Table 1. *Positional and thermal parameters*

$B_{ij}$ (Å²) are defined by $\exp[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + \cdots + 2B_{23}klb^*c^*)]$.

|   |      | $x$        | $B_{11}$  | $B_{12}$    |
|---|------|-----------|-----------|-------------|
| C | 4(a) | 0         | 1·70 (8)  | 0·20 (13)   |
| O | 8(c) | 0·1185 (3)| 2·30 (6)  | −0·32 (6)   |

corresponding values are $R_w = 0.040$ and $R'_w = 0.042$, respectively.*

**Discussion.** The structural parameters at 150 K are given in Table 1.

The C—O distance in the $CO_2$ molecule is determined as 1·155 (1) Å. This value compares well with

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35467 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the results of electron diffraction experiments which led to distances of 1·15 Å (Hassel & Viervoll, 1947) and 1·162 (±1·0) Å (Karle & Karle, 1949, 1950).

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# Single-Crystal Structure Analysis of the Spinel Copper Pentaindium Octasulphide

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**Abstract.** $Cu_{0.5}In_{2.5}S_4$, $M_r = 447.06$, cubic, $F\bar{4}3m$, $a = 10.6858$ (3) Å, $U = 1220.2$ Å³, $D_c = 4.87$ Mg m⁻³, $Z = 8$, $F(000) = 1593.9$, $\mu(\text{Mo } K\alpha) = 12.25$ mm⁻¹. The space group was assigned in a preliminary communication. The present work reports the X-ray single-crystal structural determination of the same compound and a consideration of the anharmonic lattice model found. The structure has been refined to a final $R$ of 0.056 for 242 reflections collected with a four-circle diffractometer (Mo $K\alpha$ radiation).

**Introduction.** The ideal spinel structure can be viewed as a cubic close-packed array of anions in which one eighth of the tetrahedral and one half of the octahedral interstices are occupied by cations. The general formula of a 1–3 spinel $M^+_{1/2}M^{3+}_{5/2}X^{2-}_4$ may be written as $M^+_{1/2-x}M^{3+}_{1/2+x}[M^+_x M^{3+}_{2-x}]X^{2-}_4$ where the ions in

brackets occupy octahedral sites. Different distributions of cations among the available sites are possible by varying the value of $x$ (the degree of inversion). The two extreme distributions are known as 'normal' for $x = 0$ and 'inverse' for $x = 0.5$. The cationic distribution adopted by a particular spinel depends on the interplay of several forces influencing the total internal energy of the crystal (Blasse, 1964; Gastaldi & Lapiccirella, 1978).

Although the space group $Fd3m$ has usually been assigned to spinels, in the last few years a large body of experimental evidence suggests that in many cases they crystallize with the non-centrosymmetric space group $F\bar{4}3m$ (Thompson & Grimes, 1977; Gastaldi & Scaramuzza, 1979). This lowering of symmetry can arise from a long-range cation ordering within the tetrahedral and/or octahedral sublattice and from a

displacement of the octahedral metal ions along the |111| directions (Hill, Craig & Gibbs, 1978). The space-group assignment is based on the detection of classes of reflections allowed in $F\bar{4}3m$ and forbidden in $Fd3m$. Thus, it is necessary to avoid those physical effects (mainly Renninger) which can modify the true Bragg intensity.

Data were collected at 293 K with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The unit-cell-parameter determination was reported by Gastaldi & Scaramuzza (1979).

$CuIn_5S_8$ single crystals were prepared and supplied by Drs C. Paorici and L. Zanotti of the CNR MASPEC Laboratory of Parma; analysis of the compound gave the atomic Cu/In ratio 1:5 in all tested samples (Paorici, Zanotti & Gastaldi, 1979).* The crystal chosen for data collection had an irregular shape, similar to a broken octahedron, its average radius being 0.24 mm. Despite its size, this crystal had to be used because good crystals of this material are very difficult to obtain. Satisfactory results could not be obtained using spherical crystals, even after the spheres had been annealed.

