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Structural and electronic properties of the two-dimensional superconductor CuS with $1\frac{1}{3}$-valent copper

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We present first-principles calculations of the structural and electronic properties of the CuS covellite material. The symmetry-lowering structural transition is well reproduced. However, the microscopic origin of the transition is unclear. The calculations firmly establish that the previously controversial Cu valency in this compound is 1.33. We also argue that recently reported high-temperature superconductivity (HTSC) in CuS is unlikely to occur in the stoichiometric defect-free material, since the determined Cu valency is too close to 1 to ensure proximity to a Mott-Hubbard state and superexchange spin fluctuations of considerable strength. On the other hand, one can imagine a related system with more holes per Cu in the same structural motif (e.g., due to defects or O impurities), in which case the combination of superexchange and a Fermi surface enlarged compared to that of CuS may lead to unconventional superconductivity, as in HTSC cuprates, but, unlike them, of an f-wave symmetry.

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Copper sulfide in the so-called covellite structure (Fig. 1) has recently attracted attention due to a new report about possible superconductivity at 40 K.[1] This report has been met with understandable skepticism, because previously researchers[2,3] reported reproducible superconductivity at rather low temperatures, around 1–2 K. On the other hand, inspection of the literature reveals that the reported physical properties of covellite are very different in different papers. For instance, the authors of one paper reported a well-defined Curie-Weiss magnetic susceptibility,[4] while others observed a nearly constant behavior consistent with Pauli susceptibility in the absence of any local moments.

The structural properties of covellite are also intriguing. At room temperature it consists of triangular layers of Cu and S, stacked as follows, using standard hexagonal stacking notation: Cu1 and S1 form layers A and B, at the same height, so that Cu1 has coordination of 3 and no direct overlap. Cu2 and S2 form layers B and C, so that Cu2 is directly above S1 and bonds with it, too, albeit more weakly than to S2. Thus, compared to the S2 layer, the Cu2 layer is closer to the Cu1 + S1 one, and Cu2 appears to be inside a tetrahedron, closer to its base. The next layer is again C, so that two S2 atoms are right on top of each other and form a strongly covalent bond, the shortest bond in this system, essentially making up an S_2 molecule.

At $T = 55$ K the system spontaneously undergoes a transition from a hexagonal structure to a lower-symmetry orthorhombic structure.[4] To a good approximation, the transition amounts to sliding the Cu2-S2 plane with respect to the Cu1-S1 plane by 0.2 Å, and the two neighboring Cu2-S2 planes by 0.1 Å with respect to each other, in the same direction. The bond lengths change very little; one of the three Cu2-S2 bonds shortens by 0.04 Å, and the S2-S2 bond lengthens by 0.05 Å, and all other bonds remain essentially unchanged. Note that such transitions are quite uncommon for metals, but rather characteristic of insulating Jahn-Teller systems. Transport properties are hardly sensitive to this transition,[4,5] which is, however, clearly seen in the specific heat.[6]

Thus there are three questions to be asked. First, what is the nature of the low-temperature symmetry lowering? Second, why do some experiments indicate pure Pauli susceptibility, while others observe local moments (through Curie-Weiss behavior)? Third, why does one particular experiment give indications of high-temperature superconductivity,[7] while others do not? Of, course, there is always a chance that the "outlier" experiments are simply incorrect, but it is always worth asking the question whether some sample issues may possibly account for such discrepancies.

In order to address the first question, we have performed density functional theory calculations of both hexagonal (H) and orthorhombic (O) structures. First, we optimized the crystal structure using the standard VASP program with default settings (including gradient corrections) and starting from the experimental structure as reported in Ref. 4.

After that, all calculations in the determined crystal structures were performed using the standard all-electron linear augmented plane wave code WIEN2K. We have also verified that the calculated forces in the optimized structures are small enough. As a technical note, to obtain full convergences in the energy differences we had to go up to $RK_{\max} = 9$.

