Ferromagnetic-antiferromagnetic transition in $(La\text{-}R)_4Ba_2Cu_2O_{10}$

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Cuprate $(La\text{-}R)_4Ba_2Cu_2O_{10}$ shows ferromagnetic to antiferromagnetic phase transition by replacing La ions with rare earth (R=Nd, Sm, Eu, and Gd) ions at low temperature. We propose that the transition is caused by a competition between antiferromagnetic superexchange interaction of Cu spins via La ions and ferromagnetic superexchange interaction due to Hund's rule coupling of spins of holes on oxygen ions. It is shown that the ferromagnetic interaction becomes antiferromagnetic with increasing overlap between the wave functions of oxygen and La(R) ions.

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It is well-known that high-temperature superconducting cuprates can be obtained by doping electrons or holes into antiferromagnetic insulators. In contrast to the general trend in high-T_c cuprates, $La_4Ba_2Cu_2O_{10}$ (La422) shows ferromagnetism (FM) with a Curie temperature of 5 K, and has attracted much interest for this reason.[1] The origin of the ferromagnetism has been a subject of controversy, and several mechanisms have been proposed. At the time of discovery of FM in La422, the flat-band mechanism of FM has been proposed on the basis of the characteristic lattice structure of La422.[2] Indeed, the first-principles calculation shows the presence of a flat band at the Fermi level in the paramagnetic state.[3] But this indicates a metallic FM in the paramagnetic state, which contradicts the experimental results. The flat-band mechanism can thus be ruled out. An analysis in the Hubbard model shows the presence of FM, but only for small parameter regions peculiar to real systems.[4]

In order to determine the origin of FM in La422, a detailed NMR study has been performed,[5] and NMR signals from La ions have been detected, which indicates that the La ions play an important role in FM of La422. Furthermore, FM in La422 is transformed into the antiferromagnetic (AF) state through replacement of 25%–45% of La ions with rare earth (R) ions such as Nd, Sm, Eu, and Gd. It has been further revealed that FM and AF are not affected by applied pressures of up to 6 GP, indicating that structural deformation cannot be the origin of FM.[6] In view of these experimental results, a detailed first-principles calculation has been performed, yielding values of the exchange interaction between Cu spins in La422 and Nd422.[7] The results indicate that the interaction between Cu spins along the c axis is ferromagnetic for La422, but antiferromagnetic for Nd422. The interaction on ab planes, on the other hand, is negligible for both oxides. The most interesting result is that the exchange interaction along the (101) direction is ferromagnetic for both La422 and Nd422. Ku *et al.* have concluded that the spatial extent of the wave functions of La and Nd determines the sign of the interaction between Cu spins.

The results obtained in using first principles[7] are interesting in that the second nearest-neighbor (NN) interaction is ferromagnetic, while the interaction between first NN spins along the c axis changes from ferromagnetic to antiferromagnetic through the replacement of La ions with Nd ions. An intuitive understanding of the results, however, may not be so transparent. In the present paper, we propose a clear mechanism for FM-AF transition in La-R422 by calculating the superexchange interaction between Cu spins within the framework of a simple model.

To this end, we will show that two characteristic networks of d and p orbitals of Cu-O-La-O-Cu and Cu-O-O-Cu along the c axis give rise to antiferromagnetic and ferromagnetic interactions, respectively, where the former interaction is caused by the superexchange interaction, while the latter is due to Hund's rule coupling. The magnitude of these competing interactions is strongly affected by the transfer integrals between O and La (Nd) ions, presumably due to the difference between the ionic radii of La and Nd ions, and induces a phase transition from FM to AF through replacement of La ions with Nd ions. The interaction between Cu spins on ab planes is rather subtle due to the complex bonding between Cu ions via O and La ions. Competing FM and AF interactions, however, will be shown to occur even for the interaction on ab planes.

422-cuprates show a tetragonal lattice structure, and the tetragonality c/a=0.857 and 0.869 for La422 and Nd422, respectively. The lattice structures along the (001) and (110) directions are shown in Figs. 1(a) and 1(b), respectively. Here, the lattice structure is simplified in such a way that the O-O length of the square formed by Cu and four O ions is $0.388a$, and that formed by La and four O ions is $0.513a$, which makes the angle of O1-La-O2 bonds $\pi/2$ and the tetragonality 0.901.

