

## X-ray studies on the thermal expansion of copper indium disulphide

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**Abstract.** The lattice parameters of the compound copper indium disulphide ( $\text{CuInS}_2$ ) have been measured by x-ray diffraction. The data have been used to evaluate the coefficients of thermal expansion, perpendicular and parallel to the principal axis. The thermal expansion studies revealed the anisotropy between the axial expansion coefficients having a larger coefficient of expansion along  $a$  axis than that along  $c$  axis. The anisotropic thermal expansion of this compound is interpreted in terms of the thermal expansion of the Cu-S and In-S bonds.

**Keywords.** X-ray diffraction; thermal expansion; copper indium disulphide.

### 1. Introduction

Copper indium disulphide ( $\text{CuInS}_2$ ) is a member of the class of  $A^I B^{III} C_2^{VI}$  ternary semiconducting compounds crystallizing in the chalcopyrite structure (Berger and Prochukhan 1969; Shay and Wernick 1975). In this structure, shown in figure 1 each  $A$  and  $B$  cation is tetrahedrally coordinated to four  $C$  anions, while each  $C$  anion is tetrahedrally coordinated to two  $A$  and two  $B$  cations. This tetrahedral coordination is not precisely regular, and the resulting space group is tetragonal  $I\bar{4}2d (D_{1d}^{22})$  with  $c/a$  axial ratio differing slightly from 2. As a consequence of the ordering of the two types of cations in this chalcopyrite structure, a tetragonal distortion of the lattice, defined as  $\delta = (2 - c/a)$ , results. The knowledge of the temperature dependence of this tetragonal distortion appears to be quite important in understanding the electronic properties of these widely used semi-conducting materials (Shay and Wernick 1975; Yamamoto *et al* 1979). Together with the other I-III-VI<sub>2</sub> ternaries, the  $\text{CuInS}_2$  compound has received much attention in literature for its semiconducting and non-linear optical properties, which make it a promising candidate for many technological applications (Shay and Wernick 1975; Kazmerski *et al* 1975; Bridenbaugh and Migliorato 1975; Look and Manthuruthil 1976; Bucher 1978). However, no systematic studies have been carried out on the lattice thermal behaviour of this compound. Further, our earlier studies (Kistaiah *et al* 1981a, b) on the lattice thermal behaviour of some I-III-VI<sub>2</sub> group compounds have shown that the thermal expansion coefficient is anisotropic and in some cases even negative parallel to the principal axis ( $\alpha_{\parallel}$ ) (Kistaiah *et al* 1981c,d). A knowledge of the temperature dependence of

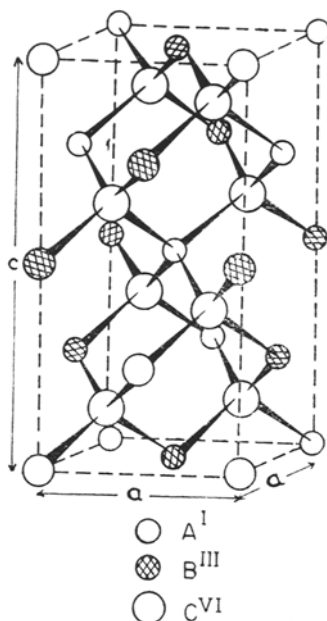


Figure 1. Unit cell of the chalcopyrite-type structure.

these coefficients of thermal expansion and their anisotropy appears to be quite important in many device applications of these materials (Bachmann *et al* 1975). The present paper gives an account of the precise determination of the lattice parameters at different temperatures and the evaluation of the coefficients of thermal expansion and the tetragonal distortion of  $\text{CuInS}_2$  at various temperatures.

## 2. Experimental procedure

A single-phase polycrystalline ingot, supplied by Dr B Tell, Bell Laboratories, USA was used. The preparation and purity of this material are as detailed in Tell *et al* (1971).

