J. Am. Chem. Soc. **1996,** *118,* 693−694

$NaCu_4S_4$, a Simple New Low-Dimensional, Metallic Copper Polychalcogenide, Structurally Related to CuS

Xiang Zhang and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

Tim Hogan and Carl R. Kannewurf

Department of Electrical Engineering and
Computer Science, Northwestern University
Evanston, Illinois 60208

Received August 28, 1995

The copper chalcogenide family consists of a relatively large number of binary and ternary members which belong to two general categories, those which are valence-precise and those which are mixed-valent. The mixed-valent compounds have been of particular interest and subject to numerous synthetic, physical, and theoretical investigations because they exhibit interesting properties, such as metallic conductivity, superconductivity,[1] and charge-density waves.[2] Examples include CuQ (Q = S, Se),[3] CuS_2,[4] CuTe,[5] $Na_3Cu_4S_4$,[6] ACu_4Q_3 (A = K, Rb, Cs; Q = S, Se),[7] $A_3Cu_8Q_6$ (A = K, Rb, Cs; Q = S, Se),[8] $Cs_2Cu_5Se_4$,[9] $K_2Cu_5Te_5$,[10] and $A_3Cu_8Te_{10}$ (A = Rb, Cs).[11] In a few instances, the mixed-valency coexists with the presence of chalcogen−chalcogen bonds as, for example, in CuQ (Q = S, Se), CuS_2, $K_2Cu_5Te_5$, and $A_3Cu_8Te_{10}$. CuS is distinguished among the binary (1:1) metal sulfides because of its unique structure, which contains both monosulfides and disulfides, and its mixed-valency. The latter is thought to be mostly associated with partial oxidation of sulfide rather than the $Cu^{+/2+}$ couple. This occurs because the energies of the Cu^+ 4d orbitals lie slightly lower relative to those of the sulfide 3p orbitals. The related valence-precise ternary compounds are semiconductors such as $NaCu_5S_3$,[12] ACuQ (A = Na, K; Q = S, Se, Te),[13] ACu_3Q_2 (A = Na, K),[14] and $K_4Cu_8Te_{11}$.[15] In this communication, we report the synthesis, structure, and properties of a new simple mixed-valent ternary copper phase, $NaCu_4S_4$, with a novel two-dimensional structure related to that of CuS.

$NaCu_4S_4$ was synthesized from a mixed Na/Ba/S flux, which was initially intended to stabilize quaternary Na/Ba/Cu/S compounds. So far, we have not been able to synthesize it from reactions of Cu with nNa_2S_x ($n = 1-3$, $x = 7-2.33$) fluxes, which generate only the known CuS. The structure of $NaCu_4S_4$ is a new two-dimensional Cu/S framework of trigonal symmetry (see Figure 1).[16] Anionic $[Cu_4(S_2)(S)_2]^-$ layers, which contain both S_2^{2-} and S^{2-}, alternate with charge-compensating Na^+ ions. The structure of the $[Cu_4(S_2)(S)_2]^-$ slab is composed of a Cu_2S_2 layer of anti-GaS structure type, sandwiched between two BN-type CuS layers. The connections are made via Cu−S bonds involving metal atoms from the anti-GaS type layer and sulfur atoms from the BN-type layers. The BN-type layers become slightly puckered, and the deviation from planarity is attributed to both ionic Na^+—S^{2-} interactions and $Na^+\cdots Cu^+$ repulsions. This results in four-coordinated monosulfide atoms with an unusual inverted (umbrella) tetrahedral geometry. The structure of $NaCu_4S_4$ is akin to that of CuS itself, in that in the binary solid, the anti-GaS type Cu_2S_2 layers alternate with the BN-type CuS layers, forming an infinite stack along the *c*-axis. In $NaCu_4S_4$, every other anti-GaS layer is missing and is replaced by a layer of Na atoms. There are two crystallographically independent Cu atoms in the structure: (a) Cu(1) is tetrahedrally coordinated by one $S(1)^{2-}$ and three $S(2)_2^{2-}$ and (b) the three-coordinated Cu(2) lies slightly above a trigonal planar environment of three $S(1)^{2-}$ ions. The Na−S distance is normal, at 2.927(4) Å. The S(2)−S(2) distance is slightly longer than a typical S−S single bond in S_2^{2-}, at 2.09(1) Å, but shorter than the 2.15 Å found in CuS.

