Tight-binding parameters and exchange integrals of Ba$_2$Cu$_3$O$_4$Cl$_2$

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Several new cuprate materials have been studied in the last years which contain modifications to the standard CuO$_2$ plane. This class includes not only the now-famous ladder compounds Sr$_{n-1}$Cu$_n$O$_{2n}$_1, but also Ba$_2$Cu$_3$O$_4$Cl$_2$ or the similar Sr$_2$Cu$_3$O$_4$Cl$_2$. The latter two compounds are antiferromagnetic insulators which are characterized by a Cu$_3$O$_4$ plane with additional Cu$_B$ atoms in the standard Cu$_4$O$_2$ plane (Figs. 1 and 6). This new class of cuprates is currently of great scientific interest since it may shed light on some of the open questions in high-$T_c$ superconductivity. The layered cuprate Ba$_2$Cu$_3$O$_4$Cl$_2$ itself is also interesting due to its rich magnetic structure and the unconventional character of its lowest energy excitations. Experimentally, two Néel temperatures have been found $T_N^A$ $\approx$ 330 K and $T_N^B$ $\approx$ 31 K (Refs. 3 and 6) connected with the two sublattices of A and B copper. The magnetic susceptibility and the small ferromagnetic moment have been explained phenomenologically together with a determination of the exchange integrals. Like in undoped Sr$_2$CuO$_2$Cl$_2$, the lowest electron removal states in Ba$_2$Cu$_3$O$_4$Cl$_2$ can be interpreted in terms of Zhang-Rice singlets with a new branch of singlet excitations connected with the B sublattice.

One might expect that the additional Cu$_B$ would give rise to considerable differences in the electronic structure in comparison with the usual CuO$_2$ plane. In particular, the amount of coupling between both subsystems would appear to be crucial. This question will be addressed here by a microscopic investigation starting from a band-structure calculation. However, as for most undoped cuprates, the local-density approximation (LDA) leads to metallic behavior, and one has to treat the electron correlation in a more explicit way. In this paper, we use band-structure calculations to determine tight-binding (TB) parameters and then add the local Coulomb correlation terms. We present here a considerable improvement of the preliminary TB fit where only the upper two bands had been fitted. Furthermore we also determine the weight of each of the relevant orbitals in the band structure (Sec. II) to obtain the TB parameters (Sec. III). In contrast to Ref. 11 we now distinguish between different oxygen orbitals. With reasonable assumptions about the local Coulomb correlation terms we estimate the exchange integrals in Sec. IV.

II. BAND-STRUCTURE CALCULATION

The tetragonal unit cell of Ba$_2$Cu$_3$O$_4$Cl$_2$ is shown in Fig. 1. We performed LDA calculations for this substance using the linear combination of atomiclike orbitals (LCAO). Due to the relatively open structure, eight empty spheres per unit cell (between Cu$_A$ and Cl) have been introduced. The calculation was scalar relativistic and we have chosen a minimal basis set consisting of Cu(4s,4p,3d), O(2s,2p), Ba(6s,6p,5d), and Cl(3s,3p) orbitals, the lower lying states were treated as core states. To optimize the local basis, a contraction potential has been used at each site. The exchange and correlation part was treated in the atomic-sphere approximation, while the Coulomb part of the potential was constructed as a sum of overlapping extended site potentials. Hence, this part of nonspherical effects determined by the crystal symmetry is taken into account self-consistently. On the other hand, the intra-atomic asphericity is suppressed by azimuthal averaging over the site-charge density during the iterations. The intra-atomic asphericity is only taken into account in the final step of calculating the weights of several orbitals in the band structure. These weights are necessary for an improvement of the preliminary TB fit.