For x-ray powder diffraction studies a part of the ingot was powdered and passed through a 325-mesh sieve. The specimen was prepared by filling this powder in a 0.05 cm diameter thin-walled quartz capillary. The powder sample was made strain-free by annealing it at approximately 400°C for about 10 hr in a high temperature powder camera chamber. Powder photographs were taken at different temperatures ranging from room temperature (28°C) to 685°C with a Unicam 19 cm high temperature powder camera and  $\text{CuK}\alpha$  radiation. The temperature calibration of the thermocouples incorporated in the camera was done by the x-ray method, using silver as the standard material. The temperature of the camera was maintained constant within  $\pm 2^\circ\text{C}$  using a stabilizer with manual control. The experimental set-up and the construction of the camera have been detailed earlier (Krishna Rao *et al* 1973).

The precision lattice parameters at different temperatures were evaluated by measuring the seven unambiguously indexed reflections recorded in the Bragg angle region (66–84°) using least squares method (Cohen 1935). The computational procedure

to evaluate lattice parameters, the standard errors in the lattice parameters and the coefficients of thermal expansion were detailed earlier (Krishna Rao *et al* 1962).

### 3. Results and discussion

In table 1, the room temperature lattice parameters obtained for  $\text{CuInS}_2$  in the present investigation are compared with earlier reported values (Wyckoff 1964; Tell *et al* 1971; Lines and Waszczak 1977; Shaukat and Singh 1978; Lines 1978; Pamplin *et al* 1979). The lattice parameters obtained in the present study are in good agreement with the values reported by Tell *et al* (1971), Lines (1978) and Shaukat and Singh (1978).

The lattice parameters determined at different temperatures and values of the unit cell volume and axial ratio are given in table 2. The  $a$  parameter increases non-linearly while the  $c$  parameter increases linearly with increasing temperature. The mean standard error of the lattice parameters, evaluated in the temperature range 28 to 685°C is about  $1 \times 10^{-4}$  Å in  $a$  parameter and about  $2 \times 10^{-4}$  Å in  $c$  parameter.

Since the  $c$  parameter with temperature varies linearly, the coefficient of thermal expansion  $\alpha_{\parallel}$ , parallel to the principal axis, remains constant throughout the range of temperature studied. The temperature dependence of the coefficient of expansion ( $\alpha_{\perp}$ ), perpendicular to the principal axis is represented by the following equation:

$$\alpha_{\perp} = [9.312 \times 10^{-6} + 2.556 \times 10^{-9}T + 2.085 \times 10^{-12}T^2]^{\circ} \text{C}^{-1}, \quad (1)$$

**Table 1.** Comparison of the lattice parameters of  $\text{CuInS}_2$  at room temperature.

Source	Lattice parameters (Å)	
	$a$	$c$
Wyckoff (1964)	5.517	11.06
Tell <i>et al</i> (1971)	5.52	11.13
Lines and Waszczak (1977)	5.53	11.08
Shaukat and Singh (1978)	5.52279	11.13295
Lines (1978)	5.522	11.133
Pamplin <i>et al</i> (1979)	5.528	11.08
Present study	5.5228	11.1321
	$\pm 0.0001$	$\pm 0.0002$

**Table 2.** Lattice parameters, unit cell volume and axial ratio of  $\text{CuInS}_2$  at different temperatures.

Temperature (°C)	Lattice parameters (Å)		$V(\text{Å}^3)$	$c/a$
	$a$	$c$		
28	5.5228	11.1321	339.5437	2.0157
116	5.5274	11.1410	340.3815	2.0156
234	5.5335	11.1531	341.5037	2.0155
346	5.5402	11.1638	342.6596	2.0151
442	5.5468	11.1757	343.8427	2.0148
566	5.5539	11.1883	345.1121	2.0145
685	5.5601	11.1984	346.1953	2.0141

where  $T$  is the temperature value. The mean coefficients of expansion over the temperature range 28 to 685°C are found to be:

$$\bar{a}_{\perp} = 10.28 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1},$$

and  $a_{\parallel} = 9.07 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}.$