We see that the Cu-O squares form a ladderlike structure along the c axis and that the Cu ions located at the center of the Cu-O square are connected via two types of paths, namely Cu1-O1-La-O2-Cu2 and Cu1-O1-O2-Cu2. Each type has two paths for the ladderlike structure. The Cu3 and O3 ions also form a ladderlike structure, which lies on a plane perpendicular to the plane of the Cu1-O1-O2-Cu2 ladder structure.

The connection of Cu1 and Cu3 on the ab plane is rather complex. A bird's eye view of the two ladderlike structures is shown in Fig. 1(c). We see that Cu1 and Cu3 are connected via O1–La–O3 bonds. Since the bonds O1–La–O3 and La–O3–Cu3 do not form right angles, the overlap between the atomic wave functions is complex. We also find that there are four possible paths for connecting Cu1 and Cu3 ions.

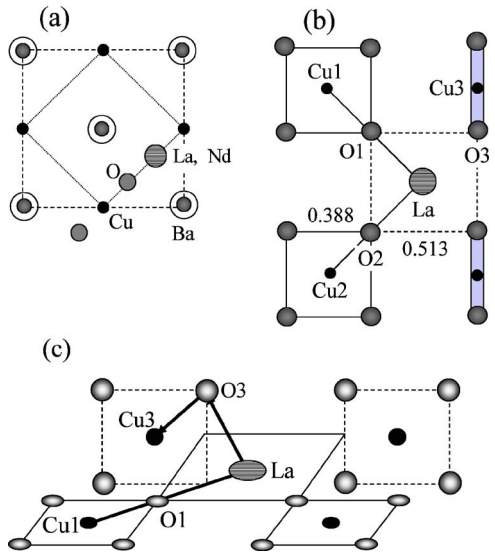

FIG. 1. (Color online) Lattice structure of La422, seen from (a) the c axis, (b) the (101) direction, and (c) bird's eye view.

$S=1/2$ spins on Cu ions may interact with each other via the superexchange process along the paths mentioned above. In order to evaluate the interaction, the overlaps between atomic wave functions should be examined. Figure 2 shows how the $d_{x^2-y^2}$ orbitals of Cu1 and Cu2 overlap with O p orbitals and La d orbitals along the c axis. Here, we take the x and y axes as shown in the figure and ignore the f orbitals of La. The $d_{x^2-y^2}$ orbitals of Cu ions hybridize strongly with p_σ orbitals of O ions (p_x orbital on O1 and p_y orbital on O2). The p_π orbital of O ions (p_y orbital on O1 and p_x orbital on O2), however, should not be neglected. Both orbitals play an important role in the competitive interactions between Cu1 and Cu2 spins; one is antiferromagnetic, while the other is ferromagnetic, as described below.

(1) The Cu1-O1-La-O2-Cu1 path gives an AF superexchange interaction: Because of the strong hybridization between the p_σ orbital and $d_{x^2-y^2}$ orbitals on Cu and La ions, a virtual process where two electrons with opposite spins reside on La ions is possible. This process induces the usual AF superexchange interaction.

(2) The Cu1-O1-O2-Cu2 path gives an FM superexchange interaction: Let us consider the case which Cu1 and Cu2 have up-spin electrons. Then, down-spin electrons may move from the p_x orbital of O1 to the Cu1 $d_{x^2-y^2}$ orbital, and from

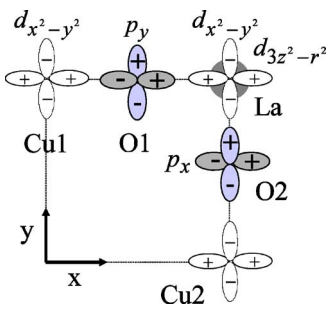

FIG. 2. (Color online) Overlap between atomic orbitals of Cu, O, and La ions.

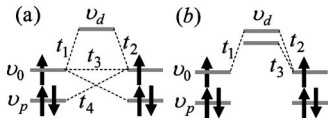

FIG. 3. Simplified model for interaction (a) along the c axis and (b) on the ab plane.

the p_y orbital of O2 to the Cu2 $d_{x^2-y^2}$ orbital. Because of the finite overlap between the p_x and p_y orbitals of O1 and O2, the down-spin electron in the p_x orbital of O2 may move to the vacant state of the p_x orbital of O1, and similarly the down-spin electron in the p_y orbital of O1 may move to the vacant p_y orbital of O2. Either case leaves two electrons with the same spin in p_x and p_y orbitals of O1 or O2. When Cu1 and Cu2 have electrons with opposite spins at the beginning, the electrons left in O ions in this process have opposite spins. Because of Hund's rule coupling of O ions, a parallel alignment of Cu spins is favored. The result agrees with the well-known Goodenough-Kanamori rule.[8,9] In this mechanism, the Hund's rule coupling between two electrons is caused by the overlap between two p_x (or two p_y) orbitals on O1 and O2 ions. Because the spins of two Cu ions interact via two oxygen ions, the resulting FM interaction would be much smaller than that in the other transition metal oxides. Consequently, the Curie temperature of La-R422 can be of a few Kelvin as observed.[6]

