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1992 J. Phys.: Condens. Matter 4 10461

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Experimental and theoretical investigation of the crystal structure of CuS

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Received 24 August 1992, in final form 14 October 1992

Abstract. The crystal structure of CuS has been confirmed experimentally using the powder diffraction method on the high-resolution powder diffractometer at the Rutherford–Appleton Laboratory. The observed crystal structure is $P6_3/mmc$. Standard density functional calculations on CuS on a variety of crystal structures are also reported. The calculations also predict $P6_3/mmc$ as the stable crystal structure. On the basis of the agreement between theory and experiment we are able to discuss the details of the bonding in this material.

1. Introduction

The crystal structure and chemistry of the copper chalcogenides has been discussed previously by several authors (Wells 1984). In particular Cu–S is a remarkably complex system existing in many phases. The low-temperature crystal structure of covellite CuS has been described by Hulliger (1968). Both the copper and sulphur atoms also occupy two crystallographically distinct sites. Essentially CuS consists of layers Cu–S₂–Cu alternating with layers of CuS. Two thirds of the sulphur atoms are really present as S₂. One third of the sulphur atoms occupy the centre of a triangle of copper atoms. The other copper atoms (in the copper layers in the Cu–S₂–Cu part of the structure) are at the centre of a tetrahedral arrangement of sulphur atoms. In this paper we report a high-resolution powder diffraction experiment which we have used to confirm and refine the previously discussed structure.

This crystal structure is unique and therefore we have also performed a number of electronic structure calculations on various crystal structures in an attempt to describe the bonding and to understand why a material with such a simple stoichiometry takes on such a complex structure. We have considered the CsCl, NaCl and two forms of the DHCP structure as well as the experimentally observed $P6_3/mmc$ structure.

2. Experimental method

A sample of high-purity copper(II) sulphide (CuS) was prepared by sealing the pure elements (Cu 99.99% and S 99.99%) in an evacuated silica glass tube, and heating

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the mixture to a temperature of 700°C for 24 h in a rocking furnace. It was then crystallized by slowly allowing the melt to cool to room temperature over a further period of 24 h. The resulting solid billet of polycrystalline CuS was then ground to a fine powder (typical grain size of approximately 0.1 mm) and annealed at 500°C for two days. The high-resolution powder diffraction patterns were obtained using the HRPD diffractometer at the ISIS neutron spallation source at the Rutherford-Appleton Laboratory, UK. The data were collected over four separate time of flight ranges (25–80, 60–105, 95–160 and 150–210 ms) which were merged and combined (after normalizing to the incident beam intensity) to give a final spectrum covering a d spacing range of 0.5 to 3.5 Å. Corrections for the wavelength-dependent efficiencies of the HRPD detectors were obtained by normalizing the spectrum with a smoothed spectrum obtained from a vanadium slab of the same dimensions as the sample. The vanadium spectrum itself was corrected for self-attenuation and multiple scattering before smoothing. Wavelength dependent self-attenuation corrections for the sample were also calculated and applied to the normalized spectrum to give a fully intensity-corrected spectrum for the sample.

3. Theoretical method

We have performed self-consistent electronic structure calculations for CuS on a variety of crystal structures. The crystal structures considered were the standard NaCl, CsCl and DHCP(1) (NiAs) structures. DHCP(2) is the same lattice as DHCP(1), but with two layers of Cu, followed by two layers of S, in planes parallel to the a - b hexagonal plane. This structure was examined because, like the measured crystal structure it allows sulphur to have nearest-neighbour sulphur atoms. This was a standard density functional calculation using the Hedin-Lundqvist approximation for the exchange-correlation energy. For a good review of the density functional method the reader is referred to the articles by von Barth (1984) and by Kohn and Vashista (1981).

The calculation was implemented using the LMTO method (Andersen 1975, 1984, Skriver 1984). Throughout a semi-relativistic approximation was used. All relativistic corrections to order $1/c^2$ except spin-orbit coupling were included.

The initial atomic charge densities were calculated using standard Hartree-Fock-Dirac programs with the initial electronic configurations core + $3d^{10}4s^1$ for copper and core + $3s^23p^4$ for sulphur. A standard frozen-core approximation was used and we iterated to self-consistency on the valence electrons only.

Self-consistency was fairly straightforward to obtain on the structures with a small number (< 5) of atoms per unit cell; however, during the iterative process on the experimentally determined structure great care was required to ensure the system relaxed to the true ground state rather than some metastable state or failing to converge altogether. This was achieved by a judicious choice of the initial values of the arbitrary parameters in the LMTO method, although these were later allowed to relax. The values used meant very small mixing ($< 4\%$) of the new charge density with the old.