A Syntex $P2_1$ diffractometer was used for the data collection, with Mo $K\alpha$ radiation and a graphite monochromator. The data were collected by the following technique, in order to reduce the errors due to the Renninger effect: each reflection was collected in the $\theta$–$2\theta$ scan mode at seven different values of the $\psi$ angle (around the scattering vector), $\Delta\psi$ being $2°$. These seven counts were averaged and values lying outside the range of $4.5\sigma(I)$ were rejected. A new average intensity was then computed using the 'good' values only.

The $hkl$ and $\bar{h}k\bar{l}$ reflections were collected up to $2\theta_{max} = 90°$ and treated separately as above, and then the symmetry-equivalent intensities were averaged. Only 253 of these, with $I \geq 3\sigma(I)$, were used in the early stages of the refinement. The following data collections were made to check that the phase of the crystal under examination was indeed cubic and of Laue class $m3m$ and to obtain information on the absorption: (i) a reflection of medium intensity with the general indices $hkl$ was chosen and all its equivalent reflections were measured: the intensities varied randomly (without any systematic relation with permutations of the indices) within 10%; (ii) the reflections of the class $0kl$, with $k + l = 4n + 2$, critical for the assignment of the $F\bar{4}3m$ space group to the structure, were measured at different positions of the azimuthal angle around the corresponding scattering vectors, as described in an earlier communication (Gastaldi & Scaramuzza, 1979); (iii) a strong reflection with $\chi$ angle $ca$ $90°$ was collected by rotation around its scattering vector up to $\psi = 180°$

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* The article contains two printing errors concerning the $a$ and $\lambda$ values used.

($\Delta\psi = 10°$): the plot of these intensities *versus* $\psi$ was relatively flat.

The first result confirmed the previous hypotheses on the crystal system and space group, whereas the $\psi$ curve induced us to apply an absorption correction for a spherical crystal. The Lorentz–polarization correction was then applied.

Since the absorption correction was undoubtedly imprecise, no extinction correction could be applied. In order to reduce these two systematic errors we have omitted reflections having $\sin\theta/\lambda \leq 0.18$ Å$^{-1}$ (Stout & Jensen, 1968), plus five low-angle reflections strongly affected by extinction. All $0kl$ 'forbidden' reflections were used for the refinement, except 002, so 242 independent non-zero reflections were used for the final calculations. The final $F_o$, $F_c$ list shows many strong reflections affected by extinction, which we consider to be the main factor limiting the accuracy of this structure determination. The refinement was carried out using the program $SHELX$ 76 (Sheldrick, 1976) on the IBM 370/168 computer of CNUCE, Pisa.

The refinement started with the following model: the two tetrahedral sites $4(a)$ and $4(c)$ both occupied by 50% Cu and 50% In atoms, the octahedral sites $16(c)$ occupied by In with $x = 0.625$, and the two anionic sites $16(e)$ occupied by S atoms with $x = 0.375$ and $0.875$.

In the refinement we included the positional parameters, the overall scale factor, the Debye–Waller

Table 1. *Fractional atomic coordinates, temperature factors* ($\times 10^4$) *and cation distribution for* $CuIn_5S_8$

E.s.d.'s are given in parentheses. The temperature factor is:
$T(hkl) = \exp|-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}ha^*kb^* + 2U_{23}kb^*lc^* + 2U_{13}ha^*lc^*)|.$

| Site | Symmetry | Atomic occupancy | | $x$ | $y = z$ | $U_{11}$ $U_{22} = U_{33}$ | $U_{12}$ $U_{13} = U_{23}$ |
|---|---|---|---|---|---|---|---|
| $4(a)$ | $\bar{4}3m$ | Cu | 0.524 (6) | 0.0 | | 4 (13) | 0 |
| | | In | 0.476 (6) | | | 215 (21) | 0 |
| $4(c)$ | $\bar{4}3m$ | Cu | 0.476 (6) | 0.25 | | 219 (53) | 0 |
| | | In | 0.524 (6) | | | 183 (38) | 0 |
| $16(e)$ | $3m$ | In | | 0.6226 (1) | | 178 (2) | 6 (1) |
| $16(e)$ | $3m$ | S(1) | | 0.3804 (3) | | 124 (4) | 17 (6) |
| $16(e)$ | $3m$ | S(2) | | 0.8672 (3) | | 114 (5) | 11 (6) |

