

Volume compression of CuCl to 7 GPa

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Abstract. The unit cell volume of CuCl as a function of pressure has been measured up to 7 GPa (giga Pascals). The compression behaviour is quite normal. The analysis of the compression data gives 40.3 ± 1.5 GPa for the bulk modulus of the zinc blende phase. The zinc blende phase transforms to a tetragonal phase at 5.5 GPa, the volume change associated with the transformation being 12%. A comparison of the bulk modulus of CuCl with those of CuBr and CuI indicates that an anomaly exists in this group.

Keywords. High pressure; cuprous chloride.

1. Introduction

Cuprous chloride crystallizes in zinc-blende structure at normal temperature and pressure and is related to the isoelectronic sequence of the group IV elements, and III-V, and II-VI semiconductors. However, many properties of CuCl are anomalous when compared with the properties of the other members of the isoelectronic sequence. Recent interest in CuCl was sparked by the claim that CuCl exhibits a dielectric to metal transition at high pressure (Rusakov *et al* 1975, 1977a, b; Serebryanaya *et al* 1979) and the high pressure phase shows anomalously large diamagnetic susceptibility (Brandt *et al* 1978) due to the onset of superconductivity. The excitonic mechanism was involved for superconductivity and a high T_c was claimed. To support the dielectric to metal transition the presence of an indirect band gap $E_{\Gamma X} \simeq 0.3\text{eV}$ in addition to a direct gap $E_D \simeq 3.4\text{eV}$ was claimed (Rusakov 1975).

However, recent experiments and band structure calculations do not support these claims for example; (i) neither the detailed band structure calculations (Doran and Woolley 1979) nor the recent optical absorption experiments (Batlogg and Remeika 1980) confirm the presence of a small indirect gap; (ii) the anomalously high diamagnetic susceptibility could not be confirmed (Guertin *et al* 1979); (iii) the conducting phase at 4 GPa appeared most probably due to the liberation of metallic copper under applied electric field which was always present while measuring the resistance (Divakar *et al* 1980), and this should not be considered as insulator \rightarrow metal transformation.

In this study we have investigated the pressure-volume behaviour of CuCl up to 7 GPa as measured by x-ray diffraction technique, and compare the various compression parameters derived from this measurement with those available in the literature.

The bulk modulus of CuCl has been compared with those of CuBr, CuI and AgI and is discussed with the help of Anderson-Nafe plot. A possible effect of pressure-induced disproportionation on the measured value of the bulk modulus is discussed.

2. Experimental details

2.1 Preparation of CuCl

On exposure to light and atmosphere, CuCl gets oxidised to CuCl₂ with the liberation of metallic copper. For this reason measurements were made on freshly prepared CuCl by the following method (Vaidya 1928). About 8 g of analytical grade CuCl₂ was heated in high purity glycerol for one hour at 180°C. The CuCl precipitate was filtered, thoroughly washed in ethanol, and dried under vacuum. The resulting white crystalline powder was heated to 200°C in quartz tube, while the tube was continuously evacuated, to remove the traces of glycerol and ethanol. The tube was then sealed and the sample end of the tube was maintained at 450°C for nearly 3 days. The vapours of CuCl deposited at the cooler regions of the tube. The condensate was removed, sealed in a second quartz tube and the process repeated. Finally, the vapour deposited CuCl was stored in sealed tubes. The x-ray diffraction patterns indicated that the phase with zinc blende structure only was present. The lattice parameter was $a = 5.413 \pm 0.002 \text{ \AA}$.

2.2 High pressure x-ray measurements

The powder patterns at high pressures were recorded using a tungsten carbide opposed anvil set-up. The gaskets made from boron-epoxy mixture were used to contain the samples under pressure. In this study the anvils of two different sizes were used. The anvils with flat face of 3 mm, and the boron-epoxy gaskets of 3 mm diameter and 0.3 mm thickness were used to record the x-ray diffraction patterns up to 7 GPa. The patterns up to 4 GPa were recorded using the anvils with 5 mm flat face and boron epoxy gaskets which were 5 mm in diameter and 0.5 mm thick.

The pressure on the sample was determined by mixing the samples with sodium chloride. The pressure experienced by NaCl was calculated from the observed change in the unit cell volume, and the knowledge of the equation of state of sodium chloride (Decker 1971). It is then assumed that the pressures on the sample and NaCl are equal. It is well-known that the presence of uniaxial stress components (usc) in the sample and the pressure marker vitiates the measured pressure volume relation (see for example Singh 1978). The correct value of the bulk modulus was deduced from the P - V data as has been discussed in § 3.

