

High-Pressure Studies of Cs_2CuCl_4 and Cs_2CoCl_4 by X-Ray Diffraction Methods

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Single crystals of Cs_2CuCl_4 and Cs_2CoCl_4 have been investigated at high pressures by X-ray diffraction techniques, using a diamond anvil cell. Increasing the pressure to just below 40 kbar caused the crystallinity of Cs_2CuCl_4 to deteriorate rapidly. This was accompanied by a color change from yellow/orange at lower pressures to deep red, suggesting, e.g., a major change of the coordination geometry around the Cu^{2+} ions. Decreasing the pressure to a few kilobars below the transition showed that the observed color change is reversible. No similar color change was observed for a Cs_2CoCl_4 specimen. Diffraction patterns collected at pressures further above the transition pressure do not indicate the formation of more crystalline new high-pressure phases. Single-crystal structure determinations of orthorhombic Cs_2CuCl_4 , space group symmetry $Pnma$, were performed just below the transition at 27, 33, and 36 kbar. Refinements, based on about 400 unique diffraction intensities to determine 41 structural parameters, converged to R values well below 0.10. The results show that the main features of the structure are rather unaffected at pressures close to the phase collapse. The main effect in the structure is a shortening of the Cs–Cl distances by 0.2 Å. The flattening of the coordination tetrahedra around Cu^{2+} decreases slightly with pressure as reflected by a decrease of 4° for one of the Cl–Cu–Cl angles. The Cu–Cl distance decreases only by about 0.02 Å from ambient to 36 kbar. Despite the detailed structural information obtained the origin of the observed color change at the phase transition is still unresolved. However, the lack of any phase transition of Cs_2CoCl_4 in the investigated pressure range suggests that the transition depends on the presence of the highly distorted coordination tetrahedra in Cs_2CuCl_4 . The structures of Cs_2CuCl_4 and Cs_2CoCl_4 both have very high compressibilities, with bulk moduli of 15.0(2) and 17(1) GPa, respectively. © 2000 Academic Press

Key Words: high-pressure structure; Cs_2CuCl_4 ; Cs_2CoCl_4 ; bulk modulus; single-crystal diffraction; powder diffraction.

INTRODUCTION

The present study has been performed as part of a research program focused on studies of the effects of high

pressure on compounds containing ions, like Cu^{2+} and Mn^{3+} , expected to introduce substantial Jahn–Teller distortions into the metal coordination geometry. Among tetrahedrally coordinated Cu^{2+} compounds Cs_2CuCl_4 is particularly attractive, as the CuCl_4^{2-} tetrahedra are “isolated” from each other in the structure by not sharing any coordination elements, giving a shortest Cu...Cu distance of above 6 Å. Structural architectures of this type are likely to reduce complicated effects of cooperative Jahn–Teller distortions and could possibly facilitate the interpretation of the pressure effects on the structure. For comparison, some investigations on the closely related phase Cs_2CoCl_4 were performed. The CoCl_4^{2-} tetrahedra in Cs_2CoCl_4 are only slightly distorted with Cl–Co–Cl angles ranging from 106 to 116°. The coordination tetrahedra Cs_2CuCl_4 show four Cl–Cu–Cl angles of around 100° and two of about 130°, values that are typical for a Jahn–Teller flattened coordination tetrahedron.

EXPERIMENTAL

Synthesis. Cs_2CuCl_4 and Cs_2CoCl_4 were prepared by high-pressure synthesis from stoichiometric mixtures of CsCl and CuCl_2 or CoCl_2 , respectively. The mixtures were kept in sealed gold ampoules. The ampoules were heated to 500°C at an external pressure of 2.5 kbar and kept under these conditions for another 24 h. The furnace was then turned off and allowed to cool down to ambient temperature before the ampoules were opened. Guinier X-ray powder diffraction patterns from the samples were identical to the pattern calculated from the data given in previously published single-crystal investigations (see, e.g., (1)).

