Ferromagnetic coupling in nonmetallic Cu^{2+} compounds

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Analytical and numerical studies of ferromagnetic coupling in nonmetallic Cu^{2+} compounds are presented. In addition to the well-known Goodenough-Kanamori-Anderson (GKA) mechanism, further possibilities for ferromagnetic interactions in insulators are investigated, using the concept of interference between inequivalent superexchange paths. The basic idea is discussed by considering Hubbard-type Hamiltonians for a simple four-site cluster with two magnetic ions and two inequivalent ligands. Here, destructive interference of hopping paths may completely suppress the antiferromagnetic coupling between the ground-state orbitals at the magnetic sites. Then, in a specific range of model parameters, ferromagnetic coupling is possible involving only ground-state orbitals. Using corresponding model Hamiltonians for realistic clusters, the range of ferromagnetic coupling in the nonmetallic ferromagnets K_2CuF_4 and La_2BaCuO_5 is investigated, both by perturbation theory and by exact diagonalization calculations. For the two compounds the in-plane coupling is ferromagnetic in accordance with the GKA rules. However, the ferromagnetic interplanar coupling is caused by interference effects.

I. INTRODUCTION

Magnetic interactions between transition metal ions in nonmetallic compounds are usually described by superexchange via intermediate ligands.[1] The use of other methods, such as spin density functional theory, is rather controversial for these materials.[2]

For most compounds, the exchange of spins leads to an antiferromagnetic coupling. Yet, there also exist ferromagnetic insulators. As pointed out by Goodenough, Kanamori, and Anderson (GKA), such ferromagnetism will occur by exchange coupling of ground- and excited-state orbitals of the magnetic ions, in the case that these orbitals exhibit appropriate symmetries.[1,3] In particular, the GKA rules explain why ferromagnetic coupling is often concomitant with the cooperative Jahn-Teller effect.[4] As an example, the Jahn-Teller compound K_2CuF_4 shows in-plane ferromagnetic coupling in accordance with the GKA rules.

However, the coupling between CuF_2 planes in K_2CuF_4 is also ferromagnetic, which *cannot* be explained by the "classical" picture of GKA. In addition, a ferromagnetic cuprate insulator La_2BaCuO_5 has been synthesized recently,[5] where the GKA rules also cannot be applied in a simple manner.

In this paper we investigate further possibilities for ferromagnetic coupling using the concept of interference between inequivalent superexchange paths. Interference between hopping paths has been discussed in the literature on magnetism, though given diverse names.[6,7] Nevertheless, we think that some important aspects of this concept have been ignored so far.

Our paper deals with analytical and numerical studies of Hubbard-type models applied to small clusters of magnetic and ligand atoms. The numerical calculations of the ground state and of low-lying excitations have been carried out by standard Lanczos technique.[8] As the analytical and numerical studies have been complementary for the main part of this paper, we will not separate the presentation of the results in the respective sections.

The paper is organized as follows. In Sec. II we will briefly discuss the origin for ferromagnetism as proposed by GKA. Then, a simple four-site model of two magnetic and two inequivalent ligand atoms will be considered, which allows for ferromagnetic coupling of the two magnetic ions even without any excited state orbitals at the magnetic sites. In Sec. III we will present our studies of ferromagnetic coupling in K_2CuF_4 and La_2BaCuO_5, based on small clusters containing two Cu^{2+} ions. Conclusions are given in Sec. IV. The model parameters employed for the calculations are listed in the Appendix. We note that the hole picture is used throughout the paper.

II. COUPLING OF SPINS

The starting point for the description of spin coupling by superexchange is a Hubbard-type Hamiltonian

$$
\begin{aligned}
H=&\sum_{\substack{i\\ \alpha,\sigma}}\epsilon_i^{\alpha}\hat{n}_{\sigma}^{\alpha}(i)+\sum_{j,\sigma}\epsilon_j\hat{n}_{\sigma}(j)\\
&+\sum_{\substack{i,j\\ \alpha,\sigma}}[t_j^{i\alpha}c_{\alpha\sigma}^{\dagger}(i)c_{\sigma}(j)+\text{H.c.}]\\
&+\frac{1}{2}\sum_{\substack{i\\ \alpha,\beta\\ \sigma,\sigma'}}U_{\alpha\beta}c_{\alpha\sigma}^{\dagger}(i)c_{\beta\sigma'}^{\dagger}(i)c_{\beta\sigma'}(i)c_{\alpha\sigma}(i)\\
&-\frac{1}{2}\sum_{\substack{i\\ \alpha\neq\beta\\ \sigma,\sigma'}}J_{\alpha\beta}c_{\alpha\sigma}^{\dagger}(i)c_{\beta\sigma'}^{\dagger}(i)c_{\alpha\sigma'}(i)c_{\beta\sigma}(i)\ . \qquad (1)
\end{aligned}
$$

Here $t_j^{i\alpha}$ is the hopping from the jth ligand (only one orbital assumed) to the αth orbital of the magnetic ion i. ϵ_i^α is the energy of orbital α at site i, ϵ_j the ligand energy. $U_{\alpha\beta}$ and $J_{\alpha\beta}$ represent the on-site Coulomb and exchange interactions at the magnetic sites. Usually, $U_{\alpha\alpha} > U_{\alpha\beta}$ leads to the first Hund's rule (maximum orbital momentum) and $J_{\alpha\beta} < 0$ to the second Hund's rule (maximum spin). Here we take for simplicity $U_{\alpha\alpha} = U_{\alpha\beta} = U$ and $J_{\alpha\beta} = J_H < 0$.

The multiband Hubbard Hamiltonian (1) is invariant under spin rotation and commutes with the z component S^z of the total spin $\mathbf{S}$ and also with the square of the total spin $\mathbf{S}^2$. These commutation rules allow us to restrict the numerical calculations to the subspace of $S^z = 0$. We note that the Heisenberg model exhibits the same commutation rules.

A. Classical ferromagnetic coupling

The simplest case is that of two magnetic sites M_1, M_2, linked by one empty ligand L. M_1 and M_2 are assumed to have two orbitals and to be occupied by one hole per site. Treating the Hamiltonian of Eq. (1) in fourth-order perturbation theory, we obtain an effective spin-$\frac{1}{2}$ Hamiltonian

$$H_{\text{eff}} = J\mathbf{S}_1 \cdot \mathbf{S}_2 \ , \tag{2}$$

where

$$\begin{aligned} \hat{n}_{i\uparrow,\downarrow} &= \frac{1}{2} \pm S_i^z \ , \\ c_{i\uparrow}^\dagger c_{i\downarrow} &= S_i^+ \ , \\ c_{i\downarrow}^\dagger c_{i\uparrow} &= S_i^- \ . \end{aligned} \tag{3}$$

There are two components of J; these are $J_{gg} > 0$ (antiferromagnetic coupling) and $J_{ge} < 0$ (ferromagnetic coupling). The first, J_{gg}, arises from hopping of spins between the ground-state orbitals (see Fig. 1) and is given by

$$J_{gg} = 2\left[\frac{1}{U} + \frac{1}{\epsilon_L}\right]\tilde{t}^2 \ , \tag{4}$$

where

$$\tilde{t} = \frac{t_{M_1 L} t_{L M_2}}{\epsilon_L} \ . \tag{5}$$

the other, J_{ge}, is due to hopping from one ground state to the neighboring excited state involving exchange (Hund's rule) coupling to the ground state (see Fig. 1). Usually, assuming $t^\alpha \approx t^\beta$,

$$J_{ge} \approx -\frac{|J_H|}{U} J_{gg} \approx -(0.1,\ldots,0.2) J_{gg} \ . \tag{6}$$

If, however, the symmetries of the ground states do not allow (or strongly reduce) the hopping from one to the other site while hopping to the excited state is of normal value, $|J_{ge}|$ may be larger than J_{gg} and the interaction is ferromagnetic.