4. Experimental results

The experimental powder diffraction obtained for CuS along with the predicted peak

positions obtained is shown in figure 1. The structure was refined to the $P6_3/mmc$ structure, see figure 2 (Wyckoff 1963, Villars and Calvert 1985), using the ISIS Rietveld refinement program TF12LS at the Rutherford Lab. The final fit to the observed diffraction pattern and the residuals to this fit are also shown in figure 1. The blank areas (for example 118–120 ms) in the residual were not considered in the final refinement. There is evidence of a small unidentified minority phase, notably the small peaks at 108 and 113 ms respectively. This phase could not be identified and was not considered in the refinement. A summary of the refined crystal parameters is given in table 1. In terms of u and v presented in table 1 the ionic positions are as follows. Cu(I) at $\pm(2/3, 1/3, 1/4)$, Cu(2) at $\pm(1/3, 2/3, u), \pm(1/3, 2/3, 1/2 - u)$, S(I) at $\pm(0, 0, v), \pm(0, 0, 1/2 - v)$, S(2) at $\pm(1/3, 2/3, 1/4)$.

Table 1. Refined crystal parameters for covellite CuS.

CuS (Covellite) Structure				
Space group $P6_3/mmc$				
Refined parameters				
Unit cell $a = b = 3.78813(1)\text{\AA}, c = 16.33307(8)\text{\AA}$				
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$				
$u = 0.10737(4), v = 0.06329(12)$				
Anisotropic temperature factors				
Atom	B11	B22	B33	B12
CU(I)	2.097(43)	2.097(43)	3.261(67)	1.048(21)
CU(II)	1.052(33)	1.052(33)	0.902(38)	0.526(16)
S(I)	1.735(67)	1.735(67)	0.483(72)	0.868(33)
S(II)	0.667(43)	0.667(43)	0.676(72)	0.334(21)

where the temperature factors are defined as :

$$\exp\left(-\frac{1}{4}(B_{11}ha^*ha^* + \dots + 2B_{23}kb^*lc^* + \dots)\right)$$

$$R(\text{profile})=3.96, R(\text{weighted,profile})=5.65, R(\text{expected})=2.23$$

where

$$R(\text{profile}) = \frac{\sum_i |Y_i(\text{obs}) - Y_i(\text{calc})|}{\sum_i Y_i(\text{obs})}$$

and

$$R(\text{weighted,profile}) = \sqrt{\frac{\sum_i w_i |Y_i(\text{obs}) - Y_i(\text{calc})|^2}{\sum_i w_i Y_i^2(\text{obs})}}$$

and

$$R(\text{expected}) = \sqrt{\frac{N-P}{\sum_i w_i Y_i^2(\text{obs})}}$$

with N and P the number of observations and fitted parameters respectively.

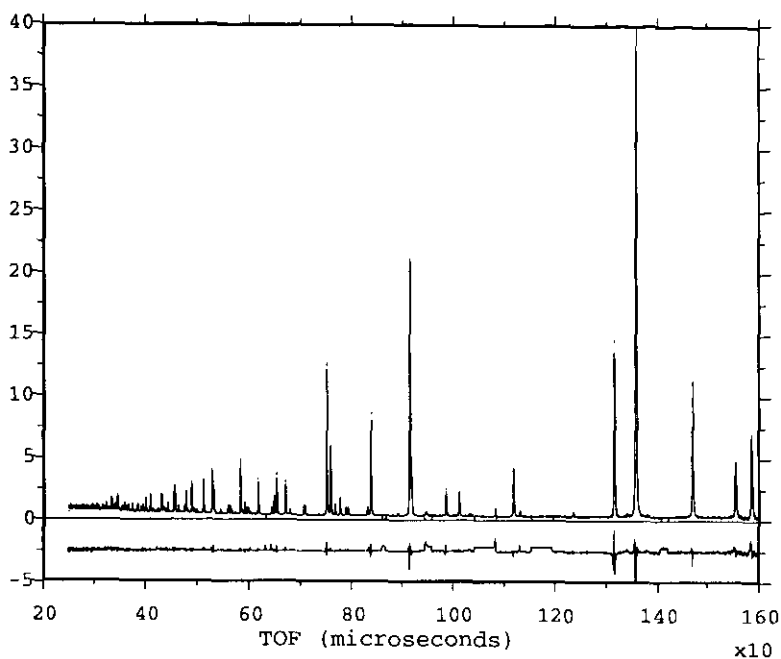


Figure 1. The experimental powder diffraction obtained for CuS.