The formal oxidation states of $NaCu_4S_4$ do not balance unless we invoke mixed-valency. If all monosulfides and disulfides are considered as 2−, then the charges on the metal reduce to $Na(Cu^+)_2(Cu^{2+})(S_2)S_2$. If, however, the metals are to be taken as 1+, then either $S^{2-/-}$ or $S_2^{2-/-}$ mixed-valency is required, which should manifest itself as holes in the sulfur-based valence band. This situation is similar to that in CuS, where the formal charge of Cu is 1+ and the average charge of S is 1−.[3] In CuS, the electron deficiency (holes) in S is partially relieved by formation of S−S bonds (for two-thirds of the S atoms) and partially delocalized through the S p-band to give the formalism of $(Cu^+)_3(S_2^{2-})(S^-)$ or $(Cu^+)_3(S_2^-)(S^{2-})$. Thus, CuS displays ideal metallic behavior. In $NaCu_4S_4$, the [CuS] framework has a 0.25− net charge, and the average charge of S is further reduced to 1.25−, still short of 2− for a filled S^{2-} p-band. The addition of extra electrons in the sulfur bands of [CuS] does not generate a valence-precise electronic structure. Instead, it

---

[1] (a) Munson, R. A.; DeSorbo, W.; Kouvel, J. S. *J. Chem. Phys.* **1967**, *47*, 1769−1770. (b) Meissner, W. *Z. Phys.* **1929**, *58*, 570. (c) Shoenberg, D. *Nature* **1938**, *142*, 874.

[2] Fleming, R. M.; ter Haar, L. W.; DiSalvo, F. J. *Phys. Rev. B* **1987**, *35*, 5388−5391.

[3] (a) Takeuchi, K.; Kudoh, Y.; Sato, G. *Z. Kristallogr.* **1985**, *173*, 119−128. (b) Fjellvåg, H.; Gronvold, F.; Stolen, S. *Z. Kristallogr.* **1988**, *184*, 111−121. (c) Stevels, A. L. N.; Jellinek, F. J. *R. Neth. Chem. Soc. Rec.* **1971**, *90*, 273−283. (d) Arunsingh; Srivastava, O. N.; Dayal, B. *Acta Crystallogr.* **1972**, *28B*, 635−638.

[4] Munson, R. A. *Inorg. Chem.* **1966**, *5*, 1296.

[5] (a) Patzak, I. *Z. Met.* **1956**, *47*, 418−420. (b) Baranova, R. V.; Pinsker, Z. G.

[6] (a) Burschka, C. *Z. Naturforsch.* **1979**, *B34*, 396−397. (b) Peplinski, Z.; Brown D. B.; Watt, T.; Hatfield, W. E.; Day, P. *Inorg. Chem.* **1982**, *21*, 1752−1755. (c) Whangbo, M. H.; Canadell, E. *Inorg. Chem.* **1990**, *29*, 1395−1397.

[7] (a) Rüdorff, W.; Schwarz, H. G.; Walter, M. *Z. Anorg. Allg. Chem.* **1952**, *269*, 141−152. (b) Brown, D. B.; Zubieta, J. A.; Vella, P. A.; Wrobleski, J. T.; Watt, T.; Hatfield, W. E.; Day, P. *Inorg. Chem.* **1980**, *19*, 1945−1950. (c) Klepp, K.; Boller, H.; Völlenkle, H. *Monatsh. Chem.* **1980**, *111*, 727−733. (d) Burschka, C. *Z. Anorg. Allg. Chem.* **1980**, *463*, 65−71. (e) Viola, F.; Schöllhorn, R. *J. Chem. Soc., Chem. Commun.* **1992**, 907−908.

[8] (a) Burschka, C. *Z. Naturforsch.* **1979**, *B34*, 675−677. (b) ter Haar, L. W.; Di Salva, F. J.; Bair H. E.; Fleming, R. M.; Waszczak, J. V.; Hatfield, W. E. *Phys. Rev. B* **1987**, *35*, 1932−1938. (c) Schils, H.; Bronger, W. *Z. Anorg. Allg. Chem.* **1979**, *456*, 187−193.

[9] Bronger, W.; Schils, H. *J. Less Common Met.* **1982**, *83*, 279−285.

[10] Park, Y.; Kanatzidis, M. G. *Chem. Mater.* **1991**, *3*, 781−783.

[11] Zhang, X.; Park, Y.; Hogan, T.; Schindler, J.; Kannewurf, C. R.; Seong, S.; Albright, T.; Kanatzidis, M. G. Submitted to *J. Am. Chem. Soc.*

[12] Effenberger, H.; Pertlik, F. *Monatsh. Chem.* **1985**, *116*, 921−926.

[13] (a) Savelsberg, G.; Schäfer, H. *Z. Naturforsch.* **1978**, *B33*, 711−713. (b) Savelsberg, G.; Schäfer, H. *Z. Naturforsch.* **1978**, *B33*, 370−373.

