Anion p-Band Hole Generation and Annihilation in Layered Potassium Trithiotetracuprate, KCu_4S_3

Frank Viola and Robert Schöllhorn*

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, D-1000 Berlin 12, Germany

Topotactic electrochemical reduction of metallic KCu_4S_3 in Cu^+ electrolytes results in the formation of semiconducting KCu_5S_3 *via* anion p-band hole annihilation in a reversible process.

The existence of p-band holes in transition metal chalcogenides[1] and oxides[2] has found increasing interest in recent years and plays a major role, *e.g.* with respect to the electronic properties of high temperature superconductors.[1–4] It has been shown by us that topotactic electron–ion transfer reactions can be correlated with the reversible formation of p-band holes and consequent changes in the magnetic ordering states of chalcogen spinels.[3–5] We have made predictions from a general model for several systems which should be able to undergo this type of reaction[4] and we report here on the case of the potassium thiocuprate, KCu_4S_3.

The structure of KCu_4S_3 (tetragonal, *P4/mmm*, $a = 388.9$, $c = 928.6$ pm) can be described as consisting of $Cu_4S_3^-$ layers held together by potassium ions[6,7] (Fig. 1). The layers consist of CuS_4 tetrahedra sharing edges and vertices. The compound exhibits metallic properties with temperature independent Pauli paramagnetism. XPS studies showed that the mixed valence metallic state is due to delocalized p-band holes (sulfur formally in two different valence states).[8] Our model for the potential reactivity of KCu_4S_3 was based on the following points: (*i*) the metallic behaviour provides bulk electronic transport, (*ii*) Cu^+ is univalent and mobile at ambient temperature in chalcogenides, (*iii*) the vacant octahedral interlayer sites (one site per formula unit) can be used for the uptake of additional Cu, (*iv*) the transfer of one electron (and one Cu^+ ion) would result in the quantitative annihilation of the sulfur p-band holes, (*v*) a metal–semiconductor transition should be observed consequently. This process is illustrated in Scheme 1 in terms of a simple ionic model.

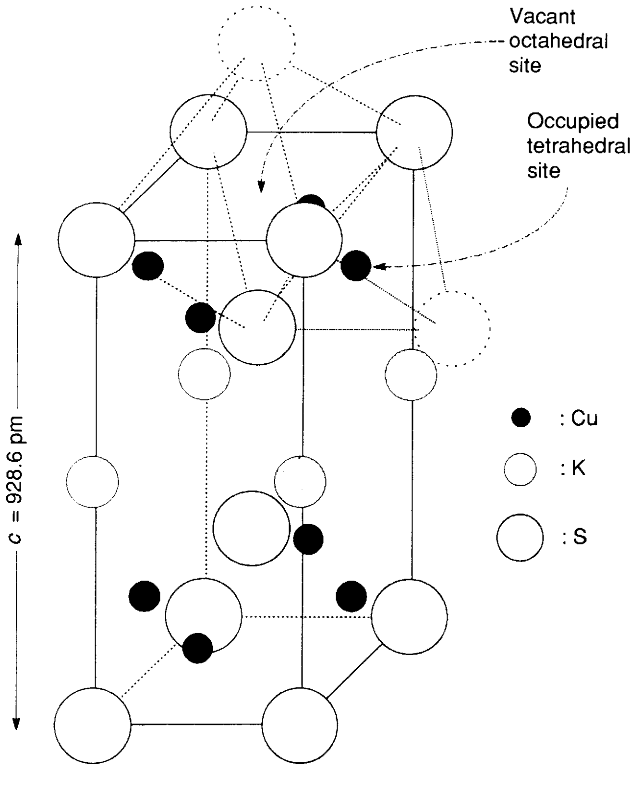

Fig. 1 Schematic structure of KCu_4S_3

Reactions were performed electrochemically in the galvanostatic or potentiostatic mode, in galvanic cells (three-electrode configuration, Cu^0/Cu^+ reference electrode) under inert gas atmosphere with an aprotic electrolyte at 300 K in a galvanic chain: $Cu^0//CuCl$, $MeCN(0.5\ mol\ dm^{-3})//KCu_4S_3$.

Working electrodes consisted of pressed polycrystalline or single crystal material. Fig. 2 shows the galvanostatic potential–charge transfer curve; after a transfer of one electron per formula unit of KCu_4S_3 a potential step indicates the end of the reaction (potential of copper deposition). The steel-blue starting material became a black phase (**I**). In agreement with the potential plateau observed (the small slope observed is a consequence of the non-equilibrium state during the reduction under current flow) the X-ray data taken at intermediate points between $n = 0$ and $n = 1$ indicate a two-phase region, *i.e.* the coexistence of KCu_4S_3 and the reaction product (**I**). This is supported also by potentiostatic studies which indi-