This mechanism is the reason for ferromagnetism in the CuF_2 planes of K_2CuF_4 where the ground-state orbitals order in such a way that neighbor orbitals are orthogonal to each other.[9,10] This is caused by the Jahn-Teller effect at the Cu sites and was discussed by Kugel and Khomskii.[11]

B. Four-site model

To describe the effect of exchanging spins between magnetic ions via more than one hopping path, we use a four-site model, as is shown in Fig. 2. A similar model has been discussed in the work of Eremin and Rakitin.[7]

We first treat the case of only one hole orbital per magnetic site. The energies of the ligand atoms are ϵ_1 and ϵ_2, respectively. $\epsilon_1 > \epsilon_2 > 0$ is assumed, so that the ligand hole states are empty. In fourth-order perturbation theory the exchange coupling is given by

$$J_{gg} = 2\left[\frac{(t+t')^2}{U} + \frac{t^2}{\epsilon_1} + \frac{t'^2}{\epsilon_2} + \left[\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2}\right] tt'\right] \ . \tag{7}$$

Here $t = t_1 t_2 / \epsilon_1, t' = t_3 t_4 / \epsilon_2$. The first term on the right-hand side (rhs) of Eq. (7) represents virtual hopping of one M spin via two ligand paths to the other M site. The second and third terms represent hopping of both spins to one or the other of the ligand sites. The fourth term represents the ring exchange. The first three terms are positive semidefinite, while the sign of the ring exchange term depends on the relative sign of t and t'. Its inclusion can lead to $J_{gg} < 0$, caused by a specific interference of the hopping paths. This can be seen more easily putting

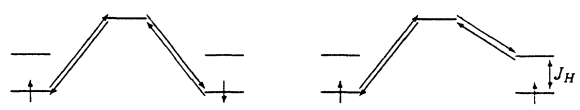

FIG. 1. Spin interaction by superexchange. Left figure depicts the antiferromagnetic interaction, right figure the ferromagnetic one. The double arrow indicates the on-site exchange J_H underlying the second Hund's rule.

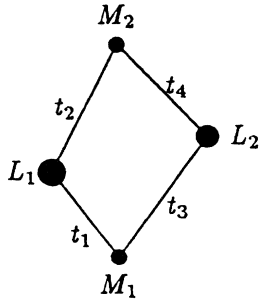

FIG. 2. Four-site model. The magnetic sites M_i are occupied by one hole and may have one or more orbitals. The (empty) ligand ions L_j are inequivalent, i.e., $\epsilon_{L_1} \neq \epsilon_{L_2}$. All hoppings t_k may be different.

$t+t'=\Delta$ and $t-t'=\delta$, which leads to

$$J_{gg}=\left[\frac{2}{U}+\frac{1}{\epsilon_1}+\frac{1}{\epsilon_2}\right]\Delta^2+\Delta\delta\left[\frac{1}{\epsilon_1}-\frac{1}{\epsilon_2}\right]. \tag{8}$$

Then, in the range of

$$0<\Delta<U\delta\frac{\epsilon_1-\epsilon_2}{2\epsilon_1\epsilon_2+U(\epsilon_1+\epsilon_2)}, \tag{9}$$

we have $J_{gg}<0$, whereby we have chosen $\delta>0$. As a consequence, a ferromagnetic interaction can be achieved without involving any excited states, i.e., without Hund's rule coupling.

The smallest J is given by

$$J_{gg}^{\min}=-\frac{\delta^2 U}{4\epsilon_1\epsilon_2}\frac{(\epsilon_1-\epsilon_2)^2}{2\epsilon_1\epsilon_2+U(\epsilon_1+\epsilon_2)}. \tag{10}$$

For equivalent ligands ($\epsilon_1=\epsilon_2$), J_{gg} is always positive. Consequently nonequivalent ligands are essential for this type of ferromagnetic interaction. We note that our result differs in this respect from the one reported in Ref. 7.

Comparing $|J_{gg}^{\min}|$ with a "typical" value of J_{gg}, given by $\delta=0,\epsilon_1\approx\epsilon_2$, leads to

$$\frac{|J_{gg}^{\min}|}{J_{gg}^{\text{typ}}}\approx\left[\frac{\epsilon_1-\epsilon_2}{4\epsilon_1}\right]^2\ll 1. \tag{11}$$

The ferromagnetic coupling can be interpreted as follows. For two parallel spins, only ring exchange is possible (see Ref. 12), where the spins never meet on the same site. On the other hand, antiparallel spins may suffer a destructive interference because additional exchange paths exist. Then, for antiparallel spins the contributions of different processes (almost) cancel each other in the range of Δ given above. As a result, the ferromagnetic state has lower energy than the antiferromagnetic one.

In the case of two orbitals at the magnetic site we have a much more complicated situation. There are eight different hopping integrals $t_j^{i\alpha}(\alpha=g,e;j=1,2;i=1,2)$. The spins can hop from one ground state to the other (J_{gg}) or to the excited orbital (J_{ge}). This leads to the following possibilities.

(a) $J_{gg}>0, J_{ge}<0, J_{gg}>|J_{ge}|$. This is the "normal" situation and leads to antiferromagnetic coupling.

(b) $J_{gg}\geq 0, J_{ge}<0, J_{gg}<|J_{ge}|$. Here J_{gg} has been reduced either by symmetry according to the GKA rules or by interference. Then the interaction is ferromagnetic.

(c) $J_{gg}<0, J_{ge}<0$. This case is only possible involving interference terms.

In addition to the analytical calculation we present exact diagonalization results for the four-site model. Figure 3 shows the region of ferromagnetic ground state in the t_{ML_1}-t_{ML_2} plane ($t_{ML_1}=t_1=t_2$ and $t_{ML_2}=t_3=-t_4$) for the four-site model with two spins and the parameters $U_M=8$, $U_L=0$, $\epsilon_M=0$, $\epsilon_1=4$, and $\epsilon_2=3$. We find good agreement between perturbation theory and numerical results, even for a relatively large hopping integral t. The ferromagnetic state has the lowest energy in a small area near the line $t_{ML_1}=t_{ML_2}$. Of course, additional higher-energy bands and Hund's rule coupling would enlarge this area.

