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Contribution from the Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204,
and Laboratorie de Chimie Théorique,[§] Université de Paris-Sud, 91405 Orsay, France

Apparent Absence of Electronic Instability in the One-Dimensional Metal $\mathrm{Na_3Cu_4S_4}$

Myung-Hwan Whangbo*[†] and Enric Canadell*[‡]

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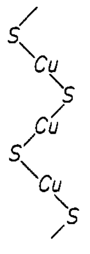
A probable cause for why a charge density wave instability is absent in the one-dimensional metal $\mathrm{Na_3Cu_4S_4}$ was examined by performing tight-binding band electronic structure calculations. Analysis of the vibrational modes needed for charge density wave formation suggests that the strain energy they are likely to induce may offset the electronic energy stabilization associated with charge density wave formation.

Most alkali-metal copper chalcogenides have a layered structure in which copper–chalcogen layers are separated by alkali-metal ions.[1-4] In contrast, KCuS[5] and $\mathrm{Na_3Cu_4S_4}$[6] do not have a layered structure. KCuS has "trans"-CuS chains (**1**) separated by $\mathrm{K^+}$ ions, while $\mathrm{Na_3Cu_4S_4}$ contains $\mathrm{Cu_4S_4^{3-}}$ columns made up of four "cis"-CuS chains (**2a**). Two adjacent cis-CuS chains of a $\mathrm{Cu_4S_4^{3-}}$ column are arranged to form nearly trigonal-planar copper centers as depicted in **3**. According to the convention in which the projection view of **2a** along the chain is given by **2b**, a $\mathrm{Cu_4S_4^{3-}}$ column can be represented by **4**. In $\mathrm{Na_3Cu_4S_4}$, $\mathrm{Na^+}$ cations separate $\mathrm{Cu_4S_4^{3-}}$ columns as shown in **5**. The copper–sulfur layers of $\mathrm{KCu_3S_2}$[1] and $\mathrm{A_3Cu_8S_6}$ (A = K, Rb, Cs)[2] contain the $\mathrm{Cu_4S_4}$ columns, which are linked by copper–sulfur chains of tetrahedrally coordinated Cu atoms, as schematically shown in **6** and **7**, respectively. The copper–chalcogen layers of $\mathrm{ACu_4X_3}$ (A = K, Cs, Rb, Tl; X = S, Se)[3] and $\mathrm{TlCu_2Se_2}$[4] contain only tetrahedrally coordinated copper atoms.



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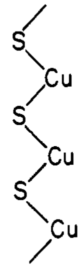

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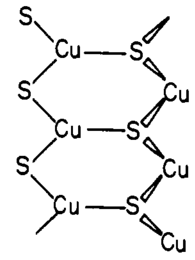
2b



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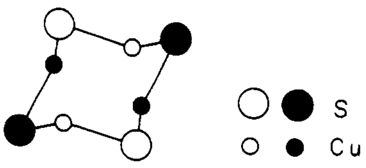

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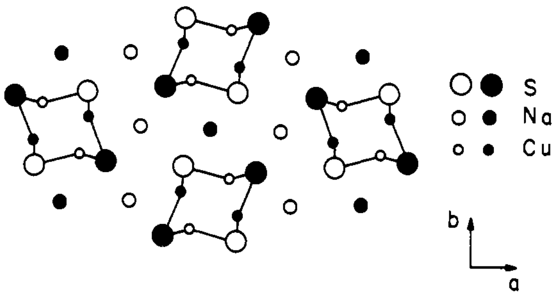

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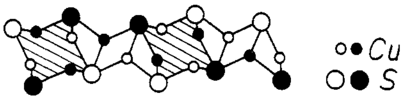

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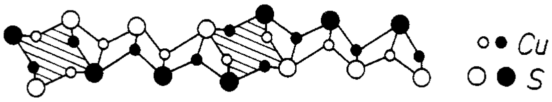

