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Electron-spin resonance and ferromagnetism in a copper oxide: $La_4Ba_2Cu_2O_{10}$

Hiromu Masuda, Fumio Mizuno, Izumi Hirabayashi, and Shoji Tanaka
Superconductivity Research Laboratory, Nagoya Division, International Superconductivity Technology Center,
2-4-1 Mutsuno, Atsuta-ku, Nagoya 456, Japan

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The electron-spin resonance (ESR) of a copper oxide $La_4Ba_2Cu_2O_{10}$, which shows a ferromagnetic transition at around 5 K, has been studied. The ESR spectra show a narrowing with decreasing temperature that is characteristic of the ferromagnetic exchange interaction. The ground state of the Cu^{2+} d hole in the $La_4Ba_2Cu_2O_{10}$ compounds is described by the wave function $d_{x^2-y^2}$, and it agrees with the results deduced from the structure. The origin of the ferromagnetism is that the d-hole orbits of the ground state are alternately orthogonal to the nearest-neighbor ones.

There have been several reports on anomalous ferromagneticlike behaviors, such as a positive divergence of the magnetic susceptibility at a finite temperature in high-T_c copper oxide superconductors. For example, it has been reported that Na-doped La_2CuO_4 prepared in an inert gas atmosphere exhibits superconductivity below 30 K with an unknown ferromagneticlike transition at about 10 K.[1] Until now, the origin of such anomalies has not been clear. Moreover, the observed anomalies have sometimes been attributed to technical problems in the magnetization measurements, such as inhomogeneity of the external field and an unsuitable size of the samples.

We have recently observed a similar ferromagneticlike behavior in the low-temperature magnetization of $LaBa_2Cu_3O_{7-y}$ prepared in a reducing atmosphere.[2] Besides the anomalous magnetization, we have found a very large magnetic signal in the specific heat at low temperature where the magnetic transition occurs, which means that an unidentified ferromagnetic object surely exists in our samples. Then we started the search for its origin. Making reference to the report by Ghandehari *et al.* that $LaBa_2Cu_3O_{7-y}$ was decomposed into barium cuprate and $La_4Ba_2Cu_2O_{10}$ (the 4:2:2 phase) when it was sintered under a He atmosphere,[3] we found that the $La_4Ba_2Cu_2O_{10}$ compound was the origin of the ferromagnetism observed in the $LaBa_2Cu_3O_{7-y}$ system.[4] According to Ref. 4, the effective magnetic moment of the 4:2:2 phase from the Curie-Weiss plot and the saturation magnetic moment are 1.66 μ_B/Cu and 0.95 μ_B/Cu, respectively. These moments indicate that almost all Cu^{2+} $\frac{1}{2}$ spins participate in the localized-type ferromagnetism of the $La_4Ba_2Cu_2O_{10}$ compound.

The 4:2:2 phase in the La-Ba-Cu-O system was first synthesized by Michel and Raveau in 1981 and its structure was analyzed with x-ray powder diffraction by them. This compound has the same stoichiometry as the green phase (the 2:1:1 phase) of the Y-Ba-Cu-O system,[5] but its structure and magnetic properties are different. The 2:1:1 phase is orthorhombic with space group *Pbnm*(62) and an antiferromagnetic transition at about 28 K.[6] The 4:2:2 phase is a tetragonal insulator with space group *P*4/*mbm*(127) and its color is not green but dark brown. Among the copper compounds in which Cu^{2+} ions show a magnetic ordering, ferromagnetic ordering is very rare. The K_2CuF_4 compound crystallizing into a K_2NiF_4-type structure is one of the most interesting ferromagnetic ones.[7] In this paper, we report an ESR investigation to clarify the relationship between ferromagnetism and the special crystal structure of the $La_4Ba_2Cu_2O_{10}$ compound with reference to the Cu ferromagnet K_2CuF_4.

The $La_4Ba_2Cu_2O_{10}$ compounds were prepared by conventional solid-state reaction from the mixture of high-purity La_2O_3, BaO_2, and CuO powders. The La_2O_3 powder was preheated at 1000 °C for 10 h in air, because La_2O_3 is highly hygroscopic. The mixed powders were calcined at 900 °C for 10 h in air. They were ground and pressed into disks, and sintered at 1000 °C for 10 h in air. The crystal structure was characterized by pulsed neutron powder diffraction. The results of the analysis gives support to the model that has been proposed by Michel *et al.* Our detailed structure analysis has been published elsewhere.[8] The result of the electron probe microanalysis (EPMA) showed that our samples were essentially the single phase of the 4:2:2 compound. The static magnetization was measured by a SQUID magnetometer. The ESR measurement was carried out with an X-band (9.097 GHz) spectrometer in the temperature range of 4.2–300 K and a Q-band (35 GHz) spectrometer at room temperature. The ESR sample in the form of fine powder was sealed to avoid humidity and freezing oxygen.

