Structural and Electronic properties of the 2D Superconductor CuS with 1\(\frac{1}{3}\)-valent Copper

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We present first principle calculations of the structural and electronic properties of the CuS covellite material. Symmetry-lowering structural transition is well reproduced. However, the microscopic origin of the transition is unclear. The calculations firmly establish that the so far controversial Cu valency in this compound is 1.33. We also argue that recently reported high-temperature superconductivity 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 combination of superexchange and an enlarged compared to CuS Fermi surface may lead to unconventional superconductivity, similar to HTSC cuprate, 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. This report has been met with understandable skepticism, because previous researches reported reproducible superconductivity at rather low temperatures, around 1-2 K. On the other hand, inspection of the literature reveals that reported physical properties of covellite are drastically different in different papers. For instance, one paper reported a well defined Curie-Weiss magnetic susceptibility, while others observed a nearly constant behavior consistent with the Pauli susceptibility in absence of any local moments.

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 Cu\(_2\)S\(_2\) bilayers (Cu2). Fat yellow sticks indicate strong covalent bonds inside the S2-S2 dumbbells.

Structural properties of the 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 three 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. 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 bonds 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, which is however clearly seen in the specific heat.

Thus there are three questions to be asked. First, what is the nature of the low temperature symmetry-lowering? Second, why some experiments indicate pure Pauli susceptibility, while others observe local moments (through Curie-Weiss behavior)? Third, why one particular experiment sees indications of high temperature superconductivity, while others do not? Of course, there is always a chance the “outliers” 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
TABLE I: The calculated total energy (meV/cell) of the low-
temperature orthorhombic and the high-temperature hexagonal
structure, using either the experimental or the calculated
optimized parameters. Structural parameters used, as well
as selected bond length (\AA) are also shown. Note that one
unit cell includes 6 formula units. The cell volume is given in
\AA^3. The last column corresponds to the orthorhombic struc-
ture with internal coordinates optimized, while keeping the
experimental unit cell.

|        | H-exp | O-exp | 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| 2×2.20 | 2×2.20 | 2×2.20 |
| \(Cu2-S1\)| 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 |
| \(S2-S2\)| 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   |

density functional calculations (DFT) of both hexagonal (H) and orthorhombic (O) structure. First, we opti-
imized the crystal structure using the standard VASP
program with default settings (including gradient correc-
tions), 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
LAPW 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 \(RK_{\text{max}} = 9\).

The results are shown in Table 1. Even though there is
some discrepancy between the calculated and the experi-
mental 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 only one paper has reported internal positions
for the orthorhombic structure, and the same paper found
a Curie-Weiss law, suggesting, as discussed below, crys-
tallographic defects in their sample, it is fairly possible
that the calculations predict the structure of an ideal
material better than this one experiment has measured.

A more important question now is, what the mecha-
nism for this well-reproduce symmetry lowering can be?
If ionic symmetry-lowering mechanisms (such as Jahn-
Teller) are excluded in a wide band metal like CuS, Typ-
ically, a lower symmetry is stabilized in a metal if it re-
sults in a reduced density of states at the Fermi level
("quasinesting mechanism"). However, the density of
states at the Fermi level does not change at this tran-
sition (Fig. 2), and the states below Fermi actually shift
slightly upward. Thus, one-electron energy is not the
reason for the transition. A look at the calculated Fermi
surfaces (Fig. 4) shows that while they become more 2D
in the orthorhombic structure (the in-plane plasma fre-
quency remains the same, \(\approx 4.0\) 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 con-
jectured in Ref. [3] (for one, it would not be reproduced
in LGA/GGA calculations with requested accuracy, and,
also, as discussed below, the interplanar bonding is cova-
lent, and not van der Waals), and not a typical metallic
mechanism driven by Fermi surface changes. One can-
didate is ionic Coulomb interaction. Indeed the calcu-
lated Ewald energy is noticeably lower in the orthorhom-
bic structure. However the Ewald energy is only part
of total electrostatic energy, so from this fact alone one
cannot derive definitive conclusions.

Let us now discuss the electronic structure. Since the
differences between the two structures are very small, we
shall limit our discussion by the high-temperature hexag-
onal structure. The calculated band structure is shown in
Fig. 3. Note two sets of bands, one at \(-7\) eV and the other at \(1\) eV, of strong S2-
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 appro-
riate ionic model. Both \((\text{Cu}^{+1})(\text{S}^{2-})^3(\text{S}^{-1})\) (Ref. [4])
and \((\text{Cu}^{+1})(\text{S}^{2-})^3(\text{S}^{-2})\) (Ref. [4]) have been discussed,
assuming monovalent copper. On the other hand, XPS

![FIG. 2: (color online) Calculated density of states in the high-temperature ("hex") and low temperature ("ortho") structures, using in both cases optimized parameters.](image-url)
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 Fermi level. Near the top of the band the dispersion is isotropic, and away from it 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 \((\text{Cu}^{+4/3})_3(S^2^{-2})_2(S^{-2})\).

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 most far in the plane, their hybridization with S is the strongest and they form the highest antibonding states near the \( \Gamma \) point, crossing the Fermi level. Integrating out the \( S \) \( p_{x,y} \) orbitals we arrive at the following model band structure:

\[
E_k = \frac{1}{2(e_d - e_p)} \left[ (3t_{pdx}^2 + 4t_{pdz}^2) \sum_i \cos(k \cdot R_i) \pm (3t_{pdx}^2 - 4t_{pdz}^2) \sqrt{\sum_i \cos^2(k \cdot R_i) - \sum_{i,j} \cos(k \cdot R_i) \cos(k \cdot R_j)} \right],
\]

where \( t \) are the Cu-S hopping amplitudes, and \( R_i \) are the three standard triangular lattice vectors, \( \sum R_i = 0 \). Note that these bands are degenerate at \( \Gamma \), 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 develops a characteristic hexagonal rosette shape (Fig. 4).

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 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 with \( U \sim 8 \) eV (as verified by direct calculations). Formation of an ordered magnetic state is additionally hindered by the fact that superexchange is 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-occucpancy and promote local magnetic moments. Note that in at least one experimental paper a Curie-Weiss behavior was reported, corresponding to 0.28 \( \mu_B/\text{Cu} \), and in another a weak, but inconsistent with the Pauli law, temperature dependence was found, while other authors reported temperature-independent susceptibility.

One can speculate that the unexpected high-temperature superconductivity observed by Raveau et al.\(^{12}\) is a phenomenon of the same sort, namely that this

FIG. 3: Calculated band dispersions in the hexagonal structure. The points \( \Gamma, M \) 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 width of the lines is proportional to the amount of the \( S_2-p_z \) character in the corresponding states.
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.

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 take place 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:

\[
J(q) = J \sum_i \cos(k \cdot R_i). \tag{2}
\]

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 picture. 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 high-\( T_c \) cuprates, where the superexchange interaction spans parts with the 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 sizeable superexchange-like magnetic fluctuations. As mentioned, our attempts to stabilize an antiferromagnetic (more precisely, ferrimagnetic, since we only tried collinear magnetic patterns) using a triple unit cell failed, even in LDA+U. One may think of a hole doped system, where superexchange is operative and the inner Fermi surfaces (albeit not the outer ones) have 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. We prefer to think about the model discussed in the previous paragraphs as inspired by the CuS covellite, but not necessary 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 the covellite, in 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 (yet unconfirmed) superconductivity in it.

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