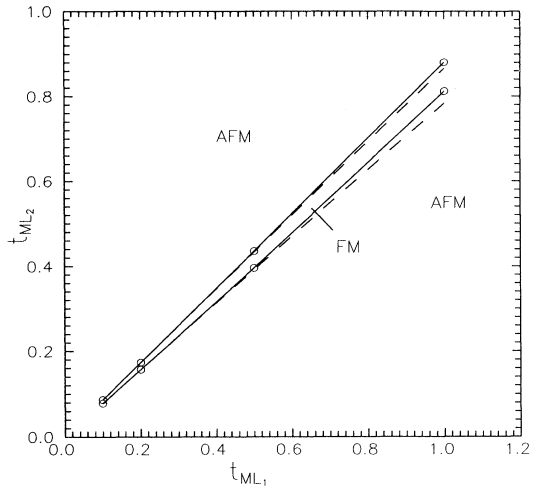

FIG. 3. Ground-state phase diagram for the four-site model (Fig. 2) with two spins, for the parameters $\epsilon_{L_1}=\epsilon_1=4$ eV, $\epsilon_{L_2}=3$ eV, $U=8$ eV, $t_{ML_1}=t_1=t_2$, and $t_{ML_2}=t_3=-t_4$. (Solid lines, exact diagonalization; dashed lines, perturbation theory).

III. FERROMAGNETIC INSULATING Cu^{2+} COMPOUNDS

A. K_2CuF_4

K_2CuF_4 has a crystal structure based on the K_2NiF_4 type (see Fig. 4), which is also the structure of the well-known cuprate La_2CuO_4. The unit cell is body-centered tetragonal with $a(=x)=b(=y)=4.1475$ Å and $c(=z)=12.734$ Å.[13] The shortest separation of Cu atoms in adjacent ab planes is 7.0 Å.

The Cu^{2+} ions are surrounded by octahedra of F^- ions which share corners in the ab plane. They are alternatively elongated (compressed) in the $a(b)$ and $b(a)$ directions. This antiferrodistortive order has been attributed to the cooperative Jahn-Teller effect,[11] so that the Cu^{2+} ions exhibit alternating occupation of z^2-x^2 and z^2-y^2 hole states, which are orthogonal to each other. As a consequence, ferromagnetic coupling in the ab plane results.[11]

K_2CuF_4 is a quasi-two-dimensional ferromagnet with a Curie temperature of $T_C=6.25$ K. The direction of magnetization is parallel to the CuF_2 planes.[9,14,15] Therefore, the ferromagnetic coupling of planes through dipole-dipole interaction can be excluded, because this would lead to an antiferromagnetic order of adjacent planes. We can also exclude direct (Coulomb) exchange because of the large separation of the Cu^{2+} ions.

Recently, spin density functional calculations for K_2CuF_4 have been reported.[16] Itinerant ferromagnetism has been proposed, with an exchange (or distortion) induced splitting in the relevant bands of ≈ 0.5 eV, leading to an energy gap of order 0.2 eV between the highest occupied and lowest unoccupied bands. In our opinion the

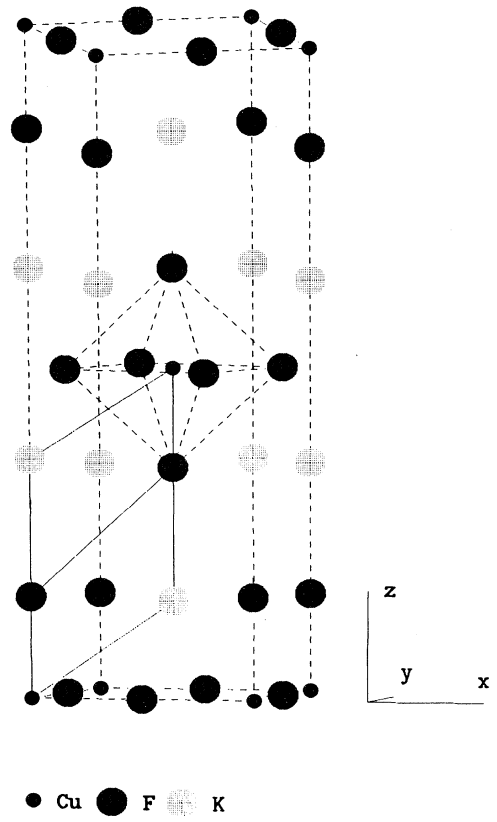

FIG. 4. Crystal structure of K_2CuF_4. The solid lines indicate the relevant cluster for interplanar spin exchange (see also Fig. 5).

single-particle band picture is inappropriate for the insulating Cu^{2+} compounds, as manifest in the failure to describe antiferromagnetism in La_2CuO_4.[17] Furthermore, band ferromagnetism resulting in a fundamental gap of ≈ 0.2 eV might be insufficient for the description of an optically transparent insulator with ≈ 5 eV energy gap. We also note that the degree of orbital order at the Cu site has not been investigated, which would be a sensitive test of the results of Ref. 16 as *complete* orbital order is found experimentally.[9,10]

In view of the above discussion we think that only kinetic exchange is left as an interplanar coupling process.

For our calculations the energy of the Cu ground state is set at zero. The excited hole states are chosen to lie at 0.5 eV for the second e_g state and at about 1.5 eV for the t_{2g} states. We note that the experimental values of the d-d excitations differ to some extent in the literature.[9,18,19] At the F sites we only take into account p_σ orbitals, with their energy at about 4 eV. The K hole states are of s-type and are doubly occupied. Their energy is put at ≈ -4 eV. For details see the Appendix. All other orbitals probably lie out of the relevant energy range.

The spin interaction of adjacent planes in K_2CuF_4 can be treated in a similar way as in our four-site model. The relevant cluster is shown in Fig. 5. The Cu^{2+} ions are coupled via a complex of ligand atoms, containing two F^- and two K^+ ions. There are three hopping paths, two of them are different (Fig. 5). One is $Cu_1 \rightarrow F_1 \rightarrow F_2 \rightarrow Cu_2$, the other $Cu_1 \rightarrow K_1 \rightarrow F_2 \rightarrow Cu_2$ (equivalent to the $Cu_1 \rightarrow F_1 \rightarrow K_2 \rightarrow Cu_2$ path). The coupling via two intermediate ligands leads to spin-spin interaction in sixth-order perturbation theory. The coupling constant J_{gg} is calculated by summing over all possibilities of exchanging the Cu spins in this order. Yet, the doubly occupied K hole states lead to a great variety of hopping paths and thus to a large number of sixth-order terms.