We construct a simple model to calculate the effective interaction between Cu spins on the basis of the electronic states in La422. As for the Cu spins along the c-axis, Cu-$d_{x^2-y^2}$, O-p_x, p_y, and La-$d_{x^2-y^2}, d_{3z^2-r^2}$ are necessary. But, we simplify the electronic state further by ignoring the La -$d_{3z^2-r^2}$ orbital and noting that the Cu-O bond forms $d^{10}\underline{L}$ hybrid states. Because the unpaired spin of the Cu-O hybrid state resides on the highest energy level (antibonding state), we take only the antibonding state into consideration, instead of the Cu-$d_{x^2-y^2}$ and O-$p\sigma$ orbitals. The energy levels of the simplified model are schematized in Fig. 3(a), where υ_d, υ_0, and υ_p are the energy levels of La-$d_{x^2-y^2}$, antibonding orbital of the hybrid state, and O-p_π orbital, respectively, and t_1, t_2, t_3, and t_4 are the hopping integrals between these orbitals. The ratios of these hopping integrals are determined from those estimated by using Harrison's table.

The overlap of atomic orbitals between Cu ions on ab planes is complex. The p_σ orbitals on O ions hybridize with $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ on La ions, but not d_{xy}, d_{yz}, and d_{zx} orbitals. However, all p orbitals on the O3 ion hybridize with all d orbitals of La because the bond angle is not $\pi/2$. In order to construct a simple model for Cu1-O1-La-O3-Cu3 bonds, we take into account their characteristic features, namely that all d orbitals on La connect with O3 p orbitals, while only the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals on La connect with O1 p orbitals, and prepare two orbitals on La ions. The antibonding state of the Cu-O1 hybrid connects with only one orbital on La, while the antibonding state of the Cu-O3 hybrid connects with both of them. Figure 3(b) shows the simple model assumed here. There might be crystal field splitting between these orbitals on La ions, which was ignored in the present model. The overlap integrals between O ions are also ignored. In the present model, three overlap integrals, t_1, t_2,

and t_3, are introduced as shown in Fig. 3(b). Although the orbitals denoted by the energy level υ_p do not play any role in determining the type of the interaction, they are included in the model since they may affect the magnitude of the interaction via the Coulomb interaction.

As for the Coulomb interaction, we consider the interactions acting on electrons on the same site and introduce the intraorbital Coulomb interaction U, the interorbital Coulomb interaction V, and the interorbital exchange interaction J. We ignore their dependence on atomic species.

The effective interaction J_{eff} can be expressed in terms of the difference between the ground state energies of the FM and AF state of the small clusters shown in Fig. 3:

$$J_{eff} = E_{AF} - E_F,$$

which will give an FM interaction when the sign is positive and an AF interaction when it is negative. The ground state energy is calculated for a given number of up- and down-spin electrons in the cluster. The FM spin state is obtained for four up- and two down-spin electrons, as shown in Fig. 3(a). The AF spin configuration will be obtained for three up- and three down-spin electrons. The total number of all spin and charge configurations is 100 for the AF state and 50 for the FM state for the model shown in Fig. 3(a), which will be reduced to 50 and 23, respectively, when we restrict the number of electrons of the two υ_p levels to 3 or 4. In the model in Fig. 3(b), the electrons at the energy level υ_p have no bearing on the sign of J_{eff}, but are included to compare the absolute value with that for the model in Fig. 3(a). The total number of the spin and charge configurations is 16 and 6 for the AF and FM states, respectively, for the model in Fig. 3(b).

Now we estimate the overlap integrals between O-p orbitals and d orbitals of Cu and La ions along the c axis using the Slater-Koster formalism with Harrison's table of band parameters.[10] They are $\sqrt{3}/2pd\sigma = 3.10$ eV for Cu-$d_{x^2-y^2}$-O-p_x, $(1/2)(pp\sigma' - pp\pi') = 1.27$ eV for O-p_x–O-p_y, $(1/2)(pp\sigma' + pp\pi') = 0.75$ eV for O-p_x–O-p_x, $\sqrt{3}/2pd\sigma'' = 4.23$ eV for O-p_x–La-$d_{x^2-y^2}$, and $-(1/2)pd\sigma'' = -2.45$ eV for O-p_x–La-$d_{3z^2-r^2}$. Since these values may be too large, we henceforth keep the ratio of these overlap integrals and make the absolute value a parameter that might be determined from other information.