[14] Klepp, K. O. *J. Less Common Met.* **1987**, *128*, 79−89.

[15] Park, Y.; DeGroot, D. C.; Schindler, J.; Kannewurf, C. R.; Kanatzidis, M. G. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1325−1328.

[16] (a) Crystal data at 23 °C (Mo Kα radiation): $a = 3.830(3)$ Å, $c = 12.074(6)$ Å, $V = 153.4(2)$ Å^3, $Z = 1$, $d_{calc} = 4.390$ g cm^{-3}, space group *P*-3*m*1 (no. 164), $2\theta_{max} = 50°$; no. of data collected, 711; no. of independent data, 137; independent data observed with $I > 3\sigma(I)$, 117; no. of variables, 15; $\mu = 149.9$ cm^{-1}; final $R = 0.045$; $R_w = 0.057$; goodness-of-fit, 2.91. The structure was solved by direct methods of SHELXS-86[16b] and refined with the TEXSAN[16c] package of crystallographic programs for the others. An empirical absorption correction based on ψ-scans was applied to the data, followed by a DIFABS[16d] correction to the isotropically refined structure. All atoms were then refined anisotropically. (b) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford, UK, 1985; pp 175−189. (c) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp. 1985. (d) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166. Experimental procedure: for the synthesis of $NaCu_4S_4$, a Pyrex tube (∼5 mL) containing Cu (0.032 g, 0.5 mmol), Na_2S (0.117 g, 1.5 mmol), BaS (0.042 g, 0.25 mmol), and S (0.096 g, 3 mmol) was evacuated and sealed under vacuum. The tube was heated at 500 °C for 4 days and then slowly cooled to 140 °C at 4 °C h^{-1}. After removal of the excess polysulfide flux with *N,N*-dimethylformamide and water under N_2 atmosphere, thin plate-like black crystals were obtained in 79% yield.

0002-7863/96/1518-0693$12.00/0

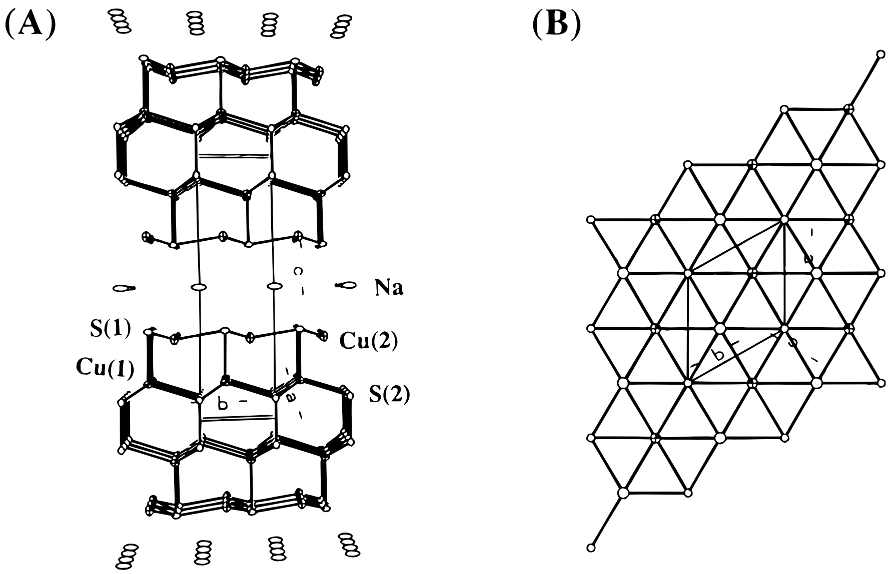

Figure 1. ORTEP representation and labeling scheme of (A) the packing diagram of $NaCu_4S_4$ and (B) one $[Cu_4S_4]^-$ layer viewed down the c−axis. Selected bond distances [Å] and angles [deg]: Cu(1)−S(1), 2.335(6); Cu(1)−S(2), 2.332(3); Cu(2)−S(1), 2.242(2); S(2)−S(2), 2.09(1); S(1)−Na, 2.927(4); Cu(2)−Na, 3.180(3); S(1)−Cu(1)−S(2), 108.5(1); S(2)−Cu(1)−S(2), 110.4(1), S(1)−Cu(2)−S(1), 117.36(9); Cu(1)−S(1)−Cu(2), 80.5(2); Cu(2)−S(1)−Cu(2), 117.36(9); Cu(1)−S(2)−Cu(1), 110.4(1).