To simplify the analytical calculation, the K sites also are treated as empty, but they remain inequivalent to the F sites. The s-type orbital is kept. In addition, only the ground-state orbitals at the Cu ions are considered. So we work with a cluster of six sites containing two holes located at the Cu sites with one orbital at the Cu sites. In a condensed notation we will indicate this by $(6+0)S2H$, where the excited Cu orbitals of one Cu ion are noted as the second part of the sum. The exchange constant of this simplified model is given by

$$J_{gg}=\frac{2}{\epsilon_F^4}\left[\frac{1}{U}+\frac{1}{\epsilon_F}\right]\left[t_{CuF}^2 t_{FF}+\frac{2\epsilon_F}{\epsilon_K}t_{CuK}t_{KF}t_{CuF}\right]^2 + \frac{8[t_{CuK}t_{KF}t_{CuF}]^2}{\epsilon_F^2\epsilon_K^3} + \frac{t_{FF}}{2\epsilon_F(\epsilon_F-t_{FF})^3}\left[t_{CuF}^2+\frac{4}{\epsilon_K}t_{CuK}t_{KF}t_{CuF}\right]^2 - \frac{t_{FF}}{2\epsilon_F(\epsilon_F+t_{FF})^3}\left[t_{CuF}^2-\frac{4}{\epsilon_K}t_{CuK}t_{KF}t_{CuF}\right]^2 . \quad (12)$$

Destructive interference is only possible for a finite contribution from the F-F path (the two K-F paths interfere constructively). Thus it is advantageous to use t_{FF} as the only variable parameter. Fixing the others to the values given in Tables V and VII, we obtain

$$J_{gg}=0.225t_{FF}^2-2.653\times10^{-3}t_{FF}+9.38\times10^{-5}[\text{eV}] . \quad (13)$$

The minimal J is found for

$$t_{FF}=0.59 \text{ eV} , \quad J^{\min}=1.6\times10^{-5} \text{ eV} . \quad (14)$$

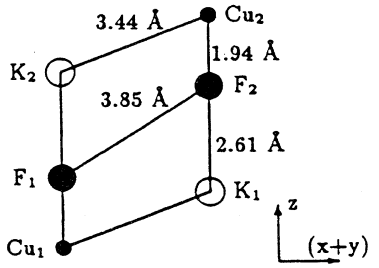

FIG. 5. The relevant cluster for interplanar spin exchange in K_2CuF_4; also given are the atomic separations.

There are four excited Cu states, $m_1,\ldots,m_4$. They all may contribute to J_{ge}. Interference is possible only for the e_g orbital m_1, but not for the t_{2g} orbitals, m_2,m_3,m_4. The reason is that $t_{m_i,\mathrm{F}}$ is zero by symmetry for $i=2,\ldots,4$, so that the remaining two paths are equivalent. This means J_{gg} (and J_{g,m_1}) may be strongly reduced by interference, but $J_{g,m_{2,\ldots,4}}$ are not, and so ferromagnetism might win.

The complete model cluster contains six spins, as the doubly occupied K hole states are included. In our condensed notation it is indicated by $(6+m)S6H,m$ counts the excited Cu orbitals of one of the two (equivalent) Cu^{2+} ions. For this cluster we have performed a numerical analysis. The ground state was calculated in the Hilbert subspace $S^z=0$. Again we studied the energy of the low-lying levels in dependence on t_{FF}. Figure 6 shows the energies of the lowest two states as a function of t_{FF} with $J_H=-1$ and $U=8$ for the $(6+4)S6H$ cluster. The state with $\mathbf{S}^2=2$ is ferromagnetic; i.e., the total spin correlation between the two copper sites

$$\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle=\sum_{\alpha,\beta}\langle \mathbf{S}^{\alpha}_{\mathrm{Cu}_1}\mathbf{S}^{\beta}_{\mathrm{Cu}_2}\rangle \tag{15}$$

is larger than zero, and the state with $\mathbf{S}^2=0$ is antiferromagnetic, i.e., $\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle<0$. Ferromagnetic correlations are stable in the region -0.135 eV $\lesssim t_{\mathrm{FF}}\lesssim 0.015$ eV. The largest energy difference between the ferromagnetic and the antiferromagnetic state is found for $t_{\mathrm{FF}}\approx -0.06$ eV, which is close to the value given by our model parameters (see Table VII).

For the total occupation number of the Cu orbitals we find $\langle n_{\mathrm{Cu}}\rangle=\sum_\alpha\langle n^{\alpha}_{\mathrm{Cu}}\rangle=0.907$ in the ferromagnetic state. Of course, the occupation number of the lowest band gives the largest contribution to $\langle n_{\mathrm{Cu}}\rangle$ (see Table I). The total spin correlation $\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle$ is practically independent of t_{FF} in the range shown in Fig. 6 and is given by $\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle_{\mathrm{FM}}=0.204$ for the ferromagnetic states and

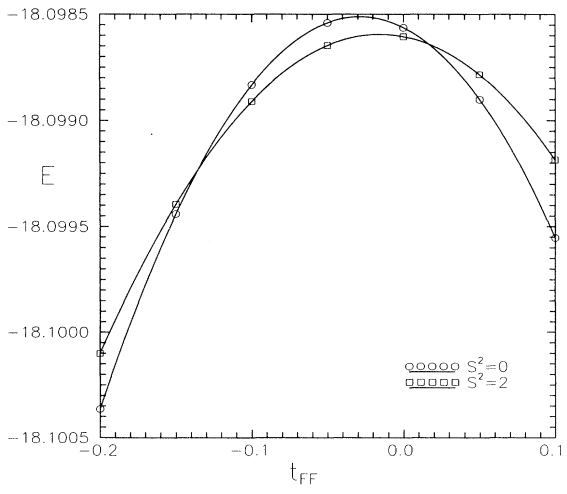

FIG. 6. Energy E as a function of t_{FF} for a K_2CuF_4 model with six spins and five orbitals per copper site.

TABLE I. Occupation number $\langle n_{\mathrm{Cu}^{\alpha}}\rangle$ of all copper orbitals α for $\mathbf{S}^2=2$ and $t_{\mathrm{FF}}=-0.05$ for the K_2CuF_4 model cluster with six spins.

	Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5
n_{Cu}	0.840 42	0.063 32	0.000 88	0.001 08	0.000 84

by $\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle_{\mathrm{AFM}}=-0.611$ for the antiferromagnetic one. The dominating contribution to $\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle$ comes for the lowest orbital as shown in Table II for the ferromagnetic state. If we scale the total spin correlation by the occupation numbers $\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle/\langle n_{\mathrm{Cu}}\rangle^2$ we find values which are close to those for the two-site Heisenberg model, where $\langle \mathbf{S}_1\mathbf{S}_2\rangle_{\mathrm{FM}}=0.25$ and $\langle \mathbf{S}_1\mathbf{S}_2\rangle_{\mathrm{AFM}}=-0.75$; see Fig. 7. Hence we can estimate the exchange integral between the Cu spins by

$$J(t_{\mathrm{FF}})=\frac{1}{2}\frac{E_{\mathrm{FM}}-E_{\mathrm{AFM}}}{\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle_{\mathrm{FM}}-\langle \mathbf{S}_{\mathrm{Cu}_1}\mathbf{S}_{\mathrm{Cu}_2}\rangle_{\mathrm{AFM}}}\ . \tag{16}$$

We find for J an almost quadratic dependence on t_{FF} (Fig. 8). The largest ferromagnetic exchange $|J|=6.67\times10^{-5}=0.77$ K is obtained for $t_{\mathrm{FF}}=-0.059$ eV. A simple mean-field estimate leads to $T_C\approx\frac{2}{3}JzS(S+1)\approx 3$ K which corresponds reasonably well to the experimental Curie temperature $T_C=6.25$ K of K_2CuF_4. ($z=8$ is the number of nearest neighbors in adjacent planes.)