By taking these values into consideration, the parameter values for model 3(a) may be given as follows: $t_1 = \alpha t$, $t_2 = -t_1$, $t_3 = (0.75/4.23)t \sim 0.2t$, and $t_4 = -(1.27/4.23)t \sim -0.3t$. We assume that $U = 5t$, $V = 4t$, and $J = t$ for the Coulomb interaction. We have adopted the ratio between U, V, and J referring to previous works.[11] The ratio between U and t, however, is rather arbitrary, but we have found no qualitative change in the results for $U = 10t$. In the following, values of α and the energy level υ_d of La ions are dealt with adjustable parameters. As for the values of t_3 and t_4, two sets of parameter values will be adopted, $(t_3, t_4) = (0.2t, -0.3t)$ and $(0.1t, -0.4t)$. The overlap integral t_3 enhances the AF interaction via O ions, while t_4 enhances Hund's rule coupling. Thus the latter parameter set is favorable for FM.

The parameter values for model 3(b) are estimated similarly to be $t_1 \equiv t$, $t_2 \sim 0.3t$, and $t_3 \sim 0.7t$. In the numerical calculation, we take υ_d and t_2 to be adjustable parameters, and assume $t_3 = t$ for simplicity. We see that FM is favored for smaller values of t_2 and larger values of t_3. The values of the Coulomb interaction are the same with those used for model 3(a).

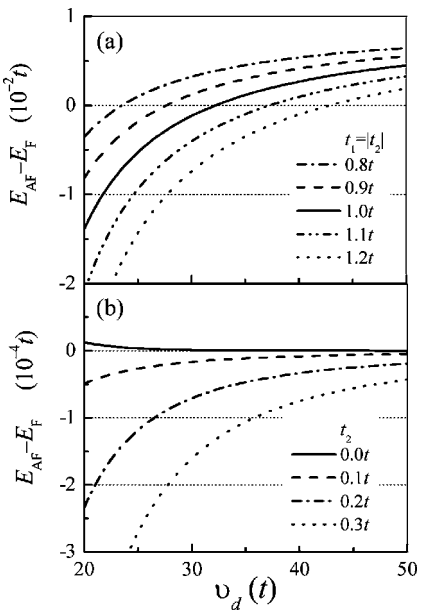

FIG. 4. Calculated results of the effective interaction (a) along the c axis and (b) on the ab plane.

Figure 4(a) shows the calculated results of $J_{eff} = E_{AF} - E_F$ along the c axis as functions of υ_d for various values of α (0.8–1.2). Here, we have used the set $(t_3, t_4) = (0.1t, -0.4t)$. With increasing υ_d, the AF superexchange interaction via La becomes weak, while the FM interaction via O ions is unchanged and thus exceeds the AF superexchange interaction. By contrast, with decreasing υ_d, the AF interaction becomes favorable. With further decrease in υ_d, the FM and AF spin configurations may no longer be well-defined since some spins reside on the La level. Such an unfavorable state occurs for $\upsilon_d \lesssim 15t$. The AF interaction is also favorable for large values of α, since the hopping integral between La and O levels increases with increasing α.

Figure 4(b) shows the calculated results of $J_{eff} = E_{AF} - E_F$ on the ab plane as functions of υ_d for various values of t_2. When $t_2 = 0$, J_{eff} is slightly positive but nearly independent of υ_d because $J_{eff}^F \sim t^2/(\upsilon_d + V - J)$ and $J_{eff}^{AF} \sim t^2/(\upsilon_d + V)$ with $\upsilon_d \gg V$. With increasing t_2, the AF interaction exceeds the FM interaction.

The calculated results shown in Fig. 4 indicate that the FM interaction changes to an AF interaction with increasing hopping integrals between La and O ions at suitable values of υ_d. The interaction along the c axis may also change with decreasing υ_d at fixed hopping integral values. The competition between the AF superexchange interaction and Hund's rule coupling is responsible for the change in the interaction. The magnetic phase transition observed for (La-Nd)422 may thus be explained by the simple mechanism of the competition between two types of interaction.