The results are shown in Table I. Even though there is some discrepancy between the calculated and the experimental low-temperature structures (mostly in terms of an overall overestimation of the equilibrium volume), the correct symmetry lowering is well reproduced. In fact, given that the authors of only one paper have reported internal positions for the orthorhombic structure, and the same authors found a Curie-Weiss law, suggesting, as discussed below, crystallographic defects in their sample, it is fairly possible that the calculations predict the structure of an ideal material better than it was measured in this one experiment.

A more important question now is what the mechanism for this well-reproduced symmetry lowering can be. Ionic symmetry-lowering mechanisms (such as Jahn-Teller distortion) are excluded in a wideband metal like CuS (in addition, 0.02 Å out of 2.33 is atypically small for Jahn-Teller systems). In metals, a lower symmetry is usually stabilized if it results in a reduced density of states at the Fermi level (either as a result of the band Jahn-Teller effect or because of partial nesting). However, the density of states at the Fermi level does not change at this transition (Fig. 2), and the states below the Fermi level actually shift slightly upward. Thus, one-electron

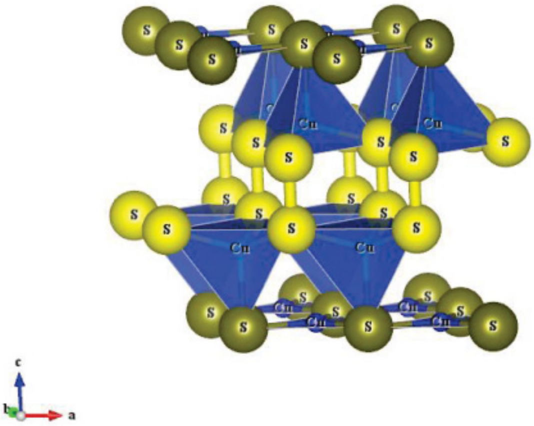

FIG. 1. (Color online) Crystal structure of covellite in the high-symmetry phase. Large yellow spheres indicate sulfur and blue spheres copper. The dark spheres form the planar CuS layers (Cu1), and the light spheres form the warped $\mathrm{Cu_2S_2}$ bilayers (Cu2). Fat yellow sticks indicate strong covalent bonds inside the S2-S2 dumbbells.

energy is not the reason for the transition (which excludes both Jahn-Teller and nesting effects). A look at the calculated Fermi surfaces (Fig. 4) shows that while they become more two dimensional in the orthorhombic structure (the in-plane plasma frequency remains the same, ≈4.0 eV, while that out of plane, 1.36 eV, drops by 12%), there is no shrinkage in their size.

We cannot say definitively what causes the low-temperature symmetry lowering in CuS, but we can say confidently that it is not van der Waals interaction as conjectured in Ref. 8 (for one reason, it would not be reproduced in local density approximation (LDA) or generalized gradient approximation calculations with the requested accuracy, and, also, as discussed below, the interplanar bonding is covalent and not van der Waals), and not a typical metallic mechanism driven by Fermi surface changes. One candidate is ionic Coulomb interaction. Indeed, the calculated Madelung energy is noticeably lower in the orthorhombic structure; however, the Madelung energy is only part of the total electrostatic energy, so from this fact alone one cannot derive definitive conclusions.

TABLE I. The calculated total energy (meV/cell) of the low-temperature orthorhombic and the high-temperature hexagonal structures, using either the experimental or the calculated optimized parameters. Structural parameters used, as well as selected bond length (Å) are also shown. Note that one unit cell includes six formula units. The cell volume is given in $\mathrm{\AA}^3$. The last column corresponds to the orthorhombic structure with internal coordinates optimized, while keeping the experimental unit cell. n/a indicates not applicable.