To study the role of Hund's rule coupling we repeated the calculations and have stepwise reduced the number of excited Cu orbitals from four to zero or, alternatively, have diminished the exchange coupling J_H. Indeed, the antiferromagnetic state becomes more stable if the number of d levels is decreased. However, even for the case of only one Cu orbital or $J_H=0$, i.e., no on-site exchange possible, we find a small region of a stable ferromagnetic ground state. The results are illustrated in Fig. 9, where the region of the ferromagnetic ground state in the t_{FF}-J_H plane is shown.

For comparison with the analytical treatment we also performed a numerical calculation for the simplified model cluster $(6+0)S2H$. We found

$$J=0.0219t_{\mathrm{FF}}^2-2.643\times10^{-3}t_{\mathrm{FF}}+7.93\times10^{-5}[\mathrm{eV}]\ . \tag{17}$$

This is very similar to Eq. (13).

B. La_2BaCuO_5

La_2BaCuO_5 has a tetragonal unit cell with lattice parameters $a=b=6.8447(9)$ Å and $c=5.8637(8)$ Å (Fig. 10). The dominant structure element are CuO_4 squares with their normals lying either along the $x=\frac{1}{2}(a-b)$ or $y=\frac{1}{2}(a+b)$ direction. In the ab plane, neighboring squares lie perpendicular to each other with a first-nearest-neighbor (1NN) Cu-Cu distance of 4.84 Å. In the $c(=z)$ direction the squares have the same orienta-

TABLE II. Spin correlations between two copper sites for $S^2=2$ and $t_{FF}=-0.05$ (fm range) for the K_2CuF_4 model cluster with six spins, $(6+4)S6H$. Subscripts denote different sites.

$\langle S_{Cu_1} S_{Cu_2} \rangle$	Orbital 1	Orbital 2	Orbital 3	Orbital 4	Orbital 5
Orbital 1	0.176 101 4	0.013 217 6	0.000 014	0.000 017	0.000 013
Orbital 2	0.013 217 6	0.000 99	0.000 001 2	0.000 001 5	0.000 001 2
Orbital 3	0.000 014	0.000 001 2	0.000 000 0	0.000 000 0	0.000 000 0
Orbital 4	0.000 017	0.000 001 5	0.000 000 0	0.000 000 0	0.000 000 0
Orbital 5	0.000 013	0.000 001 2	0.000 000 0	0.000 000 0	0.000 000 0

tion (Fig. 11); the shortest Cu-Cu distance is 5.9 Å.[20] For the other distances see Fig. 11.

La_2BaCuO_5 has a critical temperature of 5.2 K (Ref. 5) and is probably a quasi-two-dimensional ferromagnet, too.[21] The direction of magnetization is perpendicular to the *ab* plane[21] so that dipolar coupling could contribute to the ferromagnetism. Nevertheless, we think that it originates from kinetic exchange. Mizuno *et al.*[5] observe an abrupt disappearance of ferromagnetism in non-stoichiometric samples of $La_{4-2x}Ba_{2+2x}Cu_{2-x}O_{10-2x}$. Recent NMR results of Pieper *et al.*[21] indicate a large hyperfine field $B_{hf}=5.85$ T at the La sites, most probably caused by an induced spin density due to La *d* orbitals. These results are not compatible with the assumption of a dominant dipolar coupling.

The Cu^{2+} ground state hole orbitals are of *zx* or *yz* type, respectively. As a consequence they are orthogonal to each other within the *ab* plane, but are not along *c*.[5] Therefore the in-plane coupling is ferromagnetic in accordance with the GKA rules. The empty oxygen p_σ hole orbitals are $z\pm x$ or $z\pm y$ depending on the O positions. Guided by the NMR results of Ref. 21 we have taken into account the two La $5d$ orbitals which exhibit $pd\sigma$ hopping to the oxygen neighbors, but have not considered the La $6s$ orbital. Each of the $5d$ hole orbitals is doubly occupied. In a two-center approximation, the La *d* orbitals with the strongest covalent σ bond to the oxygen p_σ orbitals are of the types $d(zx)$ and $d(yz)$, respectively. The $d(3y^2-r^2)$ and $d(3x^2-r^2)$ orbitals exhibit somewhat weaker σ bonds and are assumed to lie at slightly higher (0.5 eV) orbital energies.

As we do not have any further information about the orbital energies we have chosen them similar to those of K_2CuF_4. This means $\epsilon_p=4$ eV for oxygen sites, $\epsilon_{d_1}^{La}=-2.5$ eV for the $d(zx),d(yz)$, and $\epsilon_{d_2}^{La}=-2$ eV for the $d(3y^2-r^2),d(3x^2-r^2)$ hole orbitals of La. For details see the Appendix.

The relevant cluster for the coupling in (001) direction is shown in Fig. 11. It contains eight ions, two Cu^{2+}, four O^{2-}, and two La^{3+}. These are occupied by a total of ten spins, one at each Cu ion and four at each La site (there are two fully occupied La hole orbitals to be considered). Therefore, our cluster is abbreviated as $(8+m+1)S10H$, *m* counting the excited Cu orbitals and the 1 indicating that there is one additional La orbital.

For this cluster there exists again more than one path for exchanging spins between Cu ions in adjacent planes. One is Cu→O→O→Cu, the other Cu→O→La →O→Cu (see Fig. 11). The first path gives spin-spin interaction in sixth-order perturbation theory, the second one in eighth order.

To simplify the analytical treatment, we consider the $(8+0+0)S2H$ model with empty La sites and only one La orbital. Because of the high order of the perturbation expansion we investigate only the *U* channel, that part of

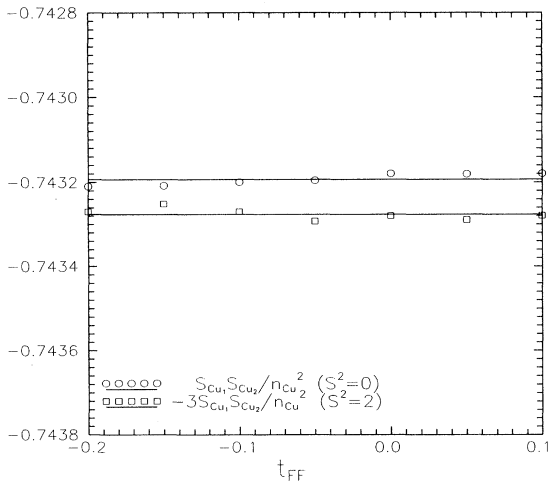

FIG. 7. Spin correlation scaled by the occupation numbers for the full K_2CuF_4 model cluster with six spins.

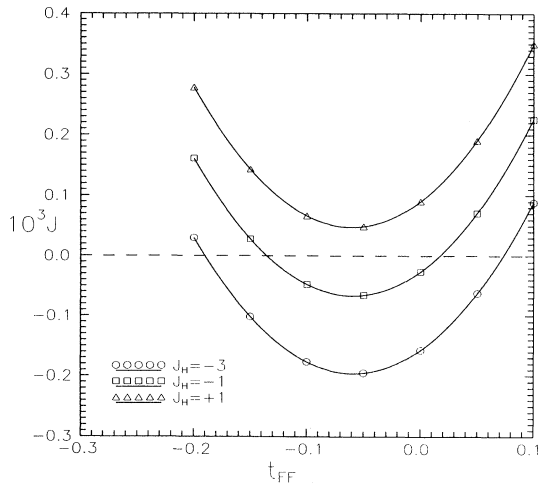

FIG. 8. Exchange integral *J* between the Cu spins as a function of t_{FF} for the full K_2CuF_4 model cluster for different Hund's rule couplings J_H.