The inverse electron spin susceptibility per molar Cu^{2+} ion of the 4:2:2 phase χ_S^{-1}, which was determined by ESR signal intensity as a function of temperature, is shown in Fig. 1(a), and that of the static magnetic susceptibility χ_M^{-1} is shown in Fig. 1(b). The absolute value of χ_S was corrected by using the Cu^{2+} signal of $CuSO_4 \cdot 5H_2O$ as a reference. The thus determined value of χ_S agrees well with the χ_M in the whole temperature range. As shown in Fig. 1(a), a slight kink anomaly in the temperature dependence of χ_S^{-1} is observed around 80 K. The line which was extrapolated from the data above 80 K crossed the abscissa at a negative temperature point, which suggests an antiferromagnetic interaction. But below 80 K, the Curie-Weiss plot showed ferromagnetic

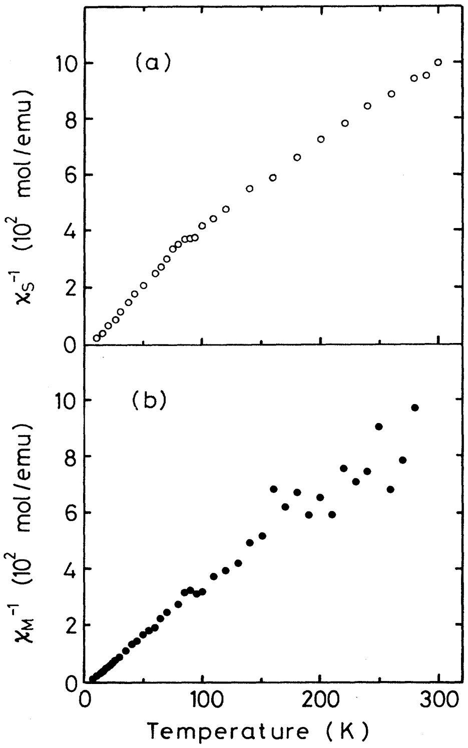

FIG. 1. The temperature dependences of the inverse molar susceptibilities for $La_4Ba_2Cu_2O_{10}$. (a) The inverse electron spin susceptibility χ_S^{-1} and (b) the inverse static susceptibility χ_M^{-1}.

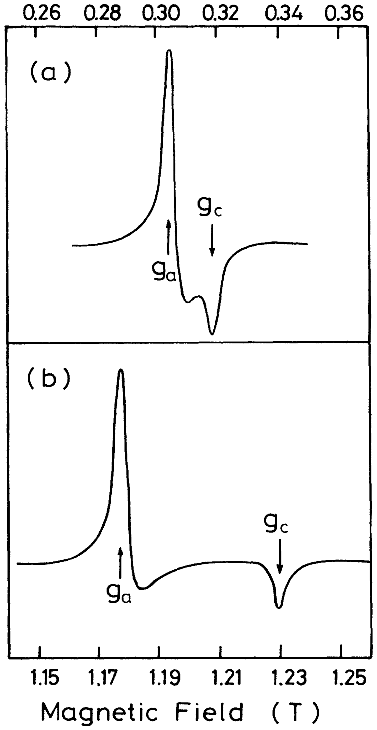

FIG. 2. The ESR powder spectra of the $La_4Ba_2Cu_2O_{10}$ at 300 K. (a) *X* band (9.097 GHz) and (b) *Q* band (35 GHz).

behavior with a Curie temperature Θ_f about 5 K. In Fig. 1(b), the temperature dependence of χ_M^{-1} shows the same behavior as χ_S^{-1}. There may be a phase transition at about 80 K, about which it is still unknown whether it is magnetic or structural. From the inverse susceptibility χ_M^{-1} below 80 K, the Curie-Weiss plot fitted to the data yields a ferromagnetic transition at $\Theta_f = 5.2$ K. Below 5.2 K, the measured susceptibility χ_M shows a sharp upturn and then a positive divergence. The effective Bohr magneton p_{eff}'s derived from the slope of χ_S^{-1} and χ_M^{-1} are 1.41 μ_B/Cu and 1.54 μ_B/Cu, respectively. If the estimated localized moment is assigned to every Cu atom, these values of effective moment are smaller than the theoretical one ($p_{\text{eff}} = \sqrt{3}$) assuming the complete quenching of the orbital angular momentum, and are also smaller than that reported in Ref. 4 (1.66 μ_B/Cu) due to the existence of an impurity phase which was observed by x-ray diffraction in the 4:2:2 sample prepared in this study.