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* $CuIn_5S_8$

$T(1)$ and $T(2)$ refer to $4(c)$ and $4(a)$ sites respectively. Superscripts refer to the following equivalent positions: (I) $x, \frac{1}{2} - y, \frac{1}{2} - z$; (II) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (III) $-x, \frac{1}{2} - y, \frac{1}{2} + z$; (IV) $x, -y, -z$; (V) $-x, -y, -z$; (VI) $\frac{1}{2} - x, y, \frac{1}{2} - z$.

| | | | |
|---|---|---|---|
| $T(1)$–S(1) | 2.413 (3) | S(1)–$T(1)$–S(1$^I$) | 109.5 (1) |
| $T(2)$–S(2) | 2.458 (3) | S(2$^{II}$)–$T(2)$–S(2$^{III}$) | |
| In–S(1) | 2.588 (3) | S(1$^{IV}$)–In–S(1$^V$) | 88.6 (1) |
| In–S(2) | 2.618 (3) | S(1$^{IV}$)–In–S(2$^{VI}$) | 93.1 (1) |
| | | S(1$^{IV}$)–In–S(2$^I$) | 177.6 (1) |
| | | S(2$^I$)–In–S(2$^{VI}$) | 85.1 (1) |

factors and the population factor for the tetrahedral sites.

An attempt to set the Cu atoms free to migrate towards the octahedral sites gave negative results. We avoided simultaneously refining the parameters which are usually strongly correlated, i.e. Debye–Waller factors and the atomic occupancy.

The final $R$ was 0·056.

The final atomic coordinates, together with atomic occupancies and $U_{ij}$'s, are listed in Table 1,* and bond distances and angles in Table 2.

Atomic scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974).

**Discussion.** An examination of the structural results obtained shows that the correct space group of the spinel $CuIn_5S_8$ is $F\bar{4}3m$. Thus, the tetrahedral sites are split into two non-equivalent groups, 4(a) and 4(c), having symmetry $\bar{4}3m$, and with an unequal distribution of Cu and In atoms over the two sites. The equipoints 4(a) are occupied to the extent of 52·4% by Cu atoms and 47·6% by In atoms. The opposite situation is found for the equipoints 4(c). As shown in Table 2, the dimensions of the two-coordinate tetrahedra are found to be different and the smaller tetrahedron accommodates the 'cation' richer in $In^{3+}$; the shrinkage of this tetrahedron therefore seems to be due mainly to electrostatic interactions.

The octahedral sites 16(e) accommodate In atoms with $3m$ symmetry. The In atom is, in fact, displaced along $|111|$ by 0·004 Å towards the face (111) of the octahedron formed by the same type of S atoms, S(1). This causes a distortion in the bond angles of the octahedron.

As well as the off-centre metal ion, the anions occupy two different groups of sites with symmetry $3m$, such that the anion lattice results in being virtually undistorted $|x_{S(1)} + x_{S(2)} = 0.248$, theoretical value $= 0.25|$.

Fig. 1 shows a portion of the structure with the two non-equivalent tetrahedra in evidence.

Finally, the structure obtained by this X-ray analysis has given results which are slightly different from those
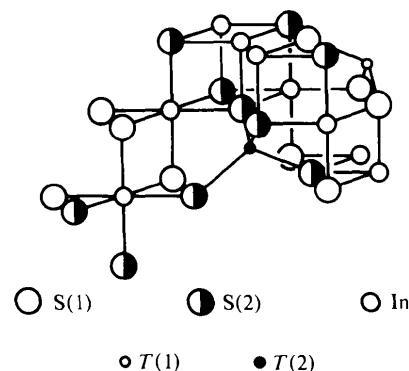
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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35310 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



Fig. 1. Portion of the structure of $CuIn_5S_8$ spinel, according to the method of representation used by Baltzer, Wojtowicz, Robbins & Lopatin (1966).

found in the literature from a powder sample (Flahaut, Domange, Guittard, Ourmichi & Kam Su Kam, 1961). The lowering of the space-group symmetry leads to an anharmonic lattice model, as found recently in a wide variety of spinel phases. The peculiarity of our case appears to be the simultaneous contribution of two effects: partial ordering in tetrahedral sites and off-centre displacement of octahedral cations.

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