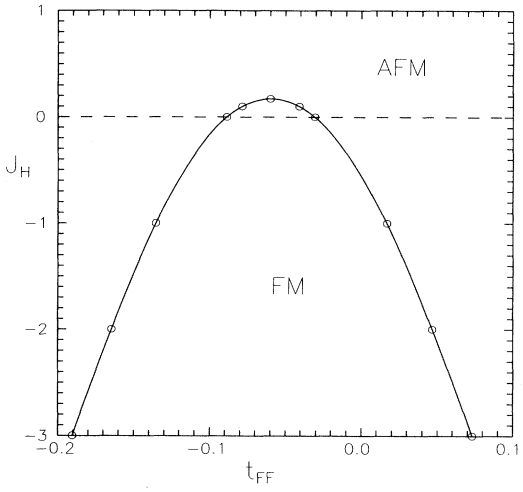

FIG. 9. Ground-state phase diagram for the K_2CuF_4 model cluster with six spins as a function of J_H and t_{FF}.

J_{gg} which is proportional to $1/U$. This term arises from the two spins meeting at one Cu ion; thus all other intermediate states are singly occupied. This simplification allows us to treat the O-La-O complex as one entity and to diagonalize it, thereby reducing the spin-spin interaction to a process of fourth order. Then we get:

$$J_{gg}^{U} \propto \frac{1}{U}\left[\frac{\epsilon_{La}t_{OO}-t_{LaO_2}t_{O_1La}}{[\epsilon_O+t_{OO}[(\epsilon_O-t_{OO})\epsilon_{La}-2t_{LaO_2}t_{O_2La}]}\right]^2 . \tag{18}$$

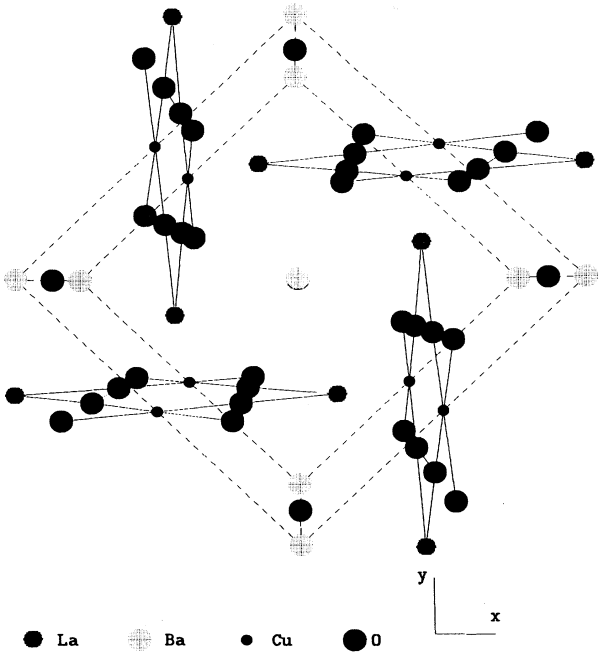

FIG. 10. Crystal structure of La_2BaCuO_5. The view is along the z axis. The main structural elements are CuO_4 squares with their normals along x or y, respectively, resulting in a ladderlike structure in the z direction. In addition there are BaO chains also directed along the z axis (see also Fig. 11).

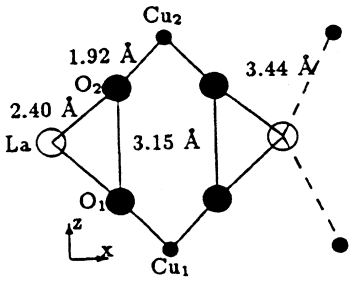

FIG. 11. The relevant cluster for spin exchange in the z direction for La_2BaCuO_5. The solid lines connecting different ions represent the hopping paths included in the calculation. Two Cu ions of an adjacent, perpendicular cluster are also indicated.

This expression involves only parameters from one O-La-O complex, since the other one is equivalent to the first. Therefore, only constructive interference can occur between the two paths. Accordingly, any destructive interference has to take place inside each O-La-O complex, as can be seen from J_{gg}^{U}, which can be made zero for appropriately chosen parameters.

For the other contributions to J_{gg} we expect similar expressions including ring exchange terms. But we cannot diagonalize the occurring matrices analytically because of their size.

For the full model of the cluster with ten spins, i.e., $(8+m+1)S10H$, we again use the numerical analysis. We study the energy of the low-lying levels in dependence on t_{OO}, as is suggested by the results of the perturbation theory. For these calculations we took into account the Cu e_g orbitals and have neglected the t_{2g} states because of the small $pd\pi$ hopping (see Tables V, VII). Figure 12 shows the energies of the lowest ferromagnetic $S^2=2$ state and the lowest antiferromagnetic $S^2=0$ state as a function of t_{OO}. In Fig. 13 the exchange constant [Eq. (16)] for the Cu spins is displayed. We find a small ferromagnetic range around $t_{OO} \approx -0.3$. This is close to

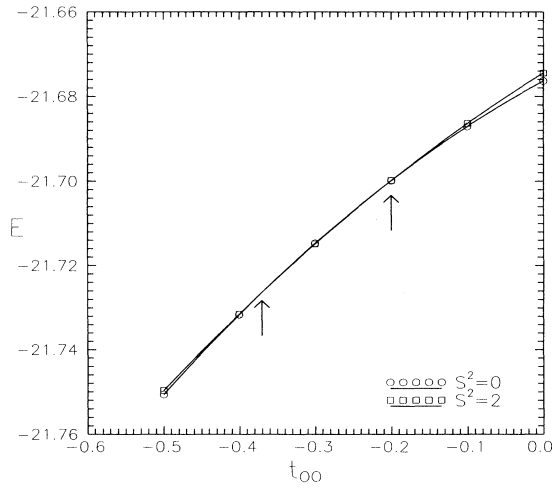

FIG. 12. Energy E as a function of t_{OO} for the La_2BaCuO_5 model of Fig. 11 with ten spins. The arrows indicate the region where the ferromagnetic state ($S^2=2$) has the lower energy.

