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Electron transfer and electronic structure of $KCuFeS_2$

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Abstract

The electron transfer that occurs in the insertion of potassium in $CuFeS_2$ has been analyzed by two different techniques. The binding energies of the core electrons of $CuFeS_2$, $KCuFeS_2$ and K_xCuFeS_2 ($x \approx 0$) has been studied by XPS experiments, while the band structure of these phases has been investigated by tight-binding EH calculations. Both experimental and numerical results strongly support the belief that the insertion reaction induces a redox process in the starting $CuFeS_2$, by which the Fe^{3+} ions are reduced to Fe^{2+}. Upon removal of the potassium ions, the Fe^{2+} ions are oxidized to Fe^{3+}. Copper atoms do not participate in the redox reaction.

Keywords: Electron transfer; Electron structure; $KCuFeS_2$

1. Introduction

The reaction of potassium with chalcopyrite, $CuFeS_2$, or with eskeborite, $CuFeSe_2$, yields new products with formula $KCuFeX_2$ (X = S or Se) which crystallize in $ThCr_2Si_2$ [1]. Following a first publication on their preparation and crystal structure [2], we report in this paper the band structure calculations based on an extended Hückel (EH) hamiltonian, and the results of XPS experiments in order to evaluate the electronic factors involved in the reaction and to get information about the oxidation states of Cu and Fe in the products and the oxidation state changes of these elements during the inclusion and extraction reactions of the alkali metal ion on the $CuFeS_2$ matrix.

2. Experimental details

The intercalation compound $KCuFeS_2$ has been synthesized and its crystal structure solved, as described in a previous work [2]. The homogeneity of the product was monitored by XRD. The oxidative extraction of the potassium ion from $KCuFeS_2$ to yield K_xCuFeS_2 ($x \approx 0$) was undertaken following the method described by Murphy et al. [3], or with a 5:95 H_2O:EtOH solution. Both procedures were carried out under Ar atmosphere.

The XPS spectra of all studied compounds were recorded on a Perkin–Elmer spectrometer. Mg Kα X-rays were used for all the measurements. Powder samples were pressed on an indium foil and then mounted on an aluminum sample holder. Crystals were fixed on the holder with an organic glue. All the samples were sputtered with an Ar beam before recording the spectra. The binding energies were referred to the C(1s) binding energy (248.8 eV) of the carbonaceous contaminant of the samples. This procedure has been demonstrated to furnish reproducible results [4]. The binding energies were determined by bisecting the curves in the vicinities of the maxima.

3. Band structure calculations

We have studied the 2-D band structure associated with a $[CuFeS_2]^{-1}$ layer of $KCuFeS_2$ by means of extended Hückel tight-binding calculations [5–9]. We have chosen for all calculations a 2-D square supercell with lattice parameter $a\sqrt{2}$ (a = 3.837 Å) with the (Cu, Fe) atoms distributed in the tetrahedral sites with an ordering pattern that produces chains of Cu and Fe atoms. The extended Hückel parameters used in the calculations are given in Table 1. These values were taken from the literature [10–11]. The off-diagonal matrix elements of the hamiltonian were evaluated by

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Table 1
Extended Hückel parameters. H_{ii} are diagonal matrix elements of the EH Hamiltonian, ξ_i are the Slater exponents, and c_i are the expansion coefficients

Atom	Orbital	H_{ii} (eV)	ξ_1	ξ_2	c_1	c_2
S	3s	−20.00	2.122			
	3p	−13.30	1.827			
Cu	4s	−11.40	2.200			
	4p	−6.06	2.200			
	3d	−14.00	5.950	2.30	0.5933	0.5744
Fe	4s	−9.10	1.900			
	4p	−5.32	1.900			
	3d	−12.60	5.350	2.00	0.5505	0.6260

means of a weighted formula [12]. A set of 120 k points in the irreducible part of the Brillouin zone was used for the density of state (DOS) calculations [13].

4. Results and discussion

The spectra obtained from the photoelectron-spectroscopic measurements are displayed in Figs. 1 and 2. The binding energies derived from these spectra are listed in Table 2.

The observed values of the binding energies for $Cu(2p_{3/2})$, $Cu(2p_{1/2})$, $Fe(2p_{3/2})$, $Fe(2p_{1/2})$ of the starting chalcopyrite, $CuFeS_2$, are in good agreement with the