In our calculation the Bloch wave function $|\mathbf{k}\nu\rangle$ is composed of overlapping atomiclike orbitals $|Lij\rangle$ centered at $\mathbf{L}_{ij}$
the atomic site \( j \) in the elementary cell \( i \) with coordinates \( \mathbf{R}_i + \mathbf{S}_j \),

\[
|\mathbf{k}\rangle = \sum_{Lij} C_{Lij}^{kv} e^{i \mathbf{k} \cdot (\mathbf{R}_i + \mathbf{S}_j)} |Lij\rangle
\]  

(1)

with the normalization condition \( \langle \mathbf{k} \mathbf{v} | \mathbf{k} \mathbf{v} \rangle = 1 \). Here, \( L = \{nlm\} \) where \( n, l, \) and \( m \) denote the main quantum number, the angular momentum, and the magnetic quantum numbers, respectively. Note that for each \( L \) only one main quantum number \( n \) is considered. With the usual definition for the density of states

\[
\rho(\omega) = \frac{1}{N_k} \sum_{k\mathbf{v}} \int d^3r \langle \mathbf{k}\mathbf{v}|\mathbf{r}\rangle \langle \mathbf{r}|\mathbf{k}\mathbf{v}\rangle \delta(\omega - E_{k\mathbf{v}}),
\]  

(2)

where \( N_k \) is the number of elementary cells equivalent to the number of \( k \) values, one can write \( \rho \) as

\[
\rho(\omega) = \frac{1}{N_k} \sum_{k\mathbf{v}} \int d^3r \sum_{Lij} C_{Lij}^{kv} e^{i \mathbf{k} \cdot (\mathbf{R}_i + \mathbf{S}_j)} \langle Lij|\mathbf{r}\rangle \times \langle \mathbf{r}|L'i'j'\rangle e^{i \mathbf{k} \cdot (\mathbf{R}_i + \mathbf{S}_j - \mathbf{R}_{i'} - \mathbf{S}_{j'})} \delta(\omega - E_{k\mathbf{v}})
\]  

(3)

or

\[
\rho(\omega) = \frac{1}{N_k} \sum_{k\mathbf{v}} \sum_{Lij} C_{Lij}^{kv} C_{L'i'j'}^{kv^*} S_{Lij,L'i'j'} \delta(\omega - E_{k\mathbf{v}}),
\]  

(4)

where \( S_{Lij,L'i'j'} \) is the overlap matrix. Now one can decompose \( \rho \) into an on-site part \((i = i' \) and \( j = j' \)) and an overlap part \((i \neq i' \) or \( j \neq j' \)). For the on-site part one finds \( S_{Lij,L'i'j'} = \delta_{LL'} \) due to the orthogonality of atomic-like orbitals at the same site. So we can define a net density of states (net-DOS)

\[
\rho_{\text{net}}(\omega) = \frac{1}{N_k} \sum_{k\mathbf{v}} \sum_{Lij} |C_{Lij}^{kv}|^2 \delta(\omega - E_{k\mathbf{v}}),
\]  

(5)

The difference between DOS and net-DOS consists in the overlap density but this difference is not very large as can be seen from Fig. 2. In the middle of the spectrum both quantities are nearly identical, whereas in the lower part the overlap density is positive and in the upper half the overlap density is negative such that the net-DOS becomes larger than the DOS. The relative difference \( (\rho - \rho_{\text{net}})/\rho \) depends on the energy in an approximately linear way.

The band structure corresponding to the DOS of Fig. 2 is shown in Fig. 3(a). Its main result are two bands crossing the Fermi surface (FS). These two bands, in common with most of the other bands, show nearly no dispersion in the \( z \) direction which justifies the restriction to the \( Cu_3O_4 \) plane in the following discussion. The two bands give rise to a peak in

![FIG. 2. LCAO-LDA DOS \( \rho \) (solid line) and net-DOS \( \rho_{\text{net}} \) (dashed line) of \( Ba_2Cu_3O_4Cl_2 \), the Fermi level is at zero energy. The scaled relative difference \( [10(\rho - \rho_{\text{net}})/\rho] \) is plotted with large black dots.](image)

\[
\rho(\omega) = \frac{1}{N_k} \sum_{k\mathbf{v}} \sum_{Lij} \sum_{L'i'j'} C_{Lij}^{kv} C_{L'i'j'}^{kv^*} S_{Lij,L'i'j'} \delta(\omega - E_{k\mathbf{v}}),
\]  