TABLE III. Occupation numbers of all orbitals for the La_2BaCuO_5 model cluster with ten spins, $(8+1+1)S10H$, as a function of t_{OO}. Superscripts denote different d orbitals. The first line for each hopping value corresponds to the lowest energy state.

t_{OO}	S^2	n_{La^1}	n_{La^2}	n_O	n_{Cu^1}	n_{Cu^2}
−0.5	0	1.872 30	1.955 59	0.144 57	0.881 51	0.001 46
	2	1.871 33	1.955 98	0.144 47	0.882 30	0.001 45
−0.4	0	1.875 16	1.954 48	0.143 30	0.882 31	0.001 44
	2	1.874 59	1.954 73	0.143 31	0.882 61	0.001 44
−0.3	2	1.877 74	1.953 43	0.142 31	0.882 79	0.001 42
	0	1.877 94	1.953 33	0.142 28	0.882 76	0.001 43
−0.2	0	1.880 63	1.952 13	0.141 48	0.882 86	0.001 41
	2	1.880 78	1.952 07	0.141 45	0.882 83	0.001 41
−0.1	0	1.883 24	1.950 89	0.140 92	0.882 62	0.001 41
	2	1.883 72	1.950 65	0.140 74	0.882 74	0.001 40
0.0	0	1.885 76	1.949 60	0.140 60	0.882 03	0.001 40
	2	1.886 55	1.949 16	0.140 18	0.882 52	0.001 40

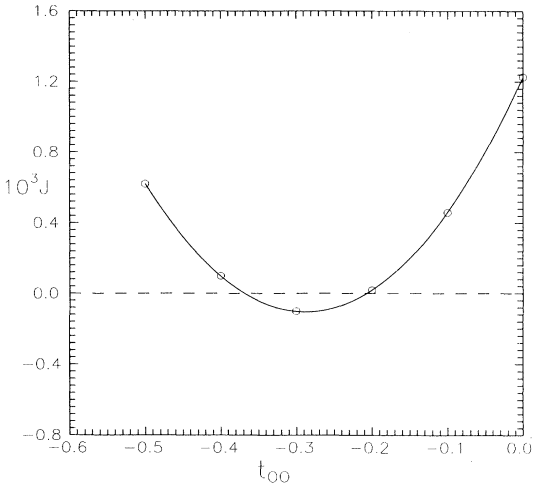

FIG. 13. Exchange integral J between the Cu spins in La_2BaCuO_5 as a function of t_{OO} for the model cluster with ten spins.

the value of t_{OO} as given in Table VII. As a consequence, the coupling between two nearest Cu atoms in (001) direction is found to be almost vanishing, but may well be antiferromagnetic. The occupation numbers and the values for local spins and for spin correlations are given in Tables III and IV.

In connection with the measurement of the hyperfine field at the La site[21] we have considered the local magnetic moment of La. For $t_{OO}=-0.2$, the ground-state expectation value is given by $\sum_\alpha \langle \mathbf{S}_{La^\alpha} \rangle \approx 0.11$, where La^α denotes different La orbitals, corresponding to a fictitious quantum number $S=0.1$ (and a magnetic moment $0.2\mu_B$). This value is compatible with the large hyperfine field of $B_{hf}=5.85$ T.[21]

In summary, ferromagnetism in La_2BaCuO_5 might occur by the following mechanism: There are three important exchange couplings between Cu spins. The hopping paths responsible for the coupling along the lattice directions (110) and (112) are topologically equivalent (see Fig. 11) and lead to a ferromagnetic coupling of spins by the classical GKA mechanism. Here the (110) coupling constant is bigger by a factor of 4 than the coupling in (112) direction, as there are two equivalent hopping paths for the (110) direction. In addition, there exists an antiferromagnetic interaction in (001) direction which by reduction through interference is smaller than the ferromagnetic exchange along (112), so that the net exchange between the planes is (weakly) ferromagnetic, leading to a two-dimensional behavior of the ferromagnetism.

IV. CONCLUSION

In this paper we have studied small clusters and various ligand geometries using Hubbard-type models in order to investigate possibilities for ferromagnetic coupling of Cu^{2+} spins. We have found that interference effects between inequivalent hopping paths may become very important, both for the sign and the magnitude of the spin interaction via superexchange. In particular, destructive interference may occur in ternary or quaternary com-

TABLE IV. S^2 and Cu-Cu spin correlation for the La_2BaCuO_5 model cluster with ten spins, $(8+1+1)S10H$. Superscripts denote different orbitals, subscripts different sites. The first line for each hopping value corresponds to the state with the lowest energy.

t_{OO}	S^2	$S^2_{La^1}$	$S^2_{La^2}$	S^2_O	$S^2_{Cu^1}$	$S^2_{Cu^2}$	$\langle \mathbf{S}_{Cu_1}\mathbf{S}_{Cu_2} \rangle$
−0.5	0	0.089 61	0.032 56	0.101 50	0.659 05	0.001 09	−0.577 47
	2	0.090 38	0.032 30	0.101 42	0.659 64	0.001 09	0.192 74
−0.4	0	0.087 74	0.033 36	0.100 69	0.659 67	0.001 08	−0.578 47
	2	0.088 24	0.033 19	0.100 68	0.659 89	0.001 08	0.192 91
−0.3	2	0.086 16	0.034 13	0.100 04	0.660 04	0.001 07	0.193 00
	0	0.085 92	0.034 18	0.100 02	0.660 02	0.001 07	−0.579 01
−0.2	0	0.084 15	0.035 03	0.099 51	0.660 10	0.001 06	−0.579 11
	2	0.084 15	0.035 10	0.099 49	0.660 09	0.001 06	0.193 03
−0.1	0	0.082 42	0.035 92	0.099 15	0.659 90	0.001 05	−0.578 76
	2	0.082 21	0.036 12	0.099 04	0.660 04	0.001 05	0.193 00
0.0	0	0.080 75	0.036 84	0.098 93	0.659 43	0.001 05	−0.577 95
	2	0.080 32	0.037 18	0.098 69	0.659 88	0.001 05	0.192 89

pounds, where both negative ions (with p valence orbitals) and positive ions (with either s or d valence orbitals) mediate the spin exchange. The interference effects may result in ferromagnetic coupling, usually through Hund's rule exchange via excited d orbitals and the magnetic sites. However, we even found a possibility for ferromagnetic coupling of spins involving ground-state orbitals only, provided that nonequivalent ligands are present.

In K_2CuF_4, interference of hopping paths leads to a ferromagnetic interaction between two Cu ions in adjacent c planes. For our study we have chosen model parameters with values close to those obtained for the isostructural La_2CuO_4. We found (including excited d orbitals) a minimal exchange constant $J \approx -6.7 \times 10^{-5}$ eV, which is of the same order of magnitude as found experimentally.

For La_2BaCuO_5, the coupling between c planes arises from two different pairs of Cu^{2+} ions. The first has its axis along (001), the second along the lattice direction (112). For the (112) pair the coupling is ferromagnetic by symmetry, while for the (001) pair our investigation indicates an almost vanishing and probably antiferromagnetic interaction. This leads to a reduction of the ferromagnetic coupling of c planes.

We note that all estimates for the model parameters as given in the Appendix are semiquantitative, at best. For a better accuracy of the exchange constants, more reliable parameters for the Hubbard-type models are required, which could be obtained by constrained-density functional calculations of the type presented in Ref. 22.

In summary, we have shown that destructive interference involving *inequivalent* hopping paths may strongly suppress the antiferromagnetic coupling of spins, leading to a weak ferromagnetic coupling. If there is a possibility to modify these interference effects, either by application of uniaxial pressure or by a magnetic field, we may restore the antiferromagnetic coupling. This may even lead to the paradox case that the application of an external magnetic field could destroy ferromagnetism. We will report about this possibility in a forthcoming paper.

TABLE V. Two-center integrals (. . .) and orbital energies ϵ for K_2CuF_4 and La_2BaCuO_5 in eV; superscripts denote different d orbitals.