	H expt.	*O* expt.	*H* calc.	*O* calc.	*O* c.o.
a	3.789	3.760	3.807	3.793	3.760
b	3.789	6.564	3.807	6.623	6.564
c	16.321	16.235	16.496	16.453	16.235
z_{Cu2}	0.1072	0.1070	0.1069	0.1077	0.1083
z_{S2}	0.0611	0.0627	0.0639	0.0646	0.0651
y_{Cu1}	n/a	0.6377	n/a	0.6227	0.6077
y_{Cu2}	n/a	0.3372	n/a	0.3410	0.3413
y_{S1}	n/a	0.3068	n/a	0.2917	0.2760
y_{S2}	n/a	0.0008	n/a	0.0064	0.0069
Cu1-S1	3 × 2.19	2 × 2.18	3 × 2.20	2 × 2.20	2 × 2.20
		2.17		2.19	2.19
Cu2-S1	2.33	2.33	2.36	2.33	2.34
Cu2-S2	3 × 2.31	2 × 2.30	3 × 2.31	2 × 2.30	2 × 2.30
		2.28		2.33	2.33
S2-S2	1.99	2.04	2.11	2.13	2.12
Volume	202.9	200.3	207.0	206.7	207.3
Energy	0	−85	−258	−265	−189

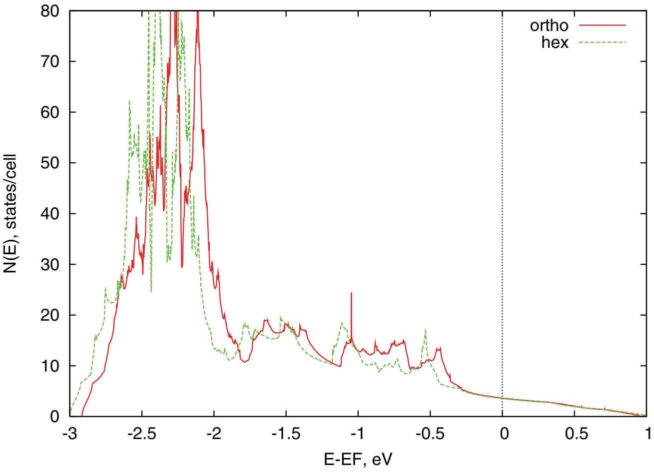

FIG. 2. (Color online) Calculated density of states in the high-temperature ("hex") and low temperature ("ortho") structures, using in both cases optimized parameters.

Let us now discuss the electronic structure. Since the differences between the two structures are very small, we shall limit our discussion to the high-temperature hexagonal structure. The calculated band structure is shown in Fig. 3. Note the two sets of bands, one at −7 eV and the other at 1 eV, of strong S2 p_z character. These are bonding and antibonding bands of the S2-S2 dumbells. Historically, there has been a heated discussion of the Cu valency in this compound, and what is an appropriate ionic model. Both $(\mathrm{Cu}^{1+})_3(\mathrm{S}_2^{2-})(\mathrm{S}^{1-})$ (Ref. 4) and $(\mathrm{Cu}^{1+})_3(\mathrm{S}_2^{1-})(\mathrm{S}^{2-})$ (Ref. 8) have been discussed, assuming monovalent copper. On the other hand, x-ray photoemission spectroscopy[9] and nuclear quadrupole resonance[10] data indicated Cu valency larger than 1 but smaller than 1.5. From our calculations it is immediately obvious that S1 is divalent while S2 is monovalent (the antibonding p_z band of the S2-S2 dimer is 1 eV above the Fermi level, while all S1-derived bands are below the Fermi level), so that Cu has valency 1.33, and the appropriate ionic model is $(\mathrm{Cu}^{4/3+})_3(\mathrm{S}_2^{2-})(\mathrm{S}^{2-})$.

This means that the Cu d band has 1/3 hole per Cu ion, 2.5 times fewer than in the high-T_c cuprates (optimal doping corresponds to 0.8–0.85 holes). This may be too far from half filling for strong correlation effects, but it is nevertheless suggestive of possible spin fluctuations. We will return to this point later.