The use of epoxy as a pressure transmitting medium is known to improve considerably the hydrostaticity (Pitt 1968). Singh and Kennedy (1977) used epoxy as a pressure medium in x-ray experiments and showed that the effect of uniaxial stress component (usc) is reduced below the limits of detection. However, CuCl showed a tendency to decompose when mixed with epoxy and hence epoxy could not be used as a pressure medium in the present experiments.

3. Results and discussion

The effect of USC on the equation of state determined by x-ray diffraction technique has been studied in detail (Singh 1978). If the USC in the sample material is larger than that in the pressure-marker material, then the x-ray methods tend to underestimate the volume decrease. Further $\Delta V/V_0$ versus P does not pass through the origin of co-ordinates. In such a case, fitting a standard equation of state such as a polynomial or Murnaghan equation results in a value of bulk modulus, B_0 which is too large and a value of the pressure derivative of the bulk modulus, B'_0 which is too small or often negative. The correct value of B_0 from such data can be derived (Singh 1978) by fitting a polynomial with an adjustable constant,

$$\Delta V/V_0 = c + aP + bP^2, \quad (1)$$

The bulk modulus can be obtained using the relation

$$\bar{B}_0 = - (a)^{-1}. \quad (2)$$

The correct value of the bulk modulus B_0 , and \bar{B}_0 are related as follows,

$$B_0 = (1 - \Delta) \bar{B}_0, \quad (3)$$

where Δ is a small positive term depending on the bulk moduli, the USCs and their pressure derivatives, and the elastic compliances of the sample and the marker material. The derivation and the detailed discussion of (1) are given by Singh (1978). To a good approximation Δ is given by the following relation

$$\Delta = 3 [\alpha_s(0) B_s(0) - \alpha_m(0) B_m(0)], \quad (4)$$

where the suffixes s and m respectively refer to the sample and the pressure marker. In (4), $B_s(0) \equiv B_0 \simeq \bar{B}_0$. Further,

$$a(0) = \left[\frac{\partial \epsilon^t(P)}{\partial P} \right]_{P=0},$$

where

$$\epsilon^t(P) = [s_{12} - (s_{11} - s_{12} - \frac{1}{2} s_{44}) \bar{\Gamma}] t(P)$$

$t(P)$ is the uniaxial stress component, and $\bar{\Gamma}$ the average value of $(h^2 k^2 + k^2 l^2 + l^2 h^2)/(h^2 + k^2 + l^2)^2$ for the observed reflections. s_{ij} denote single crystal elastic compliances.

The analysis of the CuCl data along the lines suggested by Singh and Kennedy (1976) indicates that $\alpha_s(0) \simeq \alpha_m(0) = 0.0006 \text{ (GPa)}^{-1}$. Using the elastic data on NaCl (Bartels and Schuele 1965) and CuCl (Hanson *et al* 1974), and $\alpha_s(0) = \alpha_m(0) = 0.0006 \text{ (GPa)}^{-1}$ gives a value of 0.03 for Δ .

The $(\Delta V/V_0)$ versus P data for CuCl are plotted in figure 1. It is clearly seen that the data-points, specially in the low pressure region, tend to lie on the low $\Delta V/V_0$ side. Fitting (1) by least squares to the $\Delta V/V_0$ versus P data gives $a = -0.0241$ (GPa) $^{-1}$, $b = 0.00003$ (GPa) $^{-2}$ and $c = 0.0031$. With the estimated value of $\Delta = 0.03$, (2) and (3) give 40.3 ± 1.5 GPa for the corrected value of B_0 .

A procedure for correcting B'_0 for the effect of USC is not available. It is known qualitatively that the B'_0 calculated from the values of a and b in (1) is too small, and often even negative. In the present case a value of -1 is obtained for B'_0 . This value is clearly unacceptable. When $B_0 = 40.3$ is used in a standard equation of state [$c = 0$ in (1)] and b is calculated from the experimental data, a value of 0.0009 (GPa) $^{-2}$ is obtained; this gives a value of 2 for B'_0 . However, in the absence of a valid procedure to correct B'_0 for the effect of USC, a value of 3.9 obtained by ultrasonic method will be assumed for B'_0 (Hanson *et al* 1974).

The present results are compared with those of the other investigators in table 1. It is seen that the value of B_0 is in excellent agreement with the value obtained by the