(4)
the DOS (Fig. 2) at the Fermi level. To analyze the orbital character of the two relevant bands, we write the net-DOS as

$$ \rho_{\text{net}}(\omega) = \frac{1}{N_k} \sum_{k'} \sum_{Lj} W_{Lj}^{k'} \delta(\omega - E_{k'}) $$

where we define the weight of the orbital $|Lj\rangle$ in the state $|k\rangle$ in the form:

$$ W_{Lj}^{k'} = \sum_i |c_{Lij}^{k'}|^2 $$

The sum of all weights is approximately unity, $\Sigma_{Lj} W_{Lj}^{k'} = 1$, with deviations due to the neglect of the overlap density which are linear in energy (see Fig. 2 and the discussion above).

In Figs. 4(a) and 4(b) we show the weights of the Cu\(_A\) 3d\(_{\pi z\pi z}\) and Cu\(_B\) 3d\(_{\pi z\pi z}\) orbitals, respectively. We can observe that the broadband is built up of predominantly the Cu\(_A\) 3d\(_{\pi z\pi z}\) orbital which hybridizes with one part of the planar oxygen 2p\(_{x,y}\) orbitals resulting in dp\(_{\pi}\) bonds. The corresponding oxygen orbitals, directed to the Cu\(_A\) atoms, are denoted here as p\(_{\pi}\) orbitals. Their weight is shown in Fig. 5(a). The p\(_{\pi}\) orbitals are to be distinguished from the oxygen p\(_\pi\) orbitals [Fig. 5(b)] which are perpendicular to them\(^{13}\) (see Fig. 6). These oxygen p\(_\pi\) orbitals hybridize with Cu\(_B\) 3d\(_{\pi \alpha \pi \alpha}\), building the narrow band at the FS [see Fig. 4(b)].

FIG. 3. (a) LCAO-LDA band structure of the Cu\(_3\)O\(_3\) plane of Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\), the Fermi level is at zero energy. (b) The same as in (a), but the weight of the lines is scaled with the sum of all 11 orbital projections that are used in the TB model. (c) The band structure of the TB model. The parameter set used is shown in Table I. The wave vector is measured in units of ($\pi/a, \pi/a$).

FIG. 4. Weight of (a) Cu\(_A\) 3d\(_{\pi z\pi z}\) and (b) Cu\(_B\) 3d\(_{\pi z\pi z}\) orbitals in the LCAO-LDA band structure of Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\). The wave vector is measured in units of ($\pi/a, \pi/a$).

There is generally very small weight of the p\(_{\pi}\) orbitals in this narrow band, indicating that there is only small coupling between the A and B subsystems. The only exception to this occurs around the wave vector ($\pi/a,0$). A further analysis shows that the band complex between $-1$ and $-3$ eV is predominantly built up of out-of-plane oxygen p\(_{\pi}\) together with the corresponding Cu 3d\(_{\pi \alpha \pi \alpha}\) orbitals (not shown), as well as a large contribution of Cl derived states.\(^{11}\) The in-plane oxygen orbitals contribute mainly to the lower band complex between $-4$ and $-8$ eV [see Figs. 5(a) and 5(b)].