In order to understand the Cu d bands near the Fermi level, let us consider a simple tight-binding model with two d orbitals, with $m = \pm 2$ (corresponding to combinations of the x^2-y^2 and xy cubic harmonics, which belong to the same representation in the hexagonal group). Since these orbitals are the ones spread farthest in the plane, their hybridization with S is the strongest and they form the highest antibonding states near the Γ point, crossing the Fermi level. Integrating out the S $p_{x,y}$ orbitals, we arrive at the following model band structure:

$$E_k = \frac{1}{2(\varepsilon_d - \varepsilon_p)}\left[\left(3t_{pd\sigma}^2 + 4t_{pd\pi}^2\right)\sum_i \cos(\mathbf{k}\cdot\mathbf{R}_i) \pm \left(3t_{pd\sigma}^2 - 4t_{pd\pi}^2\right)\sqrt{\sum_i \cos^2(\mathbf{k}\cdot\mathbf{R}_i) - \sum_{i>j}\cos(\mathbf{k}\cdot\mathbf{R}_i)\cos(\mathbf{k}\cdot\mathbf{R}_j)}\,\right], \qquad (1)$$

where t are the Cu-S hopping amplitudes, and $\mathbf{R}_i$ are the three standard triangular lattice vectors; $\sum_i \mathbf{R}_i = \mathbf{0}$. Note that these bands are degenerate at Γ, unless spin-orbit coupling is taken into account. Near the top of the band the dispersion is isotropic, and away from it the Fermi surface (FS) develops a characteristic hexagonal rosette shape (Fig. 4).

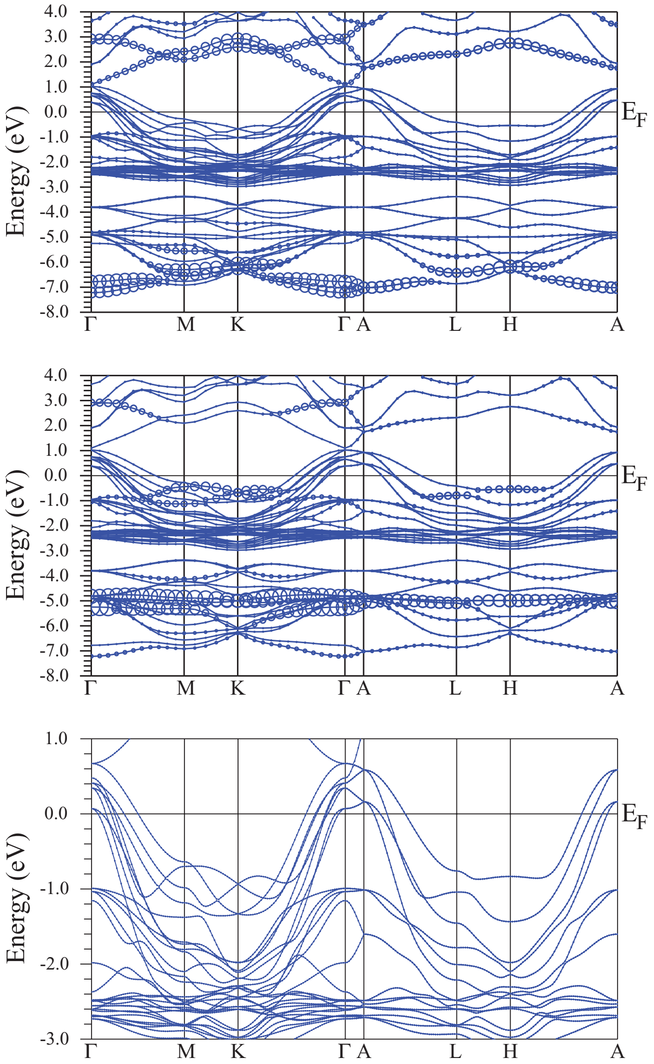

FIG. 3. (Color online) Calculated band dispersions in the hexagonal structure. The points Γ, M and K are in the central plane ($k_z = 0$) and A, L and H in the basal plane ($k_z = \pi/c$). In the top panel, the size of the markers is proportional to the amount of the S2-p_z character in the corresponding states, in the middle one, S1-p_z. One can clearly see the strong bonding-antibonding splitting and unoccupied antibonding states in the former case, and absence of such large splitting in the latter.