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According to the photoelectron spectroscopic study of Folmer and Jellinek,[7] binary and ternary copper chalcogenides requiring a mixed-valence representation are better described in terms of $\mathrm{X^{2-}}$ and $\mathrm{X^-}$ rather than $\mathrm{Cu^+}$ and $\mathrm{Cu^{2+}}$. Thus, with the formal oxidation state $\mathrm{A^+}$ for the alkali metal or Tl and $\mathrm{Cu^+}$ for copper, chalcogen is in the monovalence state $\mathrm{X^{2-}}$ for KCuS and $\mathrm{KCu_3S_2}$ but in a mixed-valence state of $\mathrm{X^{2-}}$ and $\mathrm{X^-}$ for the other alkali-metal or thallium copper chalcogenides. Consequently, it is expected that KCuS and $\mathrm{KCu_3S_2}$ are semiconductors, while $\mathrm{Na_3Cu_4S_4}$, $\mathrm{ACu_4X_3}$ (A = K, Rb, Cs, Tl; X = S, Se), $\mathrm{A_3Cu_8X_6}$ (A = K, Rb, Cs; X = S, Se), and $\mathrm{TlCu_2Se_2}$ are metals. In agreement with this prediction, $\mathrm{Na_3Cu_4S_4}$,[8] $\mathrm{KCu_4S_3}$,[3a] $\mathrm{K_3Cu_8S_6}$,[9] and Tl-

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[†] North Carolina State University.

[‡] Université de Paris-Sud.

[§] The Laboratorie de Chimie Théorique is associated with the CNRS (UA 506) and is a member of the ICMO and the IPCM (Orsay, France).

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Table I. Parameters and Exponents Used in the Calculations

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	$c_1{}^a$	$c_2{}^a$
S	3s	-20.00	1.817			
	3p	-13.30	1.817			
Cu	4s	-11.40	2.20			
	4p	-6.06	2.20			
	3d	-14.00	5.95	2.30	0.5933	0.5744

^{a}Contraction coefficients used in the double-ζ expansion.

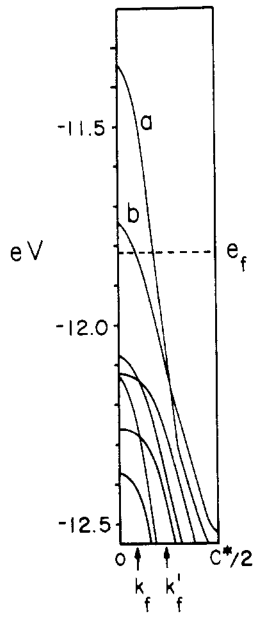


Figure 1. Dispersion reltions of the bands calculated for the $Cu_4S_4{}^{3-}$ column in the highest occupied band region, where the dashed line refers to the Fermi level. The Fermi vectors k_f and k_f' refer to the partially filled bands b and a, respectively.

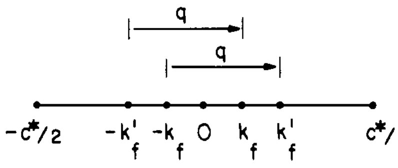
Cu_2Se_2[4a,10] are all observed to be metals. It is interesting to note that the layered compound $K_3Cu_8S_6$ exhibits a charge density wave (CDW) phenomenon,[9] which is typically found for one-dimensional (1D) metals. This observation may not be surprising in that the copper–sulfur layers **7** of $K_3Cu_8S_6$ are made up of two different types of 1D chains, one with Cu atoms of trigonal-planar coordination and the other with Cu atoms of tetrahedral coordination. The Cu_4S_4 columns of $Na_3Cu_4S_4$ are all isolated from one another, since the shortest intercolumn S···S contact distance (i.e., 4.23 Å) is well beyond the van der Waals radii sum of 3.60 Å. That is, $Na_3Cu_4S_4$ should be more strongly 1D in metallic character than is $K_3Cu_8S_6$. Consequently, $Na_3Cu_4S_4$ is expected to have an electronic instability toward a metal–insulator transition, which leads to a CDW or a spin density wave (SDW) state. However, $Na_3Cu_4S_4$ has been reported to be metallic[8] down to 13 K (the lowest temperture employed) without showing any of the resistivity anomalies that usually accompany a CDW phenomenon. In the present work, we discuss this apparently puzzling property of $Na_3Cu_4S_4$ by performing tight-binding band electronic structure calculations[11] on the basis of the extended Hückel method.[12] The atomic parameters employed in our study are summarized in Table I.