Thus it is evident that the two bands crossing the FS which we want to analyze have nearly pure 3d\(_{\pi z\pi z}\) and 2p\(_{x,y}\) character.\(^{14}\) Therefore, we have to consider all together

FIG. 5. Weight of (a) O 2p\(_{\pi}\) and (b) O 2p\(_{\alpha}\) orbitals in the LCAO-LDA band structure of Ba\(_2\)Cu\(_3\)O\(_4\)Cl\(_2\). The wave vector is measured in units of ($\pi/a, \pi/a$).
III. TIGHT-BINDING PARAMETERS

It is our main goal to find a TB description of the relevant bands crossing the FS. This task is difficult due to the large number of bands between $-1$ and $-8$ eV of Fig. 3(a). There is no isolated band complex which makes a TB analysis easy. However, we have pointed out already that the relevant bands are a nearly pure combination of Cu 3$d_{x^2-y^2}$ and O 2$p_{\sigma}$ orbitals. Thus we will only concentrate on these orbitals, thereby accepting some deviations in the lower band complex between $-3$ and $-8$ eV. The relevant orbitals are depicted in Fig. 6. The tight-binding Hamiltonian $H_{TB}$ can be written as a sum of three parts:

$$H_{TB} = H_A + H_B + H_{AB}. \quad (8)$$

We distinguish two classes of orbitals corresponding to the two different subsystems. One consists of Cu$_A$ 3$d_{x^2-y^2}$ orbitals at the sites $R$ on on-site energies $\varepsilon_d$ and oxygen 2$p_{\sigma}$ orbitals at the sites $r$ with $\varepsilon_p$:

$$H_A = \varepsilon_d \sum_{R} d_{R}^d d_{R}^d + \varepsilon_p \sum_{r} p_{r}^p p_{r}^p$$

$$+ t_{pd} \sum_{R,r} (\alpha_{R} d_{R}^d p_{r}^p + C.c.)$$

$$+ t_{pp} \sum_{R,r} (\alpha_{R} d_{R}^d p_{r}^p H.c.), \quad (9)$$

where $d_{R}^d$ and $p_{r}^p$ are the usual creation operators for Cu 3$d_{x^2-y^2}$ and O 2$p_{\sigma}$ orbitals, respectively, and $\alpha_{R}$ is a phase factor corresponding to Fig. 6 which connects only neighboring sites. The other class incorporates Cu$_B$ 3$d_{x^2-y^2}$ orbitals at the sites $G$ with on-site energies $\varepsilon_d$ and oxygen $p_{\sigma}$ orbitals at the sites $r$ with $\varepsilon_p$. One gets the Hamiltonian $H_B$ by replacing $R$ with $G$, and the on-site and transfer energies with the corresponding energies of the Cu$_B$ subsystem, respectively. The creation operators $p_{r}^p$ should then be replaced with the operators $\pi_{r}^p$ thus creating an O 2$p_{\sigma}$ orbital. The coupling between both classes of orbitals, which correspond to the Cu$_A$ and Cu$_B$ subsystems, respectively, is provided by the parameter $t_{p\pi}$:

$$H_{AB} = t_{p\pi} \sum_{R,r} (\alpha_{R} p_{r}^p \pi_{r}^p H.c.). \quad (10)$$

All together, we have to determine ten parameters, four on-site energies $(\varepsilon_d, \varepsilon_d, \varepsilon_p, \varepsilon_p)$, the nearest-neighbor transfer integrals $(t_{pd}, t_{pd})$, and several kinds of oxygen transfers $(t_{pp}, t_{p\pi}, t_{p\pi}, t_{p\pi})$.

In our analysis we found that the Cu$_A$-Cu$_B$ transfer $t_{dd}$ can be neglected since its estimation yields a value smaller than 0.08 eV. Each $p_{\sigma}$ orbital is located between two Cu$_A$ sites and we neglect the influence of different local environments on the $t_{p\pi}$ transfer integral. In the case of the $t_{p\pi}$ transfer we distinguish the two possible local arrangements, but the numerical difference between $t_{p\pi}$ and $t_{p\pi}$ is small (see Table I). The necessity to distinguish between oxygen 2$p_{\sigma}$ and 2$p_{\sigma}$ orbitals was pointed out by Mattheiss and Hamann for the case of the standard CuO$_2$ plane.

