RAPID COMMUNICATIONS

PHYSICAL REVIEW B **71**, 180415(R) (2005)

Unusual structural tuning of magnetism in cuprate perovskites

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(Received 21 March 2005; published 31 May 2005)

Understanding the structural underpinnings of magnetism is of great fundamental and practical interest. $Se_{1-x}Te_xCuO_3$ solid solutions are model systems for the study of this question, as composition-induced structural changes control their magnetic interactions. Our paper reveals that this structural tuning is associated with the position of the supposedly dummy atoms Se and Te relative to the superexchange (SE) Cu-O-Cu paths, and not with the SE angles as previously thought. We discuss the possible microscopic mechanisms responsible for this surprising effect.

DOI: 10.1103/PhysRevB.71.180415 PACS number(s): 75.10.−b, 71.27.+a, 75.30.Et, 75.80.+q

The 3*d* transition metal oxides are very important materials because they have been a source of intriguing physical phenomena such as high-T_c superconductivity, colossal magnetoresistance, and magnetoelectricity. Not surprisingly, a lot of effort is being devoted to understanding the microscopic interactions that determine the behavior of these systems. Here we are concerned with a particularly important topic, namely, the structural dependence of the magnetic couplings relevant in insulators (e.g., direct and super exchange). This question already received a lot of attention in early studies of magnetism in solids,[1] and a renewed interest in it is being driven by current intense work on magnetoelectric materials.

$Se_{1-x}Te_xCuO_3$ solid solutions (STCO)[2,3] are model systems for the study of these issues. They crystallize in a perovskite structure that is strongly distorted because both Te^{+4} and Se^{+4} are relatively small. Increasing x results in structural distortions that, in turn, switch the magnetic ground state (GS) from ferromagnetic (FM) to anti-ferromagnetic (AFM). In Ref. 2 it is proposed that the key structural modification is related to one of the Cu-O-Cu superexchange (SE) angles present in the system, α_2 in Fig. 1. The change in α_2 would cause the corresponding SE coupling (J_2 in Fig. 2) to switch sign, thus transforming the GS from FM to the AFM2 spin configuration of Fig. 2. This interpretation follows the spirit of the well-known Anderson-Goodenough-Kanemori (AGK) rules,[1] which discuss the SE sign and strength as a function of atomic species and configurations. However, we should note that, to the best of our knowledge, there is no direct experimental evidence that AFM2 is the GS of the Te-rich solid solutions, as the spin structure is yet to be determined by neutron scattering measurements.

Motivated by this appealing physical picture, we decided to study the $Se_{1-x}Te_xCuO_3$ solid solutions using density functional theory (DFT) and complementary tight-binding and effective Hamiltonian techniques. Here we report our surprising results. We find that (i) the changes in SE angles with x have negligible influence on the corresponding couplings and (ii) what controls the magnetic interactions is the position of the presumedly *dummy* atoms Se and Te with respect to the Cu-O-Cu groups. Indeed, the Se/Te atoms seem to act like a *valve*, turning the magnetic coupling from FM to AFM as they approach the Cu-O-Cu group. Our results thus draw a picture of STCO that is much more subtle than that proposed in Ref. 2. At the same time, they hint at alternate general ways of engineering magnetic couplings.

The calculations were performed within the generalized gradient approximation (GGA) (Ref. 4) to DFT. We primarily used the all-electron implementation in the WIEN2K package,[5] with a mixed basis that includes augmented plane waves and local orbitals (APW+lo). We used the so-called "LDA+U" scheme to properly treat the 3*d* electrons of Cu.[6,7] Typical cuprate values were taken for U (7.5 eV) and J (1.36 eV). We also used the ultrasoft pseudopotential[8] implementation in the plane-wave self-consistent field (PWscf) package,[9] with the LDA+U approach of Ref. 10 and $U=6$ eV. The calculation conditions[11] were converged to obtain exchange constants with an accuracy better than 1 meV. We checked that variations of 0.5–1 eV in U do not change our qualitative results. We double checked all our results by performing both WIEN2K and PWscf calculations. In all cases we got full qualitative, and reasonable quantitative, agreement.