5. Theoretical results

The density of states was calculated using the tetrahedral method to integrate the energy bands over the Brillouin zone. Eigenvalues were calculated at the vertices of each tetrahedron and a linear interpolation was performed in each. Figure 3 shows the total density of states for the experimentally observed structure. The peaks below -0.8 Ryd are the completely filled sulphur 3s states. They are not shown in subsequent diagrams as they play no significant role in bonding. The next set of peaks are predominantly sulphur p bands with some copper d states admixed in. The large peak is predominantly copper d-like with some sulphur p states included. These sulphur p-copper d hybridized bands continue up to above E_F . In figures 4-7 the local densities of states on each site are shown. Figure 4 is the density of states associated with the Cu(1) site. The three peaks between -0.4 and -0.25 Ryd are s-d bands, the larger peaks from -0.2 Ryd upwards are almost entirely d-like. In figure 5 we see the density of states around the Cu(2) site. Again the states below -0.2 Ryd are s-d-like and the states above -0.2 Ryd are almost completely d-like. There is considerably more weight in the states below -0.2 Ryd for the Cu(2) atoms than for the Cu(1) atoms. Figure 6 shows the density of states around the S(1) site. There are six peaks below -0.2 Ryd and these correspond to the sulphur p states. Above this we have mixed s and p states. Finally in figure 7 we see the density of states around the S(2) sites. Below -0.2 Ryd there are three peaks which are almost entirely p-like. There are half as many peaks as in the S(1) figure because there are half as many of this sort of atom. The states above 0.2 Ryd are mixed s- and p-like again.

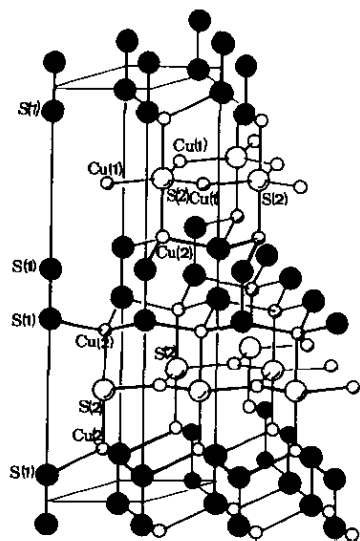


Figure 2. The measured crystal structure of CuS, the different atom types are indicated.

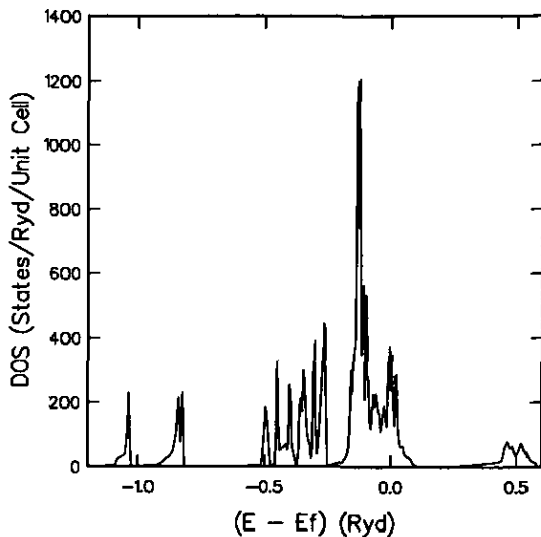


Figure 3. The total density of states for CuS.

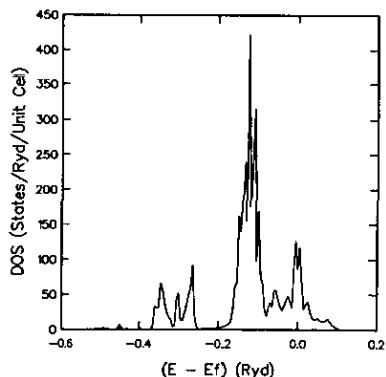


Figure 4. The local density of states on the Cu(1) site in CuS.

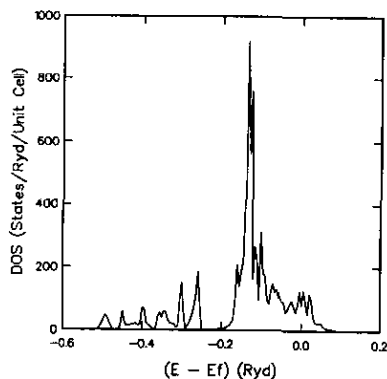


Figure 5. The local density of states on the Cu(2) site in CuS.