### Table I. Parameters of the TB fit and the proposed extended Hubbard model for the Cu$_4$O$_4$ plane in Ba$_2$Cu$_3$O$_4$Cl$_2$.\footnote{In electron representation (energy/eV)}

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$e_d^A$</th>
<th>$e_d^B$</th>
<th>$e_p$</th>
<th>$e_p$</th>
<th>$t_{pd}$</th>
<th>$t_{pd}$</th>
<th>$t_{pp}$</th>
<th>$t_{p\pi}$</th>
<th>$t_{p\pi}$</th>
<th>$t_{p\pi}$</th>
<th>$U_d$</th>
<th>$U_p$</th>
<th>$U_{pd}$</th>
<th>$U_{p\pi}$</th>
<th>$K_{pd}$</th>
<th>$K_{p\pi}$</th>
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</thead>
<tbody>
<tr>
<td>TB fit</td>
<td>-2.50</td>
<td>-2.12</td>
<td>-4.68</td>
<td>-3.73</td>
<td>1.43</td>
<td>1.19</td>
<td>0.81</td>
<td>0.41</td>
<td>0.50</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Extended Hubbard model</td>
<td>2.50</td>
<td>2.12</td>
<td>6.68</td>
<td>5.73</td>
<td>-1.43</td>
<td>-1.19</td>
<td>-0.81</td>
<td>-0.41</td>
<td>-0.50</td>
<td>-0.25</td>
<td>10.5</td>
<td>4.0</td>
<td>1.2</td>
<td>3.2</td>
<td>-0.18</td>
<td>-0.4</td>
</tr>
<tr>
<td>(energy/eV)</td>
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<td></td>
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</tr>
</tbody>
</table>
Since there is a considerable admixture of other orbitals, especially Cu $3d_{xy}$ and Cu $3d_{z^2-r^2}$, in some of the lower bands of Fig. 3(b), we cannot determine the ten TB parameters by a least-square fits of the 11 TB bands to the heavily shaded LDA bands of Fig. 3(b). Instead, at the high-symmetry points $\Gamma = (0,0)$ and $M = (\pi/a, \pi/a)$ we picked out those bands in Fig. 3(b) which have the most pure $3d_{x^2-y^2}$ and $2p_{z,x}$ character. Only those energies were compared with the TB band structure [Fig. 2(c)] derived by diagonalizing a $11 \times 11$ matrix. In this way it is possible to calculate the parameter set analytically because the TB matrix splits up into $3 \times 3$ and $4 \times 4$ matrices at the high-symmetry points $\Gamma = (0,0)$ and $M = (\pi/a, \pi/a)$. The calculated eigenvalues are given in the Appendix A. That procedure results in the parameters given in Table I. These values are similar to those which are known for the standard CuO$_2$ plane. The largest transfer integrals are $t_{pp} = 1.43$ eV and $t_{\pi\pi} = 1.19$ eV as expected. Nevertheless these values are somewhat smaller than in the previous TB fit$^{11}$ where all oxygen orbitals were treated as identical. The difference between $t_{pp}$ and $t_{\pi\pi}$ is roughly a factor of 2 in coincidence with the situation in the standard CuO$_2$ plane,$^{13}$ a fact which was not taken into account in Ref. 11. We have found that only the smallest parameter, $t_{\pi\pi} = 0.25$ eV, is responsible for the coupling between the subsystems of Cu$_A$ and Cu$_B$. Thus despite the fact that the two oxygen $p_\sigma$ and $p_\pi$ orbitals are located in real space at the same atom, they are quite far away from each other in Hilbert space.

IV. EXCHANGE INTEGRALS

Thus far we have found that the TB parameters are rather similar to the standard CuO$_2$ case and that the coupling between the Cu$_A$ and Cu$_B$ subsystem is quite small. This justifies the usage of standard parameters for the Coulomb interaction part of the Hamiltonian. Of course it would be desirable to determine these values by a constrained density-functional calculation for Ba$_2$Cu$_3$O$_4$Cl$_2$, but we expect only small changes in the estimation of exchange integrals presented below.