Raw ab initio results. We start by considering $SeCuO_3$ (SCO) and $TeCuO_3$ (TCO) in their experimental structures.[12,13] Both compounds have a 20-atom unit cell and differ only by small variations in atomic positions and lattice constants. The structure is shown in Fig. 1 and the relevant structural data is given in Table I.

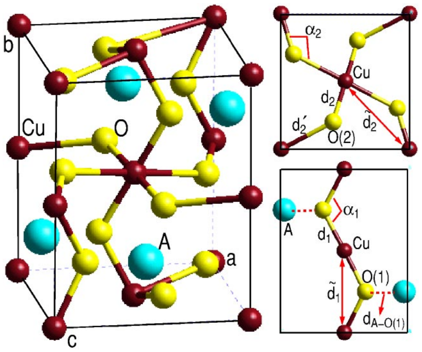

FIG. 1. (Color online) Left: Unit cell of $ACuO_3$ ($A=Se,Te$). Right top: symmetry-equivalent Cu-O(2)-Cu groups in the *ac* plane. Right bottom: Cu-O(1)-Cu chains along the *b* direction. Note there are two types of oxygens in the unit cell. Relevant structural parameters are defined.

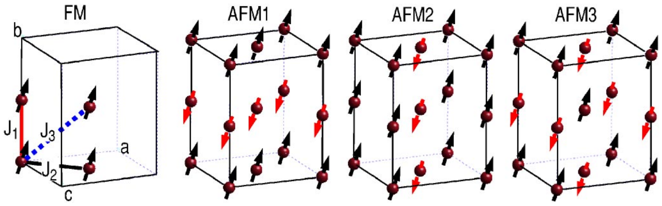

FIG. 2. (Color online) Spin structures considered in this paper. In the "FM" panel, only the four Cu atoms in the unit cell are shown, and the exchange constants are defined.

We describe the magnetic interactions by means of a Heisenberg Hamiltonian $H=1/2\sum_{i,j}J_{ij}\vec{S}_i\cdot\vec{S}_j$ in which we include the exchange constants J_1, J_2, and J_3 defined in Fig. 2. (J_1 and J_2 are, respectively, associated to SE angles α_1 and α_2.) We compute the J's by requiring that this Hamiltonian reproduces, at a classical level, the energy differences between the spin configurations in Fig. 2 calculated from first principles.

Our *ab initio* all-electron results for $SeCuO_3$ and $TeCuO_3$ are given in the first two lines of Table II. In agreement with experiment, we find the FM and AFM ground states for SCO and TCO, respectively. However, the calculations predict that the GS of TCO is AFM1, and not AFM2 as proposed in Ref. 2. Accordingly, it is J_1, not J_2, the magnetic coupling that changes sign when going from SCO to TCO. In fact, even though the change in α_1 is around three times smaller than that in α_2 (see Table I), J_1 varies by about 200% of its value, while J_2 remains almost constant. This clearly indicates that the SE angles have little influence in the magnetic couplings of these solid solutions. The last two lines of Table II show the results obtained when we consider $SeCuO_3$ in the $TeCuO_3$ structure (denoted by "SCO/TCO-st") and vice versa. The results confirm that it is the structure, and not chemical differences between Se and Te, that determines the magnetic GS.

We identify the causes of these results by examining the electronic densities that come out of the calculations. Figure 3(a) shows the spin-up density along Cu-O(2)-Cu paths in the *ac* plane of SCO (the TCO result is essentially the same). There seem to be Cu-O(2) *broken bonds*, which is not so surprising when one notes that the *broken-bond* distance, d_2', is 2.52 Å while the other Cu-O(2) distance, d_2, is only 1.92 Å (see Table I; the values for TCO are similar). The typical Cu-O distance in cuprates is 2 Å, suggesting that in SCO and TCO the SE contribution to J_2 will be unconventional and weaker than usual. In fact, it is questionable that the above-mentioned AGK rules apply in this case, and it seems reasonable that J_2 is largely independent of α_2.

TABLE I. Structural parameters defined in Fig. 1. Values taken from Refs. 12 and 13. Distances in angstroms and angles in degrees. The unit cell volume Ω is in $Å^3$.