The typical *X*-band and *Q*-band ESR spectra of the 4:2:2 phase at room temperature are shown in Figs. 2(a) and 2(b), respectively. Ganguly *et al.* reported that there was another weak structure in the ESR spectra of the 4:2:2 phase at around $g = 2.23$ besides the feature shown in Fig. 2, and they suggested that the g tensor had three different components.[9,10] They explained that this weak structure was caused by imperfections in the square planar CuO_4, i.e., displacement of a copper ion from the plane of the oxygen ions.[9] According to our neutron diffraction study,[8] the square planar CuO_4 is rectangular with dimensions 2.660×2.762 Å^2 and a copper ion placed at the center of the plane of the oxygen ions. In our refinement, such a deviation was not observed. The weak structure at around $g = 2.23$ may be caused by the barium cuprate impurities.[11] The *Q*-band spectrum shows the characteristic features that the Cu^{2+} ion in the 4:2:2 phase has the uniaxial g tensor, although the Cu site point symmetry is orthorhombic, which suggests that the g tensor has three different components. But this orthorhombicity is far smaller as compared with the anisotropy along the local principal axis perpendicular to each CuO_4 plane. Hereafter we make an assumption that the local crystal field of the cations can be approximated by a uniaxial one.

The temperature dependence of the g values and the half-width of the resonance peak ΔH are shown in Fig. 3. At room temperature, the g_a and the g_c values are 2.133 and 2.037, respectively. The g_a value gradually decreases with decreasing temperature and has a minimum value at 10 K, which is slightly higher than Θ_f. The g_c value is constant in the temperature range from 300 to 20 K. Below 20 K, it begins to increase with decreasing temperature. The half-width of the resonance peak ΔH decreases from room temperature to 10 K, and this narrowing is characteristic of the ferromagnetic exchange interaction. Below 10 K, the ΔH shows a sharp increase, which is influenced by the internal magnetic field caused by the thermal fluctuation near the transition tempera-

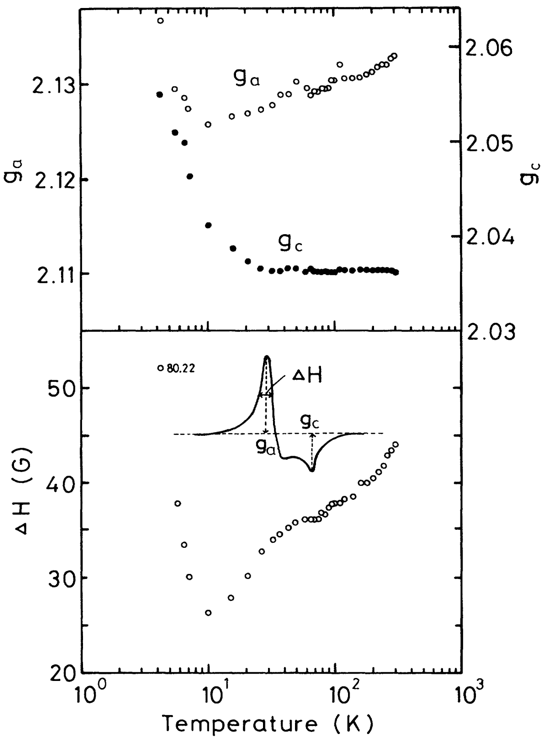

FIG. 3. The temperature dependences of the g_a,g_c values and the half-width of resonance peak ΔH for $La_4Ba_2Cu_2O_{10}$.

ture. There is no reproducibility in the ESR line shape below this temperature region. If the single crystal is used for measurements, the ΔH should be decreased even below 10 K. In the temperature dependence of the ΔH, an anomalous feature shows a slight hesitation in decreasing at around 60–80 K where χ_S^{-1} and χ_M^{-1} show kink anomalies.