6. Structure and bonding

Figure 8 is a graph of total energy against volume per formula unit for CuS for several different crystal structures. Figure 9 is a similar graph for the actual crystal structure shown in figure 1. These two figures are on the same scale and clearly the crystal structure shown in figure 9 has the lowest total energy, and hence confirms the $P6_3/mmc$ structure as the stable one. The reason all crystal structures are not displayed on the same figure is that for high volumes for the $P6_3/mmc$ structure satisfactory convergence could not be obtained. This is a well-known problem with the atomic-sphere approximation for highly anisotropic crystal structures such as this.

In this section we are going to address several points associated with the bonding

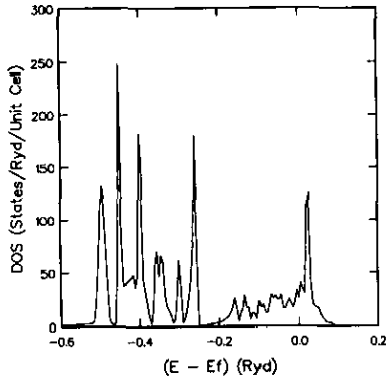


Figure 6. The local density of states on the S(1) site in CuS.

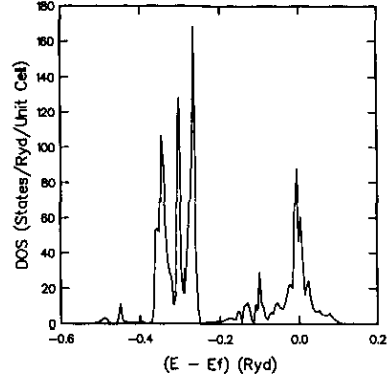


Figure 7. The local density of states on the S(2) site in CuS.

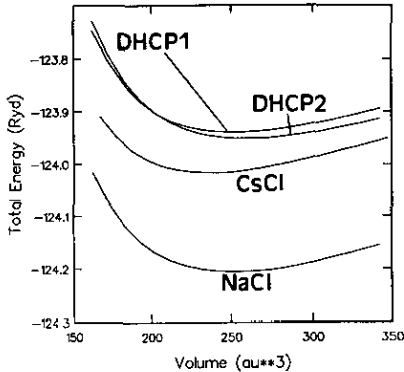


Figure 8. Total valence electron energy as a function of volume/formula unit for the CsCl, NaCl, DHCP(1) and DHCP(2) structures.

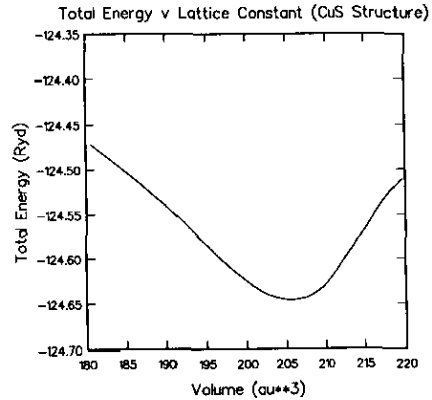


Figure 9. Total valence electron energy as a function of volume/formula unit for the observed crystal structure shown in figure 1.

and structure of this material. Firstly we consider figure 9 and ask what causes the minimum in the total energy.

If we examine the density of states at different volumes we see that the S(1) p bands are always around 0.1 Ryd below the main peaks of the Cu(2) d bands. However, we also find that the S(1) electrons are quite strongly hybridized with the Cu(2) d electrons. At the equilibrium volume this hybridization seems to be a maximum. It is at this energy that the most copper d bands are dragged down to hybridize with the sulphur p bands. Hence it is at this volume that the Cu(2) d bands have their lowest energy, and this determines the equilibrium volume.

Now let us use these facts to discuss the bonding in CuS. Clearly there are six peaks between -0.6 Ryd and -0.2 Ryd in the S(1) density of states. These correspond to sulphur p electrons. The S(1) atoms are paired in this material. It appears that these sulphur atoms are bonded covalently and should be considered as a single unit, as suggested in the introduction. Each of the atoms in the pair starts off with four electrons. The pairs accept two extra electrons, one from each of the

copper atoms in the layers above and below the S(1) pairs. They use these electrons to bond covalently. There is now a simple ionic bonding between the coppers and the covalently bonded sulphur pairs. This view is substantiated by further consideration of the densities of states. Firstly we compare the position of the S(1) p bands relative to the Fermi energy to that of the S(2) p bands. Clearly the S(1) p band centre is about 0.1 Ryd lower. This implies that the S(1) p states are filled whereas those of S(2) are not. Secondly, noting the difference in scale between figures 5 and 6 we see that there are peaks in the Cu(2) density of states corresponding with the p peaks in the S(1) density of states indicating significant hybridization between S(1) p and Cu(2) d electrons. So we have a very simplified picture of this part of the crystal structure as being ionically bonded $\text{Cu}^+-(\text{S}_2)^{2-}-\text{Cu}^+$.