Band Electronic Structure

Figure 1 shows the dispersion relations of the highest occupied bands calculated for a single $Cu_4S_4{}^{3-}$ column. The Fermi level (dashed line) cuts the top two bands (a and b), both of which are half sulfur and half copper in character. Thus, the oxidation formalism appropriate for a $Cu_4S_4{}^{3-}$ column is a hybrid of ($3Cu^+ + Cu^{2+}$) + $4S^{2-}$ and $4Cu^+$ + ($3S^{2-} + S^-$). Our band calculations on three-dimensional (3D) $Na_3Cu_4S_4$ lattice show that the dispersions of the two partially filled bands along the intercolumn directions are extremely weak, as expected from the long intercolumn S···S distances (4.23 and 4.36 Å).

The Fermi wave vectors of the two partially filled bands are calculated to be $k_f = 0.07c^*$ and $k_f' = 0.18c^*$, where $k_f + k_f' = c^*/4$ since the two bands as a whole have three electrons. Of the two partially filled bands a and b, the upper one (band a) is unfilled in the wave vector region from $-k_f'$ to k_f', and the lower one (band b) in the region from $-k_f$ to k_f. Thus the Fermi surfaces of the two bands (i.e., boundaries between filled and unfilled wave vector regions) are given by the four points $-k_f'$, $-k_f$, k_f, and k_f'.

When a piece of a Fermi surface is superposed onto another piece upon translation with a vector q, the two pieces are said to be nested by q. A normal metallic state with a nested Fermi surface is generally suspectible toward a CDW or an SDW formation associated with the nesting vector q. As shown in **8**, the Fermi surface of $Na_3Cu_4S_4$ is nested by the vector $q = k_f + k_f'$. Given two partially filled bands, it is possible to consider Fermi surface nesting within each band (a and b) thereby obtaining two separate nesting vectors $q_1 = 2k_f$ and $q_2 = 2k_f'$. However, the tendency to form a CDW or an SDW is stronger when all the Fermi surface area is nested by a single vector. For in such a case a single CDW or SDW will remove all the surface thereby more effectively lowering the electronic energy. Consequently, the nesting between the two separate bands a and b giving rise to a single nesting vector $q = k_f + k_f'$ should be energetically more favorable than the alternative nesting that leads to two different nesting vectors q_1 and q_2.



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Formation of a CDW or an SDW state originates from orbital mixing between the filled levels $\phi(\mathbf{k})$ and unfilled levels $\phi(\mathbf{k}')$ related by the nesting vectors $\mathbf{q} = \mathbf{k} - \mathbf{k}'$.[13] The driving force for the orbital mixing is the interaction energy $\langle\phi(\mathbf{k})|H'|\phi(\mathbf{k}')\rangle$, where the perturbation H' is lattice vibration for CDW formation and electron repulsion for SDW formation. The tendency to form a CDW or an SDW state becomes weak when a random potential is introduced into the lattice, since it will reduce the extent of crystallinity and hence that of orbital phase coherence in $\phi(\mathbf{k})$ and $\phi(\mathbf{k}')$, thereby making the matrix elements $\langle\phi(\mathbf{k})|H'|\phi(\mathbf{k}')\rangle$ small in magnitude. If these elements were small for a particular reason in the absence of a random potential, they would become negligible in the presence of a random potential. Therefore, the absence of a CDW formation in $Na_3Cu_4S_4$ down to 13 K despite a perfect Fermi surface nesting may be a consequence of two factors. One is that the Na positions of $Na_3Cu_4S_4$ are not completely occupied thereby providing a source of random potential. The other is that the $\langle\phi(\mathbf{k})|H'|\phi(\mathbf{k}')\rangle$ elements are small. In the following, we examine why the latter may be the case.