In the $BaCuO_{2.02}$ sample,[11] the g value of the perpendicular to the principal axis $g_a(=g_\perp)$ is smaller than that of the parallel to it $g_c(=g_\parallel)$. In the polycrystalline 4:2:2-phase sample, however, if the g_a and the g_c are assigned to $g_\perp$ and $g_\parallel$, respectively, the magnitudes of $g_\perp$ and $g_\parallel$ are reversed, i.e., the $g_\perp$ is larger than that of the parallel $g_\parallel$. According to ordinary ligand field theory, there is a relationship between the g value anisotropy and the orbitals of d holes in the ground state. If the apex anion-cation distance is elongated along the principal axis from the isotropic octahedron, the orbital of the d hole is $d_{x^2-y^2}$-like, and its g factor has a relation of $g_\parallel > g_\perp > g_e$, because the $g_\parallel$ and the $g_\perp$ are expressed as

$$g_\parallel = g_e - 8\lambda/\Delta_0 \tag{1}$$

and

$$g_\perp = g_e - 2\lambda/\Delta_1 \, , \tag{2}$$

where $g_e=2.0023$, λ is the negative spin-orbit parameter (for Cu^{2+} ion; $-828\ cm^{-1}$), Δ_0 and Δ_1 are the crystal-field-splitting energies between d_{xy} and $d_{x^2-y^2}$ orbits and d_{yz}, d_{zx}, and $d_{x^2-y^2}$ orbits for the d^9 configuration, respectively.[12] On the other hand, if the octahedron shrinks along the principal axis, the ground-state orbital becomes $d^{3z^2-r^2}$ and the g factor has a relation of $g_\perp > g_\parallel = g_e$.

From the observed ESR signal in Fig. 3, the g_a is larger than the g_c; therefore, the ground state of the d hole of the Cu^{2+} ion in the 4:2:2 phase seems to be described by the $d_{3z^2-r^2}$ orbital. According to the structural analysis of Michel *et al.*[5] and our neutron powder diffraction study of the 4:2:2 phase,[8] the square planar CuO_4 groups are so isolated that one square planar CuO_4 is orthogonal to the nearest-neighbor CuO_4, as shown in Fig. 4. The CuO_4 plane is parallel to the c axis and perpendicular to the ab plane. In the case of the CuO_4 plane, the ground state of the d hole of the Cu^{2+} ion is expected to be described by the wave function of $d_{x^2-y^2}$, which is not consistent with the ESR results. This inconsistency can be resolved if the exchange coupling is taken into account.[12]

The top view of the unit cell with the Cu^{2+} d-hole orbitals in the ground state is illustrated in Fig. 4. The g values perpendicular and parallel to the local principal axis are denoted by $g'_\perp$ and $g'_\parallel$, respectively. When the field is applied parallel to the c axis, the system responds at a field corresponding to $H=\hbar\omega/2g'_\perp\mu_B$, because both spins at the inequivalent Cu sites have the same $g'_\perp$ value. On the other hand, when the external field is applied perpendicular to the c axis, and the response frequencies are different for the inequivalent Cu spins, and the resonance occurs at different external fields corresponding to both $g'_\perp$ and $g'_\parallel$. When the exchange interaction acts between a pair of inequivalent ions and its magnitude exceeds the difference of Zeeman energy, two resonance lines amalgamate each other with increasing exchange interaction. Finally they are combined at the center of the two resonance lines. Therefore, it is straightforward to deduce the formula of the g tensor as $g_a=(g'_\perp+g'_\parallel)/2$. For the

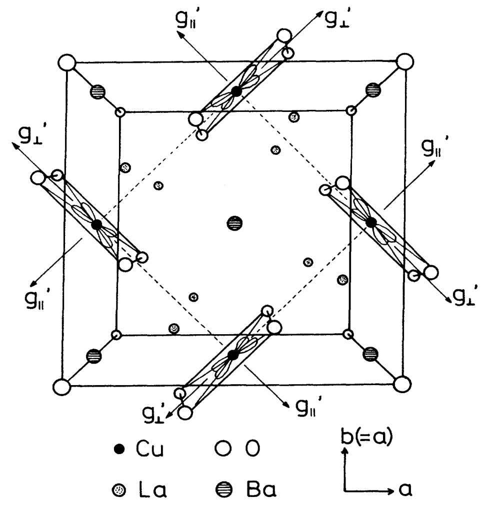

FIG. 4. Top view of the crystalline structure of $La_4Ba_2Cu_2O_{10}$. The orthogonality of the orbitals of the Cu^{2+} d hole is illustrated.