System	Ω	α_1	d_1	$\tilde{d}_1$	α_2	d_2/d_2'	$\tilde{d}_2$	$d_{A\text{-O}(1)}$
$SeCuO_3$	231	122.4	2.09	3.66	127.1	1.92/2.52	3.98	1.75
$TeCuO_3$	245	123.5	2.06	3.63	130.5	1.90/2.61	4.11	1.90

TABLE II. Exchange constants of Fig. 2 calculated for various systems (see text). The values are given in meV and the magnetic ground states (GS) are indicated. The results for SCO and TCO are consistent with high-T expansion fits of the susceptibility data in Ref. 2. In TCO there is competition between J_2 and J_3, which probably leads to interesting spin dynamics.

System	GS	J_1	J_2	J_3
SCO	FM	−4.4	−1.3	−0.8
TCO	AFM1	6.3	−1.5	−0.5
SCO/TCO-st	AFM1	17.7	−2.3	−0.6
TCO/SCO-st	FM	−14.3	1.1	−0.7

Figures 3(b) and 3(c) show the spin-up charge density along the Cu-O(1)-Cu path for SCO and TCO, respectively. As far as the Cu-O distances are concerned (see Table I), this SE path is similar in both systems and a more conventional one. However, there is a structural feature that makes a big difference between SCO and TCO, namely, the position of the neighboring A cation with respect to the O(1) atom. In SCO, $d_{A-\text{O}(1)}$ is 1.75 Å, while we have 1.90 Å in TCO. Accordingly, as the density plots in Figs. 3(b) and 3(c) suggest, the Se^{+4} cation probably perturbs the O-2p orbitals more than Te^{+4} does. One may thus hypothesize that this perturbation somehow disrupts the SE mechanism and renders a FM J_1 in SCO, while regular SE results in an AFM J_1 in TCO. To check this conjecture, we calculated the magnetic interactions in TCO as a function of the Te-O(1) distance. The results in Fig. 4 show that, indeed, when Te comes close enough to O(1) (about 1.75 Å), a FM GS results and J_1 switches sign. This is very strong evidence that we have identified the structural feature that controls the magnetic ground state in $Se_{1-x}Te_xCuO_3$ solid solutions.

Microscopic picture. The above results give no information about the electronic mechanisms by which the position of the A cation controls the sign of J_1. One would like to study such a complex problem fully *ab initio*, so that simplifying assumptions are avoided and all the possible mechanisms considered. One would compute the full electronic Hamiltonian in a basis of physically meaningful Wannier functions, so that the effect of the A atom on the electronic interactions (hoppings, Coulomb, and exchange) could be easily monitored. One would then solve these Hamiltonians and map the low-energy excitations to a Heisenberg model,

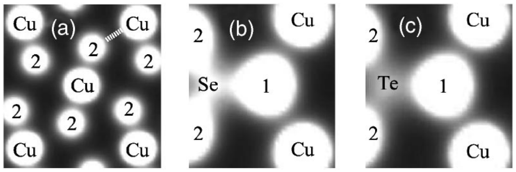

FIG. 3. (Color online) Calculated spin-up charge densities. Panel (a): Cu-O(2)-Cu groups in the *ac* plane of $SeCuO_3$ (see Fig. 1, right top). The dashed line marks one Cu-O(2) *broken bond* (see text). Panels (b) and (c): Cu-O(1)-Cu group and neighboring A cation, for $SeCuO_3$ and $TeCuO_3$, respectively (see Fig. 1, right bottom).

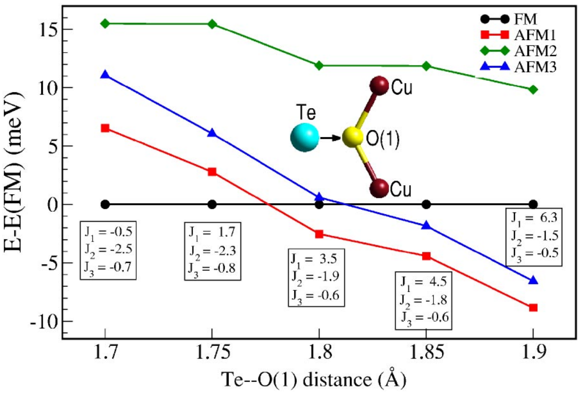

FIG. 4. (Color online) Calculated energy of spin configurations defined in Fig. 2, for $TeCuO_3$, as a function of the Te-O(1) distance. The FM configuration is taken as the zero of energy. Calculated exchange constants are given in meV.

thus obtaining exchange constants. Unfortunately, such a program is beyond our present abilities. We have tried to follow it to the greatest possible extent, and obtained a number of meaningful conclusions.