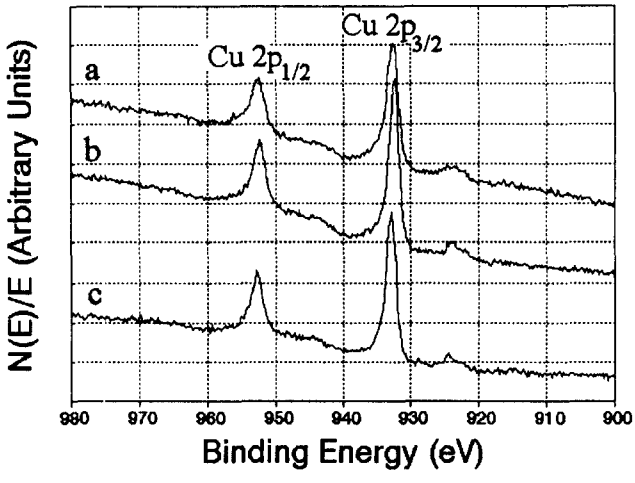

Fig. 1. X-Ray photoelectron spectrum of Cu(2p): curve (a), $CuFeS_2$; curve (b), K_xCuFeS_2 ($x \approx 0$); curve (c), $KCuFeS_2$ after bombardment with argon ions.

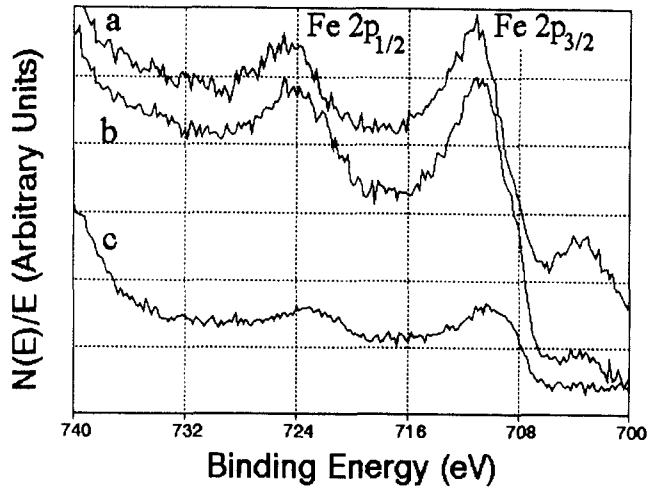

Fig. 2. X-Ray photoelectron spectrum of Fe(2p): curve (a), $CuFeS_2$; curve (b), K_xCuFeS_2 ($x \approx 0$); curve (c), $KCuFeS_2$ after bombardment with argon ions.

earlier work of Brion [14]. The full width at half maximum (FWHM) calculated for $Cu(2p_{3/2})$ is 1.8 eV. This value is also in good agreement with the reported value [15], and confirms that only Cu^{+1} is present in the parent $CuFeS_2$. Chalcopyrite has the zinc blende structure, but with ordering of the Cu^{+1}, Fe^{3+} ions within (001) layers [16].

In $KCuFeS_2$ and K_xCuFeS_2 ($x \approx 0$) phases, the binding energies of the $Cu(2p_{3/2})$ and $Cu(2p_{1/2})$ levels are nearly the same as those found in chalcopyrite. Therefore, we can conclude that upon the inclusion and removal of the potassium ion in the $CuFeS_2$ starting material, the formal oxidation state of copper does not change. Because the value for S(2p) binding energy is nearly that for S^{2-}, it seems plausible to assume that such is in fact its valence in all the three phases. This oxidation state for sulfur is consistent with the lack of S–S bonding: it is worth noting that S–S distances along the c axis (3.994 Å) as well as parallel to the (001) plane (3.837 Å) are longer than a S–S single bond [2,17]. The binding energy values corresponding to $Fe(2p_{3/2})$ and $Fe(2p_{1/2})$ show a shift of about 0.8 eV for $Fe(2p_{3/2})$ and about 2.1 eV for $Fe(2p_{1/2})$ when K is inserted in $CuFeS_2$. After the removal of the alkali metal, the binding energies of $Fe(2p_{3/2})$ and $Fe(2p_{1/2})$ core electrons show values which are similar to those corresponding to the starting $CuFeS_2$. We recall that $CuFeS_2$ has the zinc blende

Table 2
Binding energy (eV) of core electrons

Compound	$Cu(2p_{3/2})$	FWHM	$Cu(2p_{1/2})$	FWHM	$Fe(2p_{3/2})$	$Fe(2p_{1/2})$	S(2p)
$CuFe_2$	932.5	1.8	952.5	2.4	711.3	724.8	162.0
$KCuFeS_2$	932.6	1.8	952.6	2.3	710.5	722.7	162.2
K_xCuFeS_2	932.4	1.8	952.4	2.4	711.2	724.8	162.2