The error in the coefficients of thermal expansion is about  $0.06 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  in both  $a_{\perp}$  and  $a_{\parallel}$ . The mean linear expansion coefficient of this compound defined as  $\bar{a} = 1/3 (2\bar{a}_{\perp} + \bar{a}_{\parallel})$  over the temperature range covered in this investigation is  $9.88 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ . The mean temperature coefficients

$$\frac{1}{(c/a)_0} \frac{\Delta(c/a)}{\Delta T} \text{ and } \frac{1}{V_0} \frac{\Delta V}{\Delta T},$$

of the axial ratio  $c/a$  and volume of this compound over the temperature range 28 to 685°C are  $-1.21 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  and  $29.82 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  respectively. The bond expansion coefficients  $a_{\text{Cu-S}}$ ,  $a_{\text{In-S}}$  and the coefficient of parameter  $x$ , estimated by use of the relations given in Abrahams and Bernstein (1973) are found to be:

$$\frac{1}{x_0} \frac{\Delta x}{\Delta T} = 2.47 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1},$$

$$a_{\text{Cu-S}} = \frac{1}{(\text{Cu-S})_0} \frac{\Delta(\text{Cu-S})}{\Delta T} = 10.66 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1},$$

$$a_{\text{In-S}} = \frac{1}{(\text{In-S})_0} \frac{\Delta(\text{In-S})}{\Delta T} = 9.03 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1},$$

where the suffix 0 denotes the room temperature values. The parameter  $x$  denotes the location of the sulphur atom (S) relative to the copper (Cu) and indium (In) atoms by the following atomic arrangements in the chalcopyrite unit-cell,

$$\text{Cu} : (0 \ 0 \ 0), \ (0 \ \frac{1}{2} \ \frac{1}{4})$$

$$\text{In} : (0 \ 0 \ \frac{1}{2}), \ (0 \ \frac{1}{2} \ \frac{3}{4}), \ bc$$

$$\text{S} : (x \ \frac{1}{4} \ \frac{1}{8}), \ (\bar{x} \ \frac{3}{4} \ \frac{1}{8}),$$

$$(\frac{3}{4} \ x \ \frac{7}{8}), \ (\frac{1}{4} \ \bar{x} \ \frac{7}{8}), \ bc$$

with  $x = \frac{1}{4}$ , and where  $bc$  implies addition of the preceding coordinates to the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  body-centred position (Lines 1978).

The anisotropy of the thermal expansion of this compound, namely  $a_{\perp}$  greater than  $a_{\parallel}$ , is similar to that observed in its isotopic compound  $\text{CuInSe}_2$  (Kistaiah *et al* 1981b). This anisotropic thermal behaviour and the increase in the tetragonal

distortion of this compound can be explained in terms of the thermal expansion coefficients of Cu-S and In-S bonds. As seen in the bond expansion coefficients, the greater ionic Cu-S bonds have higher thermal expansion coefficients than the covalent In-S bonds. This means that the sulphur (S) atoms move relatively nearer the indium (In) cations on heating, increasing the tetragonal distortion. As pointed out by Abrahams and Bernstein (1973), the Cu-S bonds contribute more to the  $a$ -direction, while the In-S bonds to the  $c$ -direction. Hence the coefficient of thermal expansion along the  $a$ -direction ( $\alpha_{\perp}$ ) is greater than that along the  $c$ -direction ( $\alpha_{\parallel}$ ).

In conclusion, we determined the precision lattice parameters, coefficients of thermal expansion and the tetragonal distortion of the chalcopyrite ternary semiconducting compound  $\text{CuInS}_2$ . The observed anisotropy of the thermal expansion coefficients and the increase in the tetragonal distortion with temperature of this compound can be interpreted in terms of the larger thermal expansion coefficients of more ionic Cu-S bonds.

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