High-pressure studies. A diamond anvil cell (DAC) of Merrill–Bassett type (Diacell Products DXR-5 cell, 600 μm culet diameter) was used for the high-pressure studies. The Inconel gaskets used, ≈400 μm thick, were preindented before centered holes with diameters of ≈300 μm were mechanically drilled. As the solubilities of Cs_2CuCl_4 and Cs_2CoCl_4 in common pressure transmitting media like

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TABLE 1
Unit Cell Parameters (Å) and Volumes (Å³) of Cs₂CuCl₄ and Cs₂CoCl₄ at Various Pressures

Pressure	<i>a</i>	<i>b</i>	<i>c</i>	<i>V</i>
Cs ₂ CuCl ₄ , Glycerol				
0.0	9.770(1)	7.617(1)	12.413(1)	923.7(2)
3.0	9.723(4)	7.556(4)	12.356(6)	907.7(4)
6.0	9.653(6)	7.491(7)	12.290(10)	889.0(9)
15.5	9.500(3)	7.361(4)	12.086(7)	845.2(5)
18.6	9.452(3)	7.321(4)	12.044(7)	833.5(5)
25.1	9.376(4)	7.239(4)	11.926(6)	809.5(4)
27.0	9.356(2)	7.224(2)	11.898(4)	804.9(3)
32.0	9.312(5)	7.175(4)	11.826(8)	790.2(6)
33.2	9.300(2)	7.171(4)	11.824(4)	788.6(3)
35.9	9.254(3)	7.142(3)	11.787(6)	779.1(5)
38.9	9.250(6)	7.110(5)	11.760(11)	773.4(8)
Cs ₂ CuCl ₄ , Pentane + Isopentane				
23.3	9.392(3)	7.255(3)	11.953(6)	814.5(5)
Cs ₂ CuCl ₄ , Argon				
21.6	9.426(3)	7.283(2)	11.968(4)	821.5(6)
29.4	9.332(5)	7.206(2)	11.857(4)	797.4(7)
35.3	9.273(8)	7.163(3)	11.798(5)	783.6(8)
37.8	9.253(9)	7.133(3)	11.771(5)	777.0(9)
23.4	9.387(9)	7.259(3)	11.953(3)	814.6(8)
10.0	9.593(4)	7.447(3)	12.189(4)	870.8(8)
Cs ₂ CoCl ₄ , Pentane + Isopentane				
0.0	9.7690(4)	7.3992(4)	12.9723(6)	937.67(5)
4.5	9.717(8)	7.315(5)	12.802(4)	909.9(5)
10.0	9.654(8)	7.248(7)	12.645(8)	884.8(9)
14.0	9.587(9)	7.113(8)	12.403(10)	844.4(10)
30.1	9.551(8)	7.093(5)	12.255(4)	830.2(4)
40.0	9.553(10)	7.074(10)	12.082(10)	816.3(12)

Note. The esds of the pressures are about 0.6 kbar; the other esds are given within parentheses. For each set of data the pressure medium used is given. The order of the data points within a set shows in which order the points were measured. Values for 0.0 kbar denote measurements under ambient conditions outside DACs.

methanol:ethanol:water were very high, glycerol, pentane:isopentane (1:1), and/or liquid argon were used as alternative compression fluids. Liquid argon was filled by putting an almost closed DAC (<0.1 mm opening distance) into a vessel containing liquid argon. After about 5 minutes the cell was closed mechanically under liquid argon. Different pressure transmitting media were used for the studies of Cs₂CuCl₄ to ensure that the observed phase transitions did not depend on the media used. X-ray powder patterns of Cs₂CuCl₄ were recorded from well-ground samples filled into gasket holes with diameters of ≈200 μm and using pentane:isopentane (1:1) as the pressure medium.

Pressure estimates were derived from the fluorescence wavelength shifts shown by small (<20 μm) ruby crystals located close to the specimen. The radiation source was a 25 mW Ar ion laser source and the fluorescence was

analyzed with a PC-controlled spectrograph (Oriol Multi-spec) equipped with a 1024 diode array detector. A linear shift was assumed to be valid within the studied pressure range and the proportionality constant, derived by Piermarini *et al.* (2), of 2.74 GPa · nm⁻¹ was used. Pressures were determined immediately before and after the diffractometer investigations, to ensure that changes in pressure during times of data collection could be neglected.

X-ray studies. Powder patterns for Cs₂CuCl₄ were collected with λ ≈ 0.85 Å at the crystallography beamline BL711 of the 1.5 GeV synchrotron source MAX II in Lund, Sweden. The diffractometer available for this purpose was a Bruker SMART 1000 CCD, operated with a 0.1 mm collimator diameter and a specimen to detector distance of 70.0 mm.