experimental values $g_a = 2.133$ and $g_c = 2.037$ at room temperature, the local principal values of the g tensor can be calculated as $g'_\perp = g_c = 2.037$, $g'_\parallel = (2a_a - g_c) = 2.229$. From the $g'_\perp$ and the $g'_\parallel$ values, the ground state of the Cu^{2+} d hole in the 4:2:2 phase is described by the wave function $d_{x^2-y^2}$, and this agrees with the results deduced from the structure. By using the values of the $g'_\perp$ and the $g'_\parallel$, the crystal-field-splitting parameters Δ_0 and Δ_1 are calculated as 29 500 cm^{-1} (3.66 eV) and 44 900 cm^{-1} (5.56 eV), respectively.

When the d-hole orbits of the ground state are orthogonal to the nearest-neighbor copper one as shown in Fig. 4, only the potential exchange interaction acts between the Cu ions. There is no strong antiferromagnetic kinetic exchange due to the nonexistence of oxygen between Cu ions. On the other hand, although the d-hole orbitals of the ground state between the nearest-neighbor interlay Cu ions are not orthogonal, the exchange interaction is also expected to be ferromagnetic. Because the Cu ion between the interlayer is distant, the d-hole orbits of the ground state have almost no overlap. Therefore, it is reasonable to expect that the whole exchange interaction which acts between spins of the Cu^{2+} ion is ferromagnetic. The magnitude of the exchange interaction J is estimated from the formula by the molecular field approximation:

$$\Theta_f = 2zJS(S+1)/3k \ , \tag{3}$$

where Θ_f is the Curie temperature, z is the coordination number, S is the quantum number of spin, and k is the Boltzmann constant. The value of J was obtained as 2.6 K by using $z=4$ and $S=\frac{1}{2}$. Here it is instructive to compare the 4:2:2 phase with a typical Cu ferromagnet $\mathrm{K_2CuF_4}$. In $\mathrm{K_2CuF_4}$, the orbital ordering occurs due to the Jahn-Teller effect; then the ground state of the d orbital of the Cu^{2+} ion is also described by the alternately orthogonal orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$. Under this condition, the ferromagnetic exchange interaction works between the spins of $\mathrm{K_2CuF_4}$. It is similar to the case of the 4:2:2 phase.

It is important to consider the magnetic anisotropy which causes the axis or plane of easy magnetization. Since there is no one-ion anisotropy for $S=\frac{1}{2}$ Cu^{2+} spin, the higher-order anisotropic exchange and the dipole interaction cause the magnetic anisotropy. The former is expressed by $\lambda^2 J/\Delta^2$ and this value is estimated as 2–3 mK for the 4:2:2 phase using the value of J in Eq. (3). On the other hand, the latter value is estimated as 2–30 mK, which is one order of magnitude larger than that of the anisotropic exchange interaction. If the 4:2:2 phase has two dimensionality, the plane of the easy magnetization is the ab plane. In this case, the spin system can be described as Heisenberg-like, but near the Curie temperature it has an XY-like character because the effect of the isotropic energy is enhanced by the number of spins in the large ferromagnetic cluster in the fluctuation region. A similar situation occurs in the magnetic anisotropy in $\mathrm{K_2CuF_4}$. Its spin system is described by the XY model in the fluctuation region near the Curie temperature and shows the Kosterlitz-Thouless transition,[13] which has recently become interesting in the field of granular superconductivity because both XY model and granular superconductor belong to the same universality class. It has not been determined experimentally yet which type of anisotropy is realized in the 4:2:2 phase. It will be clear after some detailed measurements on the single crystals.

In summary, we have measured ESR in a ferromagnetic copper oxide: $\mathrm{La_4Ba_2Cu_2O_{10}}$. The g value, which is slightly larger than 2, shows the feature of a Cu^{2+} d^9 spin state. When the exchange coupling that occurs between a pair of inequivalent Cu^{2+} ions is taken into account, the ground state of the Cu^{2+} d hole is determined by the wave function $d_{x^2-y^2}$, which agrees with the results deduced from the structure. The location of Cu ions and the orthogonality of the wave-function ground state make the exchange interaction in the Cu plane act ferromagnetically. The origin of the ferromagnetic ordering seems to be similar to that of $\mathrm{K_2CuF_4}$.

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