Orbital Symmetry and Interaction

The two partially filled bands of Figure 1 are essentially made up of the cis-CuS chain orbital shown in **9**, which is antibonding between copper d and sulfur p orbitals. For two adjacent cis-CuS chains (e.g., **3**), their chain orbitals may be combined in phase (**10a**) or out of phase (**10b**). The bonding and antibonding

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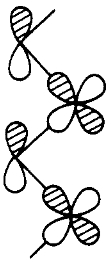

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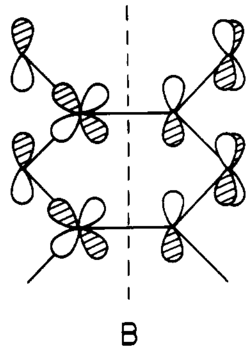

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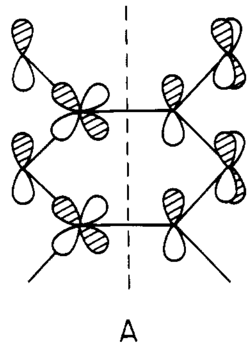
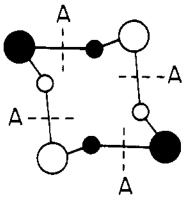
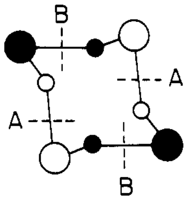


10b

between CuS chain orbitals may be denoted by the labels B and A, respectively. Then, in the vicinity of the Fermi level, all neighboring chain orbitals are combined out of phase in band a as indicated in **11a**, while bonding and antibonding combinations alternate between neighboring chains in band b as shown in **11b**. Consequently, in terms of the C_2 rotation along the chain direction (see **12**), the orbitals of band a are symmetric but those of band b are antisymmetric. Since the Fermi surface nesting $q = k_f + k_f'$ mixes the orbitals of band a with those of band b, the lattice distortion mode H', which makes the $\langle \phi(\mathbf{k})|H'|\phi(\mathbf{k}')\rangle$ elements nonvanishing, should be antisymmetric with respect to the C_2 rotation (**12**). Two examples of antisymmetric distortion in the $Cu_4S_4^{3-}$ column are schematically shown in **13a** and **13b**, where each cis-CuS chain is represented by a straight line. Such antisymmetric distortions are likely to induce a severe strain in the $Cu_4S_4^{3-}$ column. In such a case, the electronic energy stabilization resulting from the matrix elements $\langle \phi(\mathbf{k})|H'|\phi(\mathbf{k}')\rangle$ may not be large enough to compensate the strain energy even in the absence of a random potential.



11a



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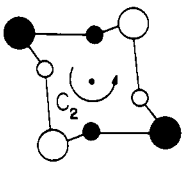

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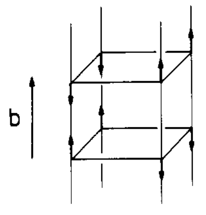

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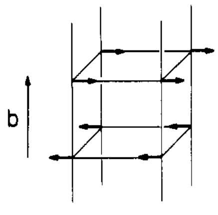

13b

Concluding Remarks

$Na_3Cu_4S_4$ contains $Cu_4S_4^{3-}$ columns separated by Na^+ cations. In agreement with this structural characteristic, our band structure calculations show that $Na_3Cu_4S_4$ is a 1D metal with nearly perfect Fermi surface nesting. Thus, it is surprising that $Na_3Cu_4S_4$ apparently does not show a CDW instability down to 13 K. According to our band orbital analysis, this can be explained if there are some Na^+ vacancies in the lattice and if the antisymmetric modes of vibration needed for a CDW formation induce a severe strain into the $Cu_4S_4^{3-}$ columns. For a 1D metal with perfect Fermi surface nesting, a SDW is an alternative state to reach.[14] Since SDW states are usually observed at low temperatures, it would be interesting to study the electronic properties of $Na_3Cu_4S_4$ below 13 K.

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