Another clue is in the charge transfer. The amount of charge transferred from one atom to another is dependent upon the arbitrary ratio chosen for the relative sizes of the spheres surrounding each atom. Hence the absolute values of the charge transfer determined in a calculation of this kind are meaningless. Furthermore, convergence of the LMTO method is facilitated if the sphere sizes are chosen in such a way as to minimize the charge transfer. Our sphere radii were selected as being approximately in proportion to the tabulated atomic volumes of copper and sulphur, Kaye and Laby (1973). For each of the crystallographically inequivalent copper atoms the radii were the same and each of the inequivalent sulphur atoms also had the same radius. Under these circumstances the magnitude of the charge transfer from one atom to another never exceeds 0.1 for the equilibrium radius. This suggests that all the copper atoms are in the same valence state. All the sulphur atoms are also in the same valence state which in general is different from that for the copper atoms.

Furthermore, as the S(1) p bands are much lower in energy than the S(2) p bands, we can infer that the S(2) p states are not filled. Examination of the densities of states in figures 4 and 7 shows that some d character is pulled off the bottom of the main d band peak of Cu(1) to hybridize with the sulphur p band, exactly as for the Cu(2)-S(1) bonding. This hybridization at low energies allows some p character from the S(2) sites to hybridize with the Cu(1) d bands around E_F . It is these latter electrons which are primarily responsible for the metallic nature of CuS. Therefore, a very simplified picture of the bonding in the Cu-S layers is a positive copper ion bound to a negative sulphur ion and both of these 'immersed' in a somewhat two-dimensional sea of conduction electrons.

If we compress this structure we find an increase in the amount of charge transferred. There are more electrons on the Cu(1) site at the expense of the S(2) site. This will lead to a decrease in the strength of the bonds in the Cu-S plane. If, on the other hand, we expand the lattice the Cu(1) site loses electrons and these move predominantly to the Cu(2) site and a little to the S(1) site. In this case the arrangement of electrons on the S(2) site also changes significantly. A significant amount of sulphur s character rises above E_F and p character comes below. This enables the S(2) p states to fill and fall further below E_F in the same way as for S(1). In this case though the decrease in the single-electron energies is offset by an increase in the Hartree energy.

The next question we address is why CuS forms this crystal structure rather than one of the simpler structures available to it. The answer to this is very straightforward. It is energetically more favourable for the sulphur atoms to bond to each other than to bond with the copper atoms. The structure illustrated in figure 2 allows two thirds of the sulphur atoms to bond covalently in pairs. This covalent bonding allows the

centre of the sulphur band to drop about 0.1 Ryd and hence lowers the total energy. This more than compensates for the increase in the Hartree contribution to the total energy. In most of the other structures examined, (see figure 8), sulphur has only copper as its nearest neighbours, hence this covalent bonding is obstructed. For the DHCP(2) structure sulphur does have some sulphur nearest neighbours and the single-electron contributions to the total energy show that this structure is favourable over the cubic structures. However this structure has a very large Hartree contribution to the energy which outweighs the one-electron energy and hence makes this structure unfavourable.

We have built up a picture of the crystal structure as being bonded $\text{Cu}^+-(\text{S}_2)^{2-}-\text{Cu}^+$. These are interleaved with Cu^+-S^- layers. Our calculations suggest this is a reasonable, but of course highly simplified, picture. If this were the full picture of the bonding in CuS we could predict that CuSe and NiS would take on similar structures. This is the case for CuSe, but not for NiS which forms the NiAs structure. Clearly a full explanation and understanding of the bonding requires calculations on these and other materials.

7. Conclusions

We have performed high-resolution powder diffraction measurements of CuS and shown that the crystal structure is that shown in figure 2. On the basis of the calculations presented here we are able to confirm the measured crystal structure and also the experimental results of Folmer and Jellinek (1980). The calculations also indicate some of the important factors to be considered when investigating the chemistry of these compounds, however comparison with other compounds, particularly NiS shows that they do not present a full picture of the complex chemistry occurring in CuS.

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