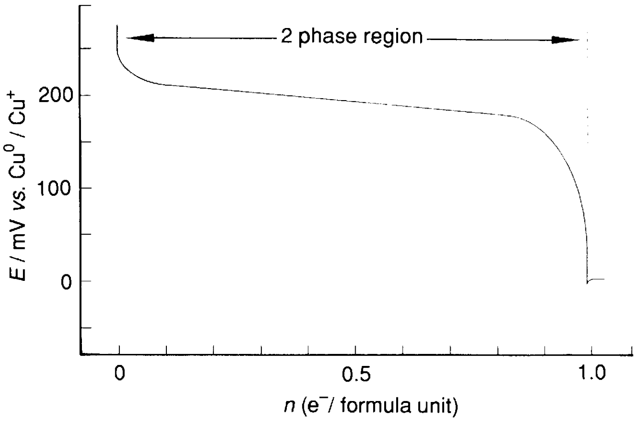

Fig. 2 Galvanostatic reduction of KCu_4S_3 in $MeCN–Cu^+$ electolyte at 300 K: potential E *vs.* charge transfer n (e^-/formula unit); nominal current density $j = 50\ \mu A\ cm^{-2}$

$$K^+[(Cu_t^{\,+})_4(S^{2-})_2(S^{\bullet -})_1] + Cu^+ + e^- \rightleftharpoons K^+[(Cu_t^{\,+})_4(Cu_o^{\,+})_1(S^{2-})_3]$$

anion mixed valence — integral valence
metal — semiconductor
Pauli paramagnetic — diamagnetic

hole annihilation →
← hole generation

Scheme 1 t and o: tetrahedral and octahedral lattice sites respectively cated similarly the existence of a two-phase region. The reaction is reversible; on anodic oxidation of (**I**) the starting material KCu_4S_3 is obtained again.

Analytical data of (**I**) (S: 23.7, K: 7.5, Cu: 68.9 wt%) yield a ratio K : Cu : S = 1 : 5 : 3; *i.e.* the composition of the new phase is KCu_5S_3. Powder X-ray data show that the tetragonal symmetry is retained; the lattice parameters are $a = 382.4$, $c = 886.5$ pm. The unit cell volume (normalized to the formula unit) decreases from $V = 140.4 \times 10^6$ pm (KCu_4S_3) to $V = 129.6 \times 10^6$ pm (KCu_5S_3), *i.e.* a change of 7%. This is attributed to a contraction of the layer units by the additional cationic charges introduced. A calculated theoretical diffractogram (LAZY PULVERIX) of KCu_5S_3 with the proposed structure model corresponds well with the observed diffractogram of KCu_5S_3 (R = 11%).

Resistivity measurements on polycrystalline KCu_5S_3 show a negative temperature coefficient in the range 80–300 K, *i.e.* semiconductor behaviour. The conductivity at 300 K decreases from $\sigma_{300} = 1363\ \Omega^{-1}\ cm^{-1}$ (KCu_4S_3) to $\sigma_{300} = 526.0\ \Omega^{-1}\ cm^{-1}$ (KCu_5S_3). The molar magnetic susceptibility was measured between 80 and 300 K; while KCu_4S_3 exhibits temperature independent paramagnetism with $\chi_{mol}(300\ K) = 2.411 \times 10^{-9}\ m^3\ mol^{-1}$, the reaction product KCu_5S_3 turns out to be diamagnetic with $\chi_{mol}(300\ K) = 2.222 \times 10^{-10}\ m^3\ mol^{-1}$ (minor paramagnetic contamination).

The experimental evidence thus supports clearly the reaction under discussion following the model outlined above. The electron–ion transfer reactions known so far are based on cation mixed valence states in the host lattice. It now becomes obvious that the physical properties of solids can be controlled reversibly also by electron transfer reactions proceeding formally *via* anion mixed valence states, *i.e.* the formation and annihilation of p-band holes in appropriate materials. Photoelectron spectroscopic studies performed by us recently on KCu_4S_3–KCu_5S_3 confirm clearly the model of a metal–semiconductor transition.[9]

Support of this work by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Received, 11th March 1992; Com. 2/01318E

References

1 F. Jellinek, *Reactivity of Solids*, 1988, **5**, 323; F. Jellinek, R. A. Pollak and M. W. Shafer, *Mater. Res. Bull.*, 1974, **9**, 845.

2 *Superconductivity*, ed. J. G. Bednorz and K. A. Müller, Springer-Verlag, Berlin–New York–Tokyo, 1990; *Crystal Chemistry of High T_c Superconducting Oxides*, ed. B. Raveau, C. Michel, M. Hervieu and D. Groult, Springer-Verlag, Berlin–New York, 1991.

3 R. Schöllhorn, *Angew. Chem.*, 1988, **100**, 1446.

4 R. Schöllhorn, *Solid State Ionics*, 1989, **32/33**, 23.

5 A. Payer, M. Schmalz, R. Schöllhorn, C. Ritter and R. Schlögl, *Mater. Res. Bull.*, 1990, **25**, 515.

6 W. Rüdorff, H. G. Schwarz and M. Walter, *Z. Anorg. Allg. Chem.*, 1952, **269**, 141.

7 W. Bronger in *Crystallography and Crystal Chemistry of Materials with Layered Structure*, ed. F. Lévy, Reidel, Dordrecht, Boston, 1976.

8 J.-C. Folmer and F. Jellinek, *J. Less-Common Met.*, 1980, **76**, 153.

9 M. Schmalz, F. Viola, R. Schöllhorn and R. Schlögl, unpublished work.