We started by computing the tight-binding (TB) Hamiltonians associated to our DFT results.[14] We considered TB models in which all valence and low-lying conduction bands are included, which allows us to compute the hybridization between Se/Te and O-2p electrons, as well as the effects of the A cation position on the Cu-3d–O-2p hoppings. As expected, we find that the two Cu-3d–O-2p hoppings along the J_2 SE path are very different. For the *broken-bond* pair (see Fig. 3) we obtain a maximum hopping of 0.35 eV, thus confirming the weakness of the bond, while we get 0.85 eV for the other Cu-O(2) pair. (These are results for SCO. The situation is similar in TCO.) Since the SE contribution to J_2 goes roughly as the fourth power of the Cu-O(2) hoppings, this result indicates that such a contribution will be relatively small.

Regarding the other SE path, the two Cu-O(1) pairs are equivalent by symmetry, and the maximum Cu-3d–O-2p hopping is 0.77 eV in SCO and 0.87 eV in TCO. On the other hand, the maximum Se-4s–O(1)-2p hopping is 4.51 eV in SCO, while for Te-5s–O(1)-2p in TCO we get 3.65 eV. Hence, it seems that the relatively strong Se-4s–O-2p interaction in SCO results in 3d-2p hoppings about 10% smaller than the corresponding ones in TCO. This result confirms quantitatively what Fig. 3 suggests, i.e., that in SCO the Se atom perturbs the Cu-O bond more than the Te atom does in TCO.

One would be tempted to neglect this 10% reduction in the 3d-2p hoppings. However, a simple estimate indicates that such a small change may be relevant in our case. The magnetic coupling J_1 is probably the result of various competing terms that are similar in magnitude. For simplicity, let us consider only two contributions: an AFM SE J_{SE} and a FM direct exchange (DE) K, so that $J_1 = -|K| + J_{SE}$. Let us take the typical values $K = 10$ meV and $J_{SE} = 15$ meV, which render an AFM coupling $J_1 = 5$ meV. From exact results for simple Cu-O-Cu SE models, we know that J_{SE} goes as t,[4] where t is the Cu-3d–O-2p hopping.[15] If t gets smaller by 10%, the corresponding reduction in J_{SE} will be around 50%. Hence, we would have $J_{SE} = 8$ meV, which would render a FM $J_1 = -2$ meV.

The above argument shows that the calculated small reduction in the 3d-2p hoppings can explain the sign change in J_1. However, it relies upon many unjustified assumptions (e.g., that we are dealing with very simple SE and DE mechanisms) and should not be taken too seriuosly. To formulate more meaningful arguments, we need to discuss *effective* electronic Hamiltonians.

Our first-principles TB Hamiltonians can be supplemented with the relevant Coulomb and exchange terms to obtain realistic models of the electronic interactions. We considered minimal models that include on-site Coulomb terms for both Cu-3d and O-2p electrons (denoted U_d and U_p, respectively) and on-site exchange for the O-2p electrons (K_p). We also considered two types of intersite exchange: between Cu-3d and O-2p electrons (K_{dp}) and, alternatively, between Cu-3d electrons of different Cu atoms (K_{dd}). (K_{dd} can be thought of as an *effective* interaction emerging from the K_{dp} couplings, which are the ones that occur in reality.) The resulting Hamiltonians can be viewed as a simplification of Eq. (4) of Ref. 15. We retained the above terms partly guided by numerical evidence that they have the largest effect in the J's. For the U and K parameters, we took typical values from the literature and assumed they do not depend critically on the position of the Se/Te atom. Such an assumption would require a first-principles justification, but that remains for future work.