Let us now look at the calculated bands (Fig. 3). It is more instructive to concentrate on the right-hand side of Fig. 3, where the k_z dispersion does not obscure the states' degeneracy. We see, as predicted by the model, three sets of nearly parabolic bands, each four times degenerate at the point $A = (0,0,\pi/c)$. One of them is below the Fermi level and two above, forming the eight FS sheets we see in Fig. 4. The middle bands are predominantly formed by the Cu1 and the lower (fully occupied) and upper ones by the Cu2, although there is a substantial mixture of all three Cu orbitals. The average occupation of Cu d orbitals, as described above, is 1/3 hole per Cu, too small to form a magnetic state, even in LDA + U calculations with $U \sim 8$ eV (as verified by direct calculations[11]). Formation of an ordered magnetic state is additionally hindered by the fact that superexchange in this case is antiferromagnetic, and frustrated, as it should be on a triangular lattice. One may think that additional hole doping, achieved through Cu vacancies, broken S-S bonds, or interstitial oxygen (note that this structures includes large pores, one per formula unit, in each Cu-S layer) should bring the d bands closer to half occupancy and promote local magnetic moments (of course, there is no guarantee that a doping level similar to

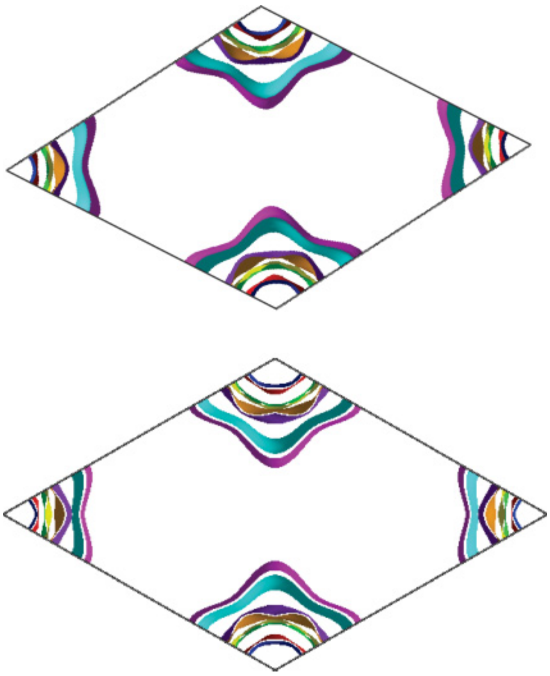

FIG. 4. (Color online) Calculated Fermi surfaces in the hexagonal (top) and orthorhombic (bottom) structure, viewed along the c-axis. Note reduced k_z dispersion in the bottom panel.

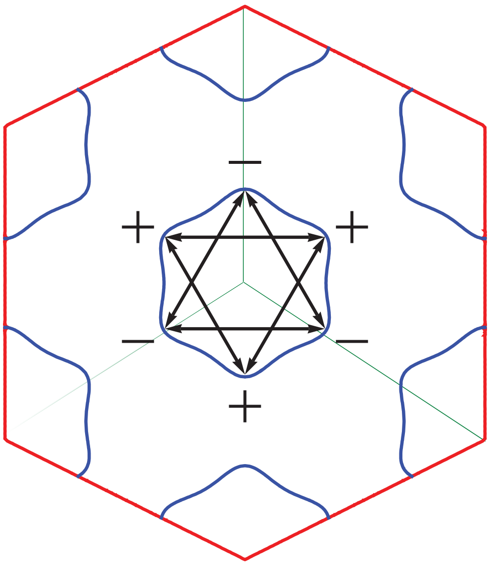

FIG. 5. (Color online) A model Fermi surface, calculated using Eq. (1), overlapped with the wave vectors corresponding to superxchange on a triangular lattice. The signs show a possible $f-$wave pairing state, consistent with superexchange-induced spin fluctuations. Three Brillouin zones are shown in the picture.

that of high-T_c cuprates will have exactly the same effect here, primarily in view of the double degeneracy of the states near the Fermi level; however, lacking more detailed knowledge, the existence of a Mott-Hubbard phase at similar dopings seems to be a fair possibility). Note that in at least one experimental paper a Curie-Weiss behavior was reported, corresponding to $0.28\mu_B/\mathrm{Cu}$,[4] and in another a weak (but inconsistent with the Pauli law) temperature dependence was found,[12] while other authors reported temperature-independent susceptibility.