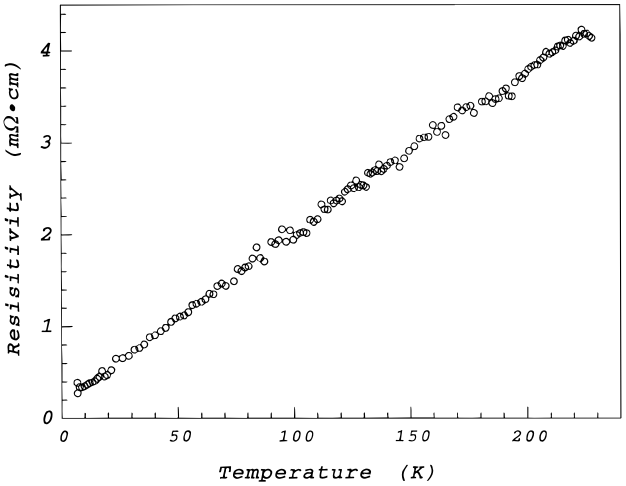

Figure 2. Four-probe electrical resistivity data as a function of temperature for a single crystal of $NaCu_4S_4$.

leads to a less localized state (now only half of the sulfur atoms form disulfides) but still with a considerable degree of delocalization. Further reduction of [CuS] by additional Na is exemplified in the known compound $Na_3Cu_4S_4$, where the average charge of S is 1.75−, and no S−S bonds exist, leaving the holes completely delocalized through the monosulfide p-band.[6]

Electrical conductivity measurements show that $Na_3Cu_4S_4$ is a metallic material (see Figure 2). The thermoelectric power is very small, at 3 μV K^{-1}, with a weak temperature dependence between 85 and 225 K, confirming the p-type metallic character. The $NaCu_4S_4$ displays temperature-independent Pauli paramagnetism, with a χ_m value of 6.2×10^{-5} emu mol^{-1}.

$NaCu_4S_4$ joins the limited number of compounds built on the $[CuQ]^{n-}$ ($n < 1$) stoichiometry, which are just $Na_3Cu_4S_4$, $TlCu_2Q_2$ (Q = S, Se),[17] and $K_2Cu_5Te_5$.[10] They can be viewed as partially reduced states of CuQ, and they are all metals despite their diverse structures. Although one might speculate on the existence of a CDW instability, there has been no experimental evidence that these metallic, low-dimensional solids are subject to one.[6c] In a recent theoretical study, it was predicted that reduction of $K_2Cu_5Te_5$ (which has one hole in the conduction band) by one electron would not yield a semiconductor; instead, a structural distortion is anticipated for it to remain metallic.[18] It appears that reduction of [CuQ] frameworks always reduces dichalcogenide groups to monochalcogenides before filling the holes in the conduction bands to generate semiconductors. Only the completely reduced $[CuQ]^-$ frameworks, such as KCuS, ACuQ,[13] and α-/β-$BaCu_2S_2$,[19] are semiconductors.

Considering the abundance of compounds in the ternary alkali Cu chalcogenide system, it is remarkable that a new structure type, a new electronic structure of $[CuS]^{0.25-}$, and a new composition of A/Cu/Q has been found. Among the plethora of A/Cu/Q phases, the metallic $NaCu_4S_4$ is a noteworthy member because of the simplicity of its structure and its close relationship to the parent CuS.

Acknowledgment. This work was supported by the National Science Foundation (DMR-92-02428). M.G.K. is a Camille and Henry Dreyfus Teacher-Scholar, 1993−1995.

Supporting Information Available: Table of atomic coordinates and anisotropic thermal parameters for $NaCu_4S_4$ (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA952982R

---

[17] (a) Berger, R.; Van Bruggen, C. F. *J. Less Common Met.* **1984**, *99*, 113−123. (b) Berger, R. *J. Less Common Met.* **1989**, *147*, 141−148.

[18] Seong, S.; Albright, T. A.; Zhang, X.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1994**, *116*, 7287−7293.

[19] (a) Iglesias, J. E.; Pachali, K. E.; Steinfink, H. *J. Solid State Chem.* **1974**, *9*, 6−14. (b) Saeki, M.; Onoda, M.; Nozaki, H. *Mater. Res. Bull.* **1988**, *23*, 603−608. (c) Onoda, M.; Saeki, M. *Mater. Res. Bull.* **1989**, *24*, 1337−1345. (d) Ouammou, A.; Mouallem-Bahout, M.; Pena, O.; Halet, J.-F.; Saillard, J. Y.; Carel, C. *J. Solid State Chem.* **1995**, *117*, 73−79.