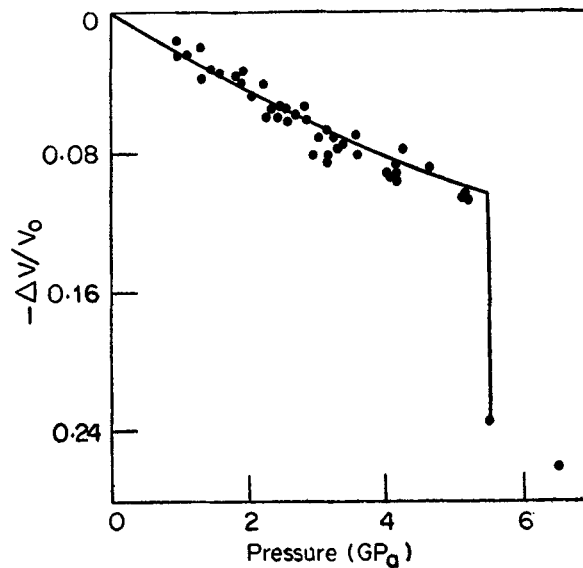


Figure 1. $(\Delta V/V_0) - P$ data for CuCl. The solid line indicates the calculated values of $(\Delta V/V_0)$ when $B_0 = 40.4$ GPa and $B'_0 = 3.9$ are used in Murnaghan equation.

Table 1. Compression parameters of CuCl.

B_0 (GPa)	B'_0	$\frac{(\Delta V)}{V_0}$ at 4.4 GPa	$\frac{(\Delta V)}{V_0}$ at trans	P_{trans} (GPa)	Reference
39.8	3.94	—	—	—	Hanson <i>et al</i> (1974)
—	—	0.085	0.12	5.3	Skelton <i>et al</i> (1980a)
—	—	0.07	0.11	4.4	Piermarini <i>et al</i> (1980)
—	—	—	0.10	5.2	Meisalo and Kalliomaki (1973)
—	—	—	0.115	4.2	Serebryanaya <i>et al</i> (1975)
40.3 ± 1.5	—	0.085	0.12	5.5	Present results

measurement of ultrasonic velocities in single crystals (Hanson *et al* 1974). There are no other measurements of B_0 and B'_0 by x-ray diffraction method reported in the literature. However, the data of Skelton *et al* (1980a) indicate a value of 0.085 for $(\Delta V/V_0)$ at 4 GPa, which agrees well with the present result.

The data of Skelton *et al* (1980a) suggest a stiffening of the lattice starting at 4 GPa and extending upto 5.3 GPa, a pressure at which zinc blende \rightarrow tetragonal transformation takes place. This stiffening of the lattice appears to be a precursor to the structural transformation. The volume anomaly in the pressure range 4–5.3 GPa is nearly 2%. Though the scatter in the present data is slightly more than that in the work of Skelton *et al* (1980b), the anomaly of such a magnitude should be easily observed. Such a lattice stiffening, however, is not observed in the present experiments.

The cuprous halides are the only halides, with the exception of γ -AgI, to crystallize in zinc blende structure. The zinc blende structure is normally exhibited by the group IV elements, and the III-V and II-VI semiconductors. However, the elastic properties of CuCl are anomalous when compared with those of the group IV elements and the III-V and II-VI semiconductors. For example, the reduced bulk modulus is considerably smaller than the value predicted by the reduced bulk modulus versus ionicity plot. The shear moduli are also unexpectedly low (Martin 1970). This anomaly may be attributed to the fact that cuprous halides and in particular, CuCl, are on the covalent side of the critical ionicity (Philips 1970).

It has been observed (Anderson and Nafe 1965) that the bulk modulus, B_0 and the specific volume per ion pair, v_0 exhibit the following relation,

$$B_0 = K v_0^{-x}, \quad (5)$$

where K and x are constants for a group of compounds; x depends on the nature of the chemical bond whereas K depends on the valency. The derivation of (5) was based on a simple relation suggested first by Bridgman (1923). By definition,

$$B_0 = -v_0 (\partial^2 F / \partial v^2) v_0, \quad (6)$$

where F is the cohesive lattice energy contribution to the free energy. In general, the lattice energy per ion pair can be expressed as follows,

$$F = -A/r + f(r), \quad (7)$$

where r is the interatomic separation.

The first term represents the Coulomb potential and the second term a repulsion potential. On combining (6) and (7) the following relation is obtained,

$$B_0 = \frac{2A}{9 \beta^{1/3} v_0^{4/3}} \left[1 + \frac{2f''(r_0)}{f'(r_0)} r_0 \right], \quad (8)$$

where β is defined by the relation $v_0 = \beta r_0^3$. Assuming that the quantity in brackets varies slowly with v_0 and therefore a constant, (8) takes the form similar to (5) with $x = 4/3$. However, in actual cases x is found to vary considerably depending on

the nature of the chemical bond. Equation (5) is an empirical relation which is supported by the data on a wide range of solids. Since x can take values very different from $4/3$, it may be argued that the quantity in the brackets in (8) is not a constant but may vary as v_0^{-m} .