Solving our effective many-body Hamiltonians for the extended systems is not feasible. Fortunately, we are dealing with insulators in which the electrons are fairly localized and, thus, it is meaningful to study spin excitations confined to small atom groups. We proceed as follows: For a Cu-O(1)-Cu group, we construct the corresponding many-body states by distributing two holes (one per Cu atom) among the Cu-3d and O-2p orbitals of the group atoms. We then construct the group Hamiltonian by projecting the full Hamiltonian onto the group states. The group Hamiltonian can be diagonalized and J_1 computed from the gap between the lowest-lying singlet and triplet states.

Using this approach, we studied the Cu-O(1)-Cu and Cu-O(2)-Cu groups, where the magnetic coupling is described by J_1 and J_2, respectively. By choosing reasonable values of the U and K parameters, we were able to obtain J_1 and J_2 exchange constants in qualitative agreement with the first-principles results for both SCO and TCO. [We used $U_d = 8-9$ eV, $U_p = 5-6$ eV, $K_p = 1-2$ eV, and $K_{dd} = 8.5-12.5$ meV (Ref. 16) (alternatively, $K_{dp} \approx 0.1$ eV).] Our analysis led us to the following conclusions: (i) the SE contribution is AFM in all the cases; (ii) the intersite exchange is necessary to obtain FM J's, and there is no qualitative difference between considering the *actual* K_{dp} or the *effective* K_{dd}; (iii) the structural changes tune the magnetic couplings via their effect on the magnitude of the Cu-3d–O-2p hoppings. Smaller hoppings result in a smaller SE singlet-triplet splitting and, thus, make it easier for the intersite exchange to turn the exchange constant FM.

We also checked whether the Se/Te atom provides alternative paths leading to nonconventional SE couplings. The best candidate is the Cu-O(2)-Se/Te-O(2)-Cu path, which is associated with J_1. (In this case, the group states are constructed by distributing two holes among the Cu-3*d*, O-2*p*, and Se-3*d*/Te-4*d* orbitals.) However, we found its contribution to be negligible. In fact, we found that Se/Te-mediated paths are *inert* because of the large energy cost of creating holes in the Se/Te cations.

Given the drastic approximations underlying our effective electronic Hamiltonians and the simplifications involved in the way we solve the models, the physical picture proposed above should be taken with caution. One should note, however, that our analysis shows that the proposed, relatively simple, mechanism *works*. Moreover, it seems to be quite robust, in the sense that an effect not considered here (e.g., the dependence of the *U* and/or *K* parameters on the *A* cation position) should be quite pronounced to become the dominant mechanism.

In summary, we have studied the $Se_{1-x}Te_xCuO_3$ solid solutions in which the magnetic interactions are controlled by composition-dependent structural changes. Our LDA+U results show that the key structural feature is the position of the supposedly *dummy* atoms Se and Te relative to the Cu-O-Cu SE paths. As the Se/Te atom approaches the Cu -O-Cu group, it acts like a magnetic valve and switches the sign of the magnetic interaction. This is quite a surprising mechanism, as a more conventional one related to the SE angles might have been expected and, in fact, was proposed in the literature.[2] A theoretical analysis, using tight-binding and effective Hamiltonian methods, suggests an appealing physical explanation of the effect: the proximity Se/Te atom weakens the antiferromagnetic superexchange contribution to the magnetic coupling, thus rendering a ferromagnetic interaction. Further theoretical work is required to confirm this picture.

We thank Art Ramirez, Collin Broholm, and David Vanderbilt for useful comments.

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[11] More technical details follow. Brillouin zone integrals: tetrahedron method, 4×4×3 grid. WIEN2K details follow. Semicore orbitals: Cu 3*s* and 3*p*, Se 3*d*, and Te 4*p* and 4*d*. Muffin-tin sphere radii: $R_{Cu}=R_{Se}=1.8$ a.u. and $R_O=1.4$ a.u. for $SeCuO_3$; $R_{Cu}=R_{Te}=1.9$ a.u. and $R_O=1.6$ a.u. for $TeCuO_3$. For modified structures, smaller values are used as needed. The plane-wave cutoff is $K_{max}=7/R_{min}$. PWscf details follow. Valence orbitals: Te 4*d*, 5*s*, and 5*p*; Se 3*d*, 4*s*, and 4*p*; Cu 3*d* and 4*s*; and O 2*s* and 2*p*. Partial core corrections used. Plane-wave cutoff: 30 Ry.

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