The Coulomb interaction also changes the on-site copper and oxygen energies. Their difference, given in the first line of Table I, is too small to explain the charge-transfer gap of $\sim 2$ eV in Ba$_2$Cu$_3$O$_4$Cl$_2$. Adding 2 eV to the on-site oxygen energies, the difference $\Delta = e_p - e_d$ (in hole representation which is chosen from now on) becomes similar to the standard value derived by Hybertsen $et \ al.$ for La$_2$CuO$_4$. Our proposal of on-site energies for the multiband Hubbard model $H = H_{TD} + H_{int}$ are given in the second line of Table I. We have used the values of Ref. 17 also for the parameters of the Coulomb interaction part

$$ H_{int} = \sum_i U_i n_i n_i + \frac{1}{2} \sum_{ij} U_{ij} n_i n_j + \sum_{ij} K_{ij} S_i S_j, $$

(11)

where $n_i$ is the occupation operator of the orbital $i$ with the spin $s$ and $S_i$ the corresponding spin operator. From Ref. 17 we know the values for $U_d$, $U_p$, $U_{pd}$ and $K_{pd}$. Since we now have two oxygen orbitals at one site we also have to take into account the corresponding Hund’s rule coupling energy which is in the notation of Eq. (11) $K_{\pi\pi}$. That correlation energy is not given in Ref. 17 and we use here the simple rule $K_{\pi\pi} = -0.1 U_p$. The Coulomb repulsion between two oxygen holes in $p_\sigma$ and $p_\pi$ orbitals is assumed to be $U_{\pi\pi} = U_p + 2K_{\pi\pi}$, which is a valid approximation given degenerate orbitals. In the second line of Table I we combine the TB parameters derived from the band structure of Ba$_2$Cu$_3$O$_4$Cl$_2$ (now in hole representation) with the standard Coulomb correlation terms. This parameter set then defines an 11-band extended Hubbard model for the Cu$_3$O$_4$ plane which is used for the following estimation.

The exchange integrals have been calculated using the usual Rayleigh-Schrödinger perturbation theory on small clusters (Fig. 7). All transfer integrals (and $K_{\pi\pi}$) have been considered as a perturbation around the local limit. We calculated all exchange integrals in the corresponding lowest order (see Appendix B). The exchange $J_{AA} = t_{pd}^2 \Delta^3$ between two Cu$_A$ spins is given in fourth order for the simple Cu$_A$-O-Cu$_A$ cluster. It turns out that the influence of intersite Coulomb and exchange terms $U_{pd}$ and $K_{pd}$ is rather large, decreasing $J_{AA}$ from 246 to 99 meV (see Table II). In spite of

<table>
<thead>
<tr>
<th>Exchange integral</th>
<th>Without $U_{pd}$, $K_{pd}$</th>
<th>All parameters</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{AA}$</td>
<td>246</td>
<td>99</td>
<td>$130 \pm 40$</td>
</tr>
<tr>
<td>$J_{BB}$</td>
<td>17</td>
<td>12</td>
<td>$10 \pm 1$</td>
</tr>
<tr>
<td>$J_{AB,of}^{(1)}$</td>
<td>6.9</td>
<td>4.6</td>
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</tr>
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<td>$J_{AB,if}^{(1)}$</td>
<td>-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$J_{AB}^{(1)}$</td>
<td>-15</td>
<td>-12 $\pm$ 9</td>
<td></td>
</tr>
<tr>
<td>$J_{AB,of}^{(3)}$</td>
<td>1.4</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>
our rather approximate procedure, the latter value agrees quite reasonably with the phenomenological value (130±40)
meV (Ref. 7) for Sr$_2$Cu$_3$O$_4$Cl$_2$. $J_{AA}$ is thus also quite close to the standard value of the CuO$_2$ plane [$\sim$ 140 meV (Ref. 17)].