In transition metal cuprates, $t = 0.1$ to 0.2 eV. Thus the

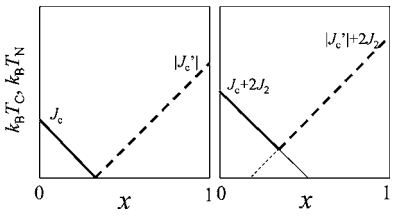

FIG. 5. Magnetic phase diagram obtained by the mean-field approximation for (a) $J_2=0$ and (b) $J_2\neq 0$.

small change in the hopping integrals, e.g., $t_1=t_2=1.0t \rightarrow 1.0t\pm 0.1t$ changes J_{eff} (along the c axis) by ± 0.3 to ± 0.6 meV, which is the right order of magnitude given the observed Curie and Neel temperatures. The energy level of v_d is higher than that of v_0 by a few eV, and v_p is assumed to be lower than v_0 by $0.5t$. These values may not be unreasonable, however, a more sophisticated model needs to be adopted to get quantitative estimates of these values. Our results suggest that the interaction changes from FM to AF with increasing hopping integrals between La and O ions. Because the ionic radius of La is larger than that of Nd, the simple argument that the hopping integral is larger for larger ions may break down. One should, however, take into account the anisotropic distribution of the wave functions of La and Nd ions, as expected by the first-principles calculation.[7]

Ku *et al.*[7] performed a detailed calculation of the effective interaction using first principles and showed that the interaction along the c axis is FM in La422, but AF in Nd422, and that the NN interaction on the ab plane is small. Our results agree with these first-principles results. The most interesting result obtained by the first-principles calculation is that the second NN interaction along (101) is always FM and rather large in magnitude. The present analysis, however, may not yield such a large value for the second NN FM interactions.

FM interaction between second NN spins may give rise to a first-order transition between FM and AF states. Let the interaction along the c axis be J_c and J_c' for La422 and Nd422, respectively, and the interaction between second NN spins J_2. Ignoring the ab plane interactions, which are very small, we obtain the FM and AF interactions along the c axis:

$$J_{FM}=4[xJ_c'+(1-x)J_c+2J_2],$$

$$J_{AF}=-4[xJ_c'+(1-x)J_c-2J_2],$$

respectively, for $(La_{1-x}Nd_x)422$. Phase diagrams calculated by the mean-field approximation are shown in Fig. 5 for $J_2=0$ and $\neq 0$. When $J_2\neq 0$, a first-order transition may occur between FM and AF phases, as shown in Fig. 5(b). The second NN interaction seems to be necessary for explaining the magnetic phase transition in (La-Nd)422. Further confirmation that the second NN interaction is nonzero is desirable.

In conclusion, we have proposed a simple picture for the transition from ferromagnetic to antiferromagnetic state in La-Nd422 systems by replacing La ions with Nd ions. There are two competing mechanisms for mediating the interaction between Cu spins: the standard AF superexchange interaction via La ions and the FM interaction due to Hund's rule coupling of O ions. It has been shown that the ferromagnetic interaction between Cu spins becomes antiferromagnetic with increasing overlap between the wave functions of oxygen and La(Nd) ions.

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[1] F. Mizuno, H. Masuda, I. Hirabayashi, S. Tanaka, M. Hasegawa, and U. Mizutani, Nature (London) **345**, 788 (1990).
[2] H. Tasaki, Phys. Rev. Lett. **69**, 1608 (1992).
[3] V. Eyert, K.-H. Hock, and P. S. Riseborough, Europhys. Lett. **31**, 385 (1995).
[4] S. Feldkemper, W. Weber, J. Schulenburg, and J. Richter, Phys. Rev. B **52**, 313 (1995).
[5] M. W. Pieper, E.-G. Gaspary, P. Adelmann, and G. Roth, J. Magn. Magn. Mater. **135**, 319 (1994).
[6] H. Nozaki, H. Ikuta, Y. Yamada, A. Matsushita, H. Takahashi, I. Hirabayashi, and U. Mizutani, Phys. Rev. B **62**, 9555 (2000).
[7] W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. **89**, 167204 (2002).
[8] J. B. Goodenough, J. Phys. Chem. Solids **6**, 287 (1958).
[9] J. Kanamori, J. Phys. Chem. Solids **10**, 87 (1959).
[10] W. A. Harrison, *Electronic Structure and the Properties of Solids* (W. H. Freeman and Company, San Francisco, (1980).
[11] See, e.g., B. H. Brandow, Adv. Phys. **26**, 651 (1977).