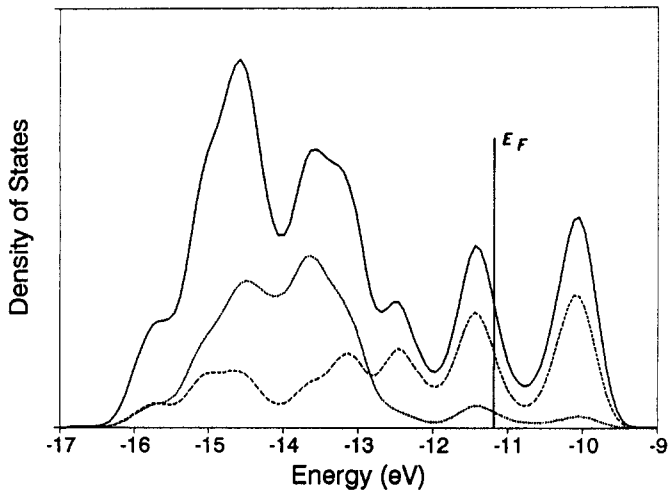

Fig. 3. Density of states of the $[CuFeS_2]^{-1}$ single layer (continuous line), and contributions of the Fe AOs (broken line) and Cu AOs (dotted line). The Fermi energy is indicated by the label E_F.

structure, while the deintercalated phase K_xCuFeS_2 ($x \approx 0$) displays a layered structure. The XPS spectrum data for iron show that the insertion reaction of potassium ion in $CuFeS_2$ can be related to a change in the oxidation state from Fe^{3+} to Fe^{2+} in the final product $KCuFeS_2$. Furthermore, the removal of the alkali metal ion occurs with the oxidation of Fe (Fe^{2+} to Fe^{3+}). From these experimental data it is clear that copper does not participate in the redox process.

The results obtained from the XPS spectrum data are consistent with the calculated band structure of a $[CuFeS_2]^{-1}$ layer as model for $KCuFeS_2$. The DOS curve and the projected DOS distributions for Fe and Cu atomic orbitals (AOs) are shown in Fig. 3.

The projected DOS curve indicates that the energy bands at the Fermi level have mainly Fe 3d character. The maximum in the DOS curve associated to the Cu 3d orbitals is found about 3 eV below the Fermi level. By the formation of $KCuFeS_2$, the electron transfer from the K atoms towards the Cu–Fe–S framework is almost complete. The computed atomic net charges are $(K)^{+0.80}[(Fe)^{-0.80}(Cu)^0(S_2)^0]^{-0.80}$. As expected, the Fe 3d orbitals participate to a larger extent than the Cu 3d ones.

However, the removal of one electron from the unit cell of the $[CuFeS_2]^{-1}$ layer shows that the electronic charge is removed from the Fe atoms. This result is in line with the reduction and oxidation of Fe found in the XPS experiments upon insertion and removal of K atoms in chalcopyrite. These results are comparable with those found for the other alkali metal–copper–iron sulfides, $LiCuFeS_2$ and $NaCuFeS_2$ [18].

Finally, it is worth noting that the arrangement observed in $KCuFeS_2$, analogous to that of $ThCr_2Si_2$, is rather scarce for d^{10} transition metals.

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References

[1] Z. Ban and M. Sikirica, *Acta Crystallogr., 18* (1965) 594.
[2] C. Mujica, J. Paéz and J. Llanos, *Mater. Res. Bull., 29* (1994) 263.
[3] D.W. Murphy, C. Cros, F.J. di Salvo and J.V. Waszczak, *Inorg. Chem., 16* (1977) 3027.
[4] G.E. Murch and R.J. Thorn, *J. Phys. Chem. Solids, 41* (1980) 2850.
[5] N.W. Ashcroft and N.D. Mermin, *Solid State Physics*, Holt, Rinehart and Winston, New York, 1977.
[6] M.-H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc., 100* (1978) 6093.
[7] M.-H. Whangbo, R. Hoffmann and R.B. Woodward, *Proc. R. Soc. Lond., 23* (1979) 366.
[8] R. Hoffmann and W.N. Lipscomb, *J. Chem. Phys., 36* (1962) 2176.
[9] R. Hoffmann, *J. Chem. Phys., 39* (1963) 1397.
[10] P.J. Hay, J.C. Thibeault and R. Hoffmann, *J. Am. Chem. Soc., 97* (1975) 4844.
[11] R.H. Summerville and R. Hoffmann, *J. Am. Chem. Soc., 98* (1976) 7240.
[12] J.H. Ammeter, H.-B. Bürgi, J. Thibeault and R. Hoffmann, *J. Am. Chem. Soc., 100* (1978) 3686.
[13] R. Ramírez and M.C. Böhm, *Int. J. Quantum Chem., 30* (1986) 391.
[14] D. Brion, *Appl. Surf. Sci., 5* (1980) 133.
[15] D. Cahen, P.J. Ireland, L.L. Kazmerski and F.A. Thiel, *J. Appl. Phys., 57* (1985) 4761.
[16] F.D. Bloss, *Crystallography and Crystal Chemistry*, Holt, Rinehart and Winston, New York, 1971.
[17] F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1988.
[18] J. Llanos, A. Buljan, C. Mujica and R. Ramírez, *Mater. Res. Bull., 30* (1995) 43.