splits into two distinct peaks as the angle θ increases indicating that Δg becomes large. The absorption of the low-field side peak is stronger than that at the high-field side, which is different from Fig. 2 in Ref. 13. This discrepancy arises from the high-temperature approximation

$$x=\hbar\omega_0/k_bT\ll 1 \tag{3}$$

used in the theory of Anderson, where ω_0 is the angular frequency of the submillimeter wave radiation. The parameter x is between 0.4 and 0.5 in the present experiments. A more advanced treatment that can be appropriate under the low-temperature condition has been given by Hamano and Shibata.[16,17] In their theory, it is expected that the peak in the low-field side becomes stronger than that in the high-field side when the exchange coupling is antiferromagnetic, which is consistent with the present result. The observed double-peak absorption spectra are fitted with double Lorentzians and thus the two resonance fields for No. 1 and No. 2 are obtained. The splitting of the two peaks is plotted in Fig. 4 as a function of the exchange-splitting energy. Since we cannot separate the signals into two peaks in 0.693 and 1.02 THz, we plot the full width of the half maximum in these two frequencies. The horizontal axis of Fig. 4 is $\Delta g\mu_BH_0/\sqrt{2}$ where H_0 is the average of the two resonances and Δg is taken from the calculation by Yamamoto *et al.*[12] The agreement between these calculated g values and the experimental values obtained by NMR measurements are very good.[18] Consequently, the use of g values given in Ref. 12 does not

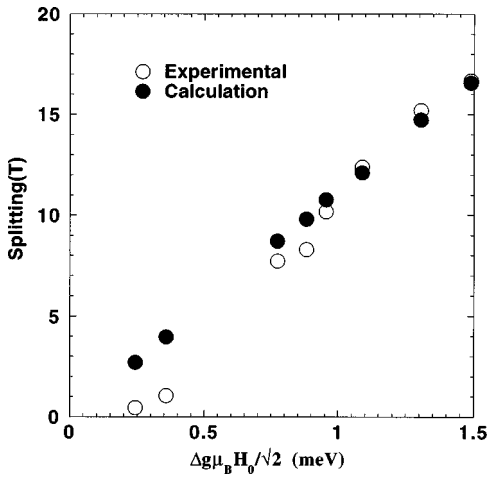

FIG. 4. The plot of the experimentally obtained splitting between the two peaks against $\Delta g\mu_BH_0/\sqrt{2}$ (open circles). The splitting calculated for $J_b=0$ is shown by closed circles. The crossover between the exchange-narrowed regime and the exchange-splitting regime is shown at around $\Delta g\mu_BH_0/\sqrt{2}\sim 0.9$ meV.

cause ambiguity in evaluating J_b. Assuming $J_b=0$, we can observe the two resonance peaks at $H_1=\omega/g_1\mu_BS$ and $H_2=\omega/g_2\mu_bS$. The splitting between H_1 and H_2 is also plotted in Fig. 4 by closed circles. In the exchange-narrowed regime, the experimental splitting is expected to be smaller than the splitting calculated assuming $J_b=0$. When the exchange splitting occurs, the experimental splitting is expected to approach this calculated value because the condition $J_b\ll\Delta g\mu_BH/\sqrt{2}$ holds. In Fig. 4, this transition from the exchange-narrowed regime to the exchange-splitting regime is observed around $\Delta g\mu_B/\sqrt{2}\sim 0.9$ meV. From the accuracy of the field measurement and the scattering of the data in Fig. 4, we can conclude that the error in the estimation of this value does not exceed 7%. This indicates that $J_b\sim 0.9$ meV with an accuracy of 7%. This value is nearly the same as $J_b\sim 1.0$ meV obtained by neutron-scattering experiment.[2] But J_b is expected to be smaller than $J_b\sim 0.9$ meV when we consider the molecular field caused by J_c as shown in Ref. 14.

Finally, we discuss the one dimensionality of $CuGeO_3$. By using the present value of $J_b\sim 0.9$ meV and $J_c=15.8$ meV,[7] we obtained a ratio of $J_b/J_c\sim 0.06$. This value is slightly smaller than that of 0.1 assessed by the neutron-scattering experiment, but it shows that the one dimensionality of $CuGeO_3$ is poor. In a typical quasi-one-dimensional antiferromagnet $KCuF_3$, the intrachain exchange coupling and the ratio of the interchain coupling to the intrachain coupling have been evaluated to be $J_c=35.0$ meV and $J_a/J_c=0.01$, respectively. This compound shows an antiferromagnetic order below $T_N=39.8$ K. It shows the contrast with $CuGeO_3$ in which no antiferromagnetic order is observed in spite of the poor one dimensionality. A quantitative analysis of this problem may contribute to the understanding of the competing next-nearest-neighbor exchange interaction that can prevent the three-dimensional magnetic ordering.

To summarize, the exchange splitting of EPR has been observed in ultrastrong magnetic field. The interchain exchange coupling has been evaluated as $J_b\sim 0.9$ meV from this splitting and it is not far from the value obtained by

neutron inelastic scattering measurements. We obtained a ratio of $J_b/J_c \sim 0.06$. It shows that the one dimensionality of $CuGeO_3$ is weaker than other typical one-dimensional systems.

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