K_2CuF_4		La_2BaCuO_5	
	(. . .)		
$(pp\sigma)$(F-F)	−0.2	$(pp\sigma)$ (O-O)	−0.32
$(pp\pi)$ (F-F)	0.1	$(pp\pi)$ (O-O)	0.03
$(sp\sigma)$ (K-F)	−1.5		
		$(dp\sigma)$ (La-O)	−1.4
		$(dp\pi)$ (La-O)	0.7
$(dp\sigma)$ (Cu-F)	−1.6	$(dp\sigma)$ (Cu-O)	−1.6
$(dp\pi)$ (Cu-F)	0.6	$(dp\pi)$ (Cu-O)	0.6
$(ds\sigma)$ (Cu-K)	0.5		
	ϵ		
$2p$(F)	4.0	$2p$(O)	4.0
$4s$(K)	−4.0	$5d^1$(La)	−2.5
		$5d^2$(La)	−2.0
$3d^1$(Cu)	0.0	$3d^1$(Cu)	0.0
$3d^2$(Cu)	0.5	$3d^2$(Cu)	0.5
$3d^3$(Cu)	1.4		
$3d^4$(Cu)	1.5		
$3d^5$(Cu)	1.6		

TABLE VI. Direction cosines for the relevant bonds; the first four bonds belong to K_2CuF_4, the last three to La_2BaCuO_5.

	l	m	n
F-F	0.54	0.54	0.65
K-F	0	0	1
Cu-F	0	0	1
Cu-K	0.60	0.60	0.53
O-O	0	0	1
La-O	0.75	0	0.66
Cu-O	0.68	0	0.72

ACKNOWLEDGMENTS

Helpful discussions with A. L. Shelankov are appreciated. This work was supported in part by the Deutsche Forschungsgemeinschaft and by the European Community Project No. CHRX-CT93-0332.

APPENDIX: MODEL PARAMETERS

For the numerical calculations, the hopping integrals between the different ions, the values of the energy levels, the on-site interaction energies U and J_H, and information on the orbital symmetry are required. Assuming a two-center approximation, the symmetry part of the hopping integrals can be taken from Table I of Slater and Koster.[23] The two-center matrix elements are taken from the tight-binding model used for calculations of the electron-phonon coupling in La_2CuO_4.[24] We assume that their values are quite similar for La_2CuO_4, K_2CuF_4 and La_2BaCuO_5, apart from distance effects. Any changes of the two-center matrix elements due to bond length changes are incorporated via the gradients used to calculate the electron-phonon coupling. Changes in bond an-

TABLE VII. Resulting hopping integrals of K_2CuF_4 and La_2BaCuO_5 in eV; superscripts denote different d orbitals.

K_2CuF_4		La_2BaCuO_5	
	t		
F-F	−0.03	O-O	−0.2
K-F	−1.5	La^1-O	1.2
		La^2-0	−0.7
Cu^1-F	−1.4	Cu^1-O	−1.3
Cu^2-F	0.8	Cu^2-O	0.8
Cu^3-F	0	Cu^3-O	−0.2
Cu^4-F	0	Cu^4-O	−0.2
Cu^5-F	0	Cu^5-O	0
Cu^1-K	−0.033		
Cu^2-K	0.022		
Cu^3-K	0.25		
Cu^4-K	0.28		
Cu^5-K	0.25		

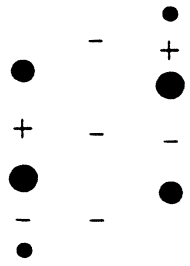

FIG. 14. Signs of hopping integrals for K_2CuF_4 referring to the ground state at the magnetic sites. Relative signs for ground and excited states can be taken from Table VII.

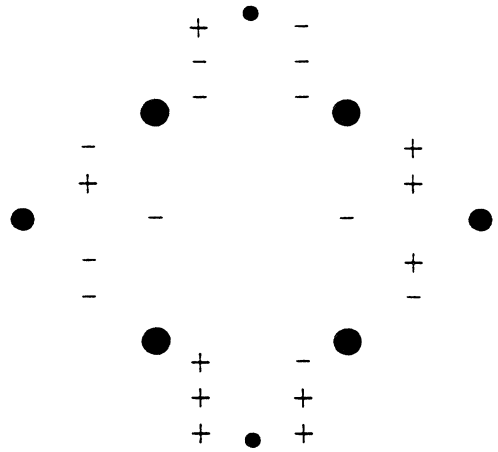

FIG. 15. Signs of hopping integrals for La_2BaCuO_5; the top sign of a column represents the ground state, the other ones the excited states.

gles are accounted for by the modified direction cosines entering the expressions of Table I in Ref. 23. The two-center integrals involving s orbitals at K are assumed to be the same as the corresponding integrals involving La d orbitals, i.e., $(dd)=(ds),(pd)=(ps)$. As the hole picture is used here, while in Ref. 24 the electron picture was employed, the signs of the hopping integrals have to be reversed.

In Table V we give the values of the two-center integrals for K_2CuF_4 and La_2BaCuO_5 using the data of Ref. 24. The direction cosines for the different bonds are shown in Table VI. The resulting hopping integrals are listed in Table VII for K_2CuF_4 and La_2BaCuO_5. Here $Cu^{1,\ldots,5}$ mean the five Cu d orbitals, with the ground state Cu^1 and the four excited states $Cu^{2,\ldots,5}$. The signs of the hopping integrals for the individual bonds can be seen in Fig. 14 for K_2CuF_4 and Fig. 15 for La_2BaCuO_5.

Coulomb interaction energies U are chosen to be 8 eV for the Cu sites, equal for all orbitals, in accordance with the usual values proposed for La_2CuO_4.[18,22] The Hund's rule exchange constant at the Cu sites is taken as $J_H=-1$ eV.[11] For the ligands $U=0$ was assumed; also any intersite interaction was neglected for simplicity.

The ligand energies are also supposed to be similar to the values of La_2CuO_4. A constrained density functional calculation in the hole picture by Hybertson *et al.*[22] leads to a value of $\epsilon_O=3.6$ eV for the bare oxygen energy, measured from the lowest Cu d state. Using this value one gets very good agreement between the calculated and the experimentally found superexchange constant $J=0.13$ eV in the CuO_2 planes of La_2CuO_4.[25]

For K_2CuF_4, we chose $\epsilon_F(\text{hole})=4$ eV and $\epsilon_K(\text{hole})=-4$ eV. The latter value is somewhat arbitrary, but ensures that the K 4s orbital is occupied by two holes. In addition, energy band calculations in the electron picture for K_2CuF_4 indicate $\epsilon_F(\text{electron})=-\epsilon_K(\text{electron})$,[26] which result was transferred to the hole picture.

For La_2BaCuO_5 the ligand energies, and also the two-center integrals, are even less well known. Especially, the crystal symmetry and thus the local environment of the atoms are considerably different from the case of La_2CuO_4. To get better parameters, a tight-binding analysis of a density functional calculation is required, which, so far, has not been carried out. For these reasons we assume similar values as in K_2CuF_4. Only the energies of the La d orbitals is raised somewhat to get a higher magnetic moment at the La site. We take $\epsilon_{d_1}^{La}=-2.5$ eV for the lower La state and $\epsilon_{d_2}^{La}=-2$ eV for the higher one.

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