The exchange $J_{BB}$ is given only in sixth order for a larger cluster of two Cu$_B$, one Cu$_A$ and four oxygen orbitals. Correspondingly, it is roughly one order of magnitude smaller, $J_{BB}$\$\sim$ 12 meV (Table II). For $J_{AB}$ we need to distinguish between antiferromagnetic and ferromagnetic contributions. There are two antiferromagnetic couplings between nearest-neighbor copper atoms $J_{AB,af}^{(1)}$ and third-nearest-neighbor copper atoms $J_{AB,af}^{(3)}$, both being comparably small at 4.6 and 0.8 meV, respectively. The ferromagnetic contribution $J_{AB,f} = -20$ meV between nearest-neighbor copper spins arises in fifth order and is provided by Hund’s rule coupling of two virtual oxygen holes sitting at the same oxygen. Since $K_{\pi\pi}$ is known with less accuracy than the other interaction parameters, this value has to be taken with care.

V. SUMMARY

Summarizing, we have presented an LCAO-LDA bandstructure calculation for Ba$_2$Cu$_3$O$_4$Cl$_2$. Deriving TB parameters from it, we found only a weak coupling between the two sets of orbitals connected with the subsystems of copper $A$ (Cu$_A$ 3$d_{x^2-y^2}$ and O 2$p_x$) and copper $B$ (Cu$_B$ 3$d_{x^2-y^2}$ and O 2$p_x$). Furthermore, we derived exchange integrals $J_{AA}$, $J_{BB}$, and $J_{AB}$ in reasonable agreement with phenomenologically derived values from magnetic-susceptibility data if we add to the TB parameters the standard local Coulomb correlation energies. One should note, however, that we used a rather approximate perturbative procedure to estimate the exchange integrals. We expect that the Rayleigh-Schrödinger perturbation theory provides us with the right order of magnitude, but it may fail in the correct numbers. In that sense the agreement of the theoretical exchange integrals with the experimental ones should not be overinterpreted. On the other hand, the TB parameters were obtained by fitting to a first-principles band structure and they are accurate within the chosen orbital set.

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APPENDIX A: EIGENVALUES

As written in Sec. III, at the high-symmetry points $\Gamma'=(0,0)$ and $M=(\pi/\alpha,\pi/\alpha)$ the tight-binding matrix is block diagonal, so it is possible to calculate the eigenvalues analytically. In the following these eigenvalues are listed corresponding to the different parts of the tight-binding Hamiltonian.

Eigenvalues at $k = (0,0)$:

Cu$_A$ subsystem:

\[ e_d^A, \]
\[ e_p - 4t_{pp}, \]
\[ \frac{1}{2}(e_d^A + e_p + 4t_{pp} \pm \sqrt{(\Delta_A + 4t_{pp})^2 + 32t^2_{pd}}). \]

Cu$_B$ subsystem:

\[ e_\pi - 2t^+_{\pi\pi}, \]
\[ \frac{1}{2}(e_d^B + e_\pi + 2t^+_{\pi\pi} \pm \sqrt{(\Delta_B + 2t^+_{\pi\pi})^2 + 16t^2_{pd}}). \]

coupling between the subsystems:

\[ 1/2(e_p + e_\pi \pm \sqrt{(\Delta_{\pi\pi} + 64t^2_{p\pi})}). \]

The eigenvalues in Eq. (A3) are twofold degenerated.

Eigenvalues at $k = (\pi,\pi)$:

Cu$_A$ subsystem:

\[ \frac{1}{2}(e_d^A + e_\pi \pm \sqrt{\Delta^2_{\pi\pi} + 16t^2_{pd}}). \]

Cu$_B$ subsystem:

\[ e_\pi + 2t^+_{\pi\pi}, \]
\[ \frac{1}{2}(e_d^B + e_\pi - 2t^+_{\pi\pi} \pm \sqrt{(\Delta_B - 2t^+_{\pi\pi})^2 + 16t^2_{pd}}). \]

coupling between the subsystems:

\[ e_p, \]
\[ e_\pi, \]

where $\Delta_A = e_p - e_d^A$, $\Delta_B = e_\pi - e_d^B$, $\Delta_{AB} = e_\pi - e_d^A$, $t_{p\pi}^d = t_{p\pi}$.