One can speculate that the unexpected high-temperature superconductivity observed by Raveau *et al.*[1] is a phenomenon of the same sort, namely, that this superconductivity forms in a portion of a sample, the same portion where some previous researchers observed local magnetic moments. As discussed above, it is highly unlikely that a stoichiometric, defectless CuS sample would support either local moments or unconventional superconductivity. However, it is of interest to consider a hypothetical situation that would occur if such moments were present. Indeed in that case one can write down the superexchange interaction between the nearest neighbors as antiferromagnetic Heisenberg exchange, in which case in the reciprocal space it will have the following functional form:

$$J(\mathbf{q}) = J\sum_i \cos(\mathbf{k}\cdot\mathbf{R}_i). \tag{2}$$

In Fig. 5 we show an example of a Fermi surface generated for the model band structure [Eq. (1)], for the simplest case of $t_{pd\pi}=0$. The wave vectors corresponding to the peaks of the superexchange interaction (2) are shown by arrows. An interesting observation is that for this particular doping this superexchange interaction (or, better to say, spin fluctuations generated by this superexchange) would be pairing for a triplet f state shown in the same figure.[13] Indeed, the superexchange vectors always span the lobes of the order parameter with the same sign. Since in a triplet case spin fluctuations generate an attractive interaction, it will be pairing for the geometry shown in Fig. 5. Note that this is opposite to the situation in high-T_c cuprates, where the superexchange interaction occurs between opposite parts of the d-wave order parameter, but in a singlet channel this interaction is repulsive, and therefore pairing when the corresponding parts of the Fermi surface have opposite signs of the order parameter.

While the model Fermi surface shown in Fig. 5 is roughly similar to that calculated in the stoichiometric CuS, the system at this doping is too far from the ordered magnetism to let us assume sizable superexchangelike magnetic fluctuations. Indeed our attempts to stabilize a magnetic solution using a triple unit cell failed, even in a LDA + U calculation. However, one may think of a hole-doped system, where superexchange is operative and the inner Fermi surfaces (albeit not the outer ones) have a geometry similar to that featured in Fig. 5.

Of course, it may not be possible to stabilize a system at sufficient hole doping and retain the required crystallography. Furthermore, in the absence of Jahn-Teller distortion (0.02 Å difference in the bond lengths is very small) the highest occupied band is doubly degenerate ($m=\pm 2$), which may prevent the system from developing strong correlations even if doped to the same level as high-T_c cuprates. Thus, we prefer to think about the model discussed in the previous paragraphs as *inspired* by the CuS covellite, but not necessarily applicable to actual materials derived from this one. The reason we paid so much attention to it is that this is a simple generic model, describing any triangular planar structure with transition metals and ligands in the same plane, as in covellite, in the case where correlations are sufficiently strong to bring about spin fluctuations controlled by superexchange. It is quite exciting that, compared to the popular spin-fluctuation scenario of superconductivity in cuprates, to which it is conceptually so similar, this simple generic model results in a completely different superconducting state, triplet f as opposed to singlet d. This finding may have implications far beyond this particular material and (the yet unconfirmed) superconductivity in it.

Note added. Recently, the authors of Ref. 1 published a Comment on their own paper,[15] (where they effectively withdrew the original claim of superconductivity at 40 K. This is consistent with our conclusion, made prior to learning about this withdrawal, that high temperature superconductivity in pristine CuS is unlikely.

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