Thus (5) suggests that a plot of $\log B_0$ against $\log v_0$ for a group of similar compounds will result in a straight line with a slope $-x$. To compare the bulk moduli of the cuprous halides, $\log B_0$ has been plotted against $\log v_0$ in figure 2. The data points fall on a straight line with a slope -0.35 . This slope is considerably lower than -1 observed for alkali halides and -1.3 for covalent compounds (Anderson and Nafe 1965). In fact, such a low value of x has not been observed so far for any other group of compounds and could be regarded highly anomalous. However, if a variation of 5% is allowed in the values of B_0 for CuBr and CuI, then a line (shown dashed in figure 2) with slope -1 can be made to pass through the CuBr and CuI data points. (It may be noted that a variation of 5% in the values of B_0 is not unreasonable in view of the fact that the uncertainty in the values of B_0 is of this order). In such a case, the measured value of B_0 for CuCl will fall nearly 20% lower than the value predicted by the line of slope -1 . Thus, either the B_0 values for all the cuprous halides are anomalous in a sense that a very small value of x is obtained, or the data points for CuBr and CuI are taken to fall on a line with slope -1 and the B_0 value of CuCl alone is anomalously low. This ambiguity can be resolved if the B_0 values for some more isostructural halides become available. However, the only other isostructural halide is AgI. The elastic data for zinc blende phase are unfortunately not available. Assuming that B_0 for the zinc blende phase is not very different from that for the Wurtzite phase, one more point on the $\log B_0$ vs $\log v_0$ plot is obtained.

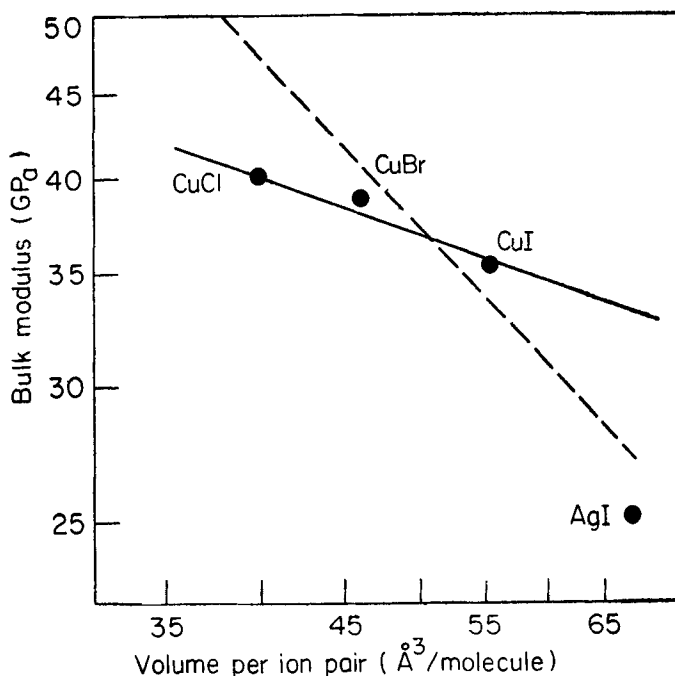


Figure 2. A plot of $\log B_0$ against $\log v_0$. The values of the bulk modulus for CuBr and CuI are from Hanson *et al* (1972) and for AgI from Davis and Blair (1968).

This point falls close to the line with slope -1 . This then suggests that the B_0 values of CuBr and CuI are most probably normal and B_0 for CuCl alone is abnormally low.

The cuprous chloride is known to undergo a disproportionation reaction as follows:



This reaction results in a volume decrease of nearly 2% and therefore favoured at high pressure. The high pressure behaviour of CuCl, specially the appearance of the conducting phase at 4 GPa, could be an outcome of this reaction (Blount and Philips 1978; Divakar *et al* 1980; Wilson 1978). If such a reaction takes place at high pressure, it will lead to a decrease in volume in addition to a volume decrease arising from the normal compressibility. This in turn will lead to a decrease in the value of B_0 . If the difference between the value of B_0 estimated from figure 2 and the measured value is attributed to the disproportionation, then it turns out that nearly 20% of CuCl will disproportionate at 1 GPa. Though the presence of very small quantities of Cu^{++} has been detected under pressure in *in-situ* ESR experiments (Skelton *et al* 1980b), such large amount of disproportionation is not observed. The difference between the observed value of B_0 and that predicted by figure 2 is thus too large to be explained on the basis of disproportionation.

4. Conclusions

(a) The pressure-volume relation for the zinc blende phase of CuCl is normal. The stiffening of the lattice prior to the cubic-tetragonal transition reported earlier (Skelton *et al* 1980a) is not observed in the present experiments.

(b) It is well-known that the reduced bulk modulus of CuCl is anomalously low compared with those of other isostructural compounds. A comparison of the bulk modulus of CuCl with those of CuBr, CuI using Anderson-Nafe plot indicates that an anomaly exists within this group.

(c) Disproportionation under pressure of CuCl is too small to lower significantly the bulk modulus.

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