The eigenvalues in Eqs. (A4) and (A6) are twofold degenerated.

APPENDIX B: EXCHANGE INTEGRALS

\[ \Delta_A = e_p - e_d^A, \quad \Delta_B = e_\pi - e_d^B, \]
\[ \Delta_{AB} = e_\pi - e_d^A, \]
\[ t_{p\pi}^d = t_{p\pi}, \quad t_{p\pi} = t_{p\pi}, \]
\[ J^{(4)}_{AA} = \frac{4t_{pdA}^2}{(\Delta_A + U_{pd})^2} \times \frac{K_{pd} + 2t_{pdA}^2 + t_{pdA}^2 + \frac{K_{pd}^2}{U_{pd} + \Delta_A + U_{pd}}}{\Delta_A + U_{pd}}. \]
\[ J_{BB}^{[6]} = \frac{8t_{p pd}^2(U_p^1)^2}{\Delta_B^2} \times \left\{ \frac{1}{(\Delta_B + U_p)} \left( K_{pd} + \frac{2t_{p pd}^2}{U_d} \right) + \frac{K_{pd}^2}{(\Delta_B + U_p)^3} \right\} \]

\[ J_{AB}^{[3][6]} = \sum_{A-B} \frac{2t_{p \pi}^2 t_{pd}^2 K_{pd}}{(\Delta_B + U_p)^2} \left( \frac{1}{\Delta_B + U_p} \right) + \sum_{A-B} \frac{2t_{p \pi}^2 t_{p d}^2 t_{pd}^2}{\Delta_B^2(\Delta_B + \Delta_A + U_p)} \left( \frac{1}{\Delta_B + \Delta_A + U_p} \right)^2 \]

\[ J_{BB}^{[1][6]} = \sum_{A-B} \frac{4t_{p \pi}^2 t_{p d}^2 K_{pd}}{\Delta_B^2(\Delta_B + U_p)} \left( \frac{1}{\Delta_B + U_p} \right) + \sum_{A-B} \frac{4t_{p \pi}^2 t_{p d}^2 t_{pd}^2}{\Delta_B^2(\Delta_B + \Delta_A + U_p)} \left( \frac{1}{\Delta_B + \Delta_A + U_p} \right)^2 \]

\[ J_{AB}^{[1][5]} = \frac{4t_{p pd} t_{p d}^2 K_{pd}^2}{(\Delta_B + \Delta_A + U_p)^2} \left( \frac{1}{\Delta_B + \Delta_A + U_p} \right)^2 \]

14. The corresponding band complex with nearly pure $3d_{x^2-y^2}$ and $2p_{x,y}$ character includes also a third band just below the FS. It has Cu$_4$ 3$d_{x^2-y^2}$ and O $p_x$ character similar to the broad band crossing the FS. This can be understood since there are two Cu$_4$ in the elementary cell of Cu$_2$O$_4$.
15. The parameter $t_{dd}$ can be roughly estimated by the weight of the Cu$_4$ in the Cu$_4$ band crossing the Fermi level at the $\Gamma = (0,0)$ point of the Brillouin zone. At this point the coupling via $t_{p x}$ is not possible due to symmetry.
19. The anisotropic coupling $J = -20 \mu eV$ which was found to be responsible for the small ferromagnetic moment in Sr$_2$Cu$_2$O$_4$Cl$_2$ cannot be estimated within the model proposed here. It requires a more refined treatment incorporating spin-orbit coupling and more orbitals at the Cu site.