Single-crystal X-ray intensity data were collected with a four-circle diffractometer (Siemens P4/RA) with MoKα radiation from a rotating anode X-ray generator operated at 5.0 kW. The filament size was 0.3 × 3 mm and the collimator had a diameter of 0.3 mm. Unit cell parameters of a selected crystal at different hydrostatic pressures (Table 1) were refined from 15 well-centered reflections (10° < 2θ < 25°). Cell parameters were determined at pressures up to 38.9 kbar. The unit cell parameters at ambient pressure agree within a few estimated standard deviations (esds) with those previously published. At 36 kbar the crystal quality deteriorated significantly and just above 40 kbar the reflection profiles became too broad and diffuse to allow any centering of the reflections. The intensities of the reflections also decreased dramatically. The behavior above ≈40 kbar indicates that the specimen undergoes a phase transition that involves a major structural change leading to a collapse of the single crystal.

Three sets of single-crystal diffraction data (see Table 2) were collected at different pressures before the phase collapse pressure, viz., at 27.7, 33.3, and 35.9 kbar. The reflection intensities were measured by the conventional ω, 2θ

TABLE 2
Experimental Characteristics of the High-Pressure Single-Crystal Investigations of Cs₂CuCl₄

	Pressure (kbar)		
	27.7	33.2	35.9
Unit cell dimensions, <i>a</i>	9.356(2)	9.300(2)	9.254(3)
<i>b</i>	7.224(2)	7.171(4)	7.142(3)
<i>c</i>	11.898(4)	11.824(4)	11.787(6)
Unit cell volume, <i>V</i>	804.9(3)	788.6(3)	779.1(5)
Collected refls	1622	1354	1474
Observed unique refls	406	405	389
No. of parameters	41	41	41
<i>R</i>	0.052	0.061	0.094

TABLE 3
Fractional Coordinates and Thermal Displacement Parameters with esds in Parentheses Obtained for the High-Pressure Single-Crystal Investigations of Cs₂CuCl₄

(a) Parameters at 27.7 kbar							
Atom	x	y	z				
Cs1	0.1316(2)	0.25	0.1073(2)				
Cs2	− 0.0046(2)	0.75	0.3330(2)				
Cu	0.2300(4)	0.25	0.4204(3)				
Cl1	0.3498(9)	0.25	0.5819(7)				
Cl2	− 0.0039(9)	0.25	0.3810(8)				
Cl3	0.2998(7)	− 0.0174(8)	0.3531(5)				
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{23}	U_{eq}
Cs1	0.028(2)	0.039(1)	0.027(2)	0	0.002(1)	0	0.032(1)
Cs2	0.028(2)	0.038(1)	0.025(2)	0	0.002(1)	0	0.031(1)
Cu	0.022(3)	0.026(2)	0.022(3)	0	− 0.003(1)	0	0.023(2)
Cl1	0.032(8)	0.048(4)	0.022(8)	0	− 0.006(2)	0	0.034(4)
Cl2	0.018(8)	0.051(4)	0.039(7)	0	− 0.002(3)	0	0.036(4)
Cl3	0.034(6)	0.030(3)	0.041(6)	− 0.010(3)	− 0.001(2)	0.001(2)	0.035(3)
(b) Parameters at 33.2 kbar							
Atom	x	y	z				
Cs1	0.1312(2)	0.25	0.1076(2)				
Cs2	− 0.0040(4)	0.75	0.3342(2)				
Cu	0.2292(4)	0.25	0.4203(3)				
Cl1	0.3520(9)	0.25	0.5823(7)				
Cl2	− 0.0052(9)	0.25	0.3804(8)				
Cl3	0.3008(7)	− 0.0187(7)	0.3522(5)				
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{23}	U_{eq}
Cs1	0.024(2)	0.041(1)	0.029(2)	0	0.001(1)	0	0.031(1)
Cs2	0.027(2)	0.040(1)	0.023(2)	0	0.001(1)	0	0.030(1)
Cu	0.021(3)	0.030(2)	0.024(3)	0	− 0.005(2)	0	0.025(2)
Cl1	0.031(6)	0.042(4)	0.025(6)	0	− 0.007(3)	0	0.033(3)
Cl2	0.028(7)	0.044(4)	0.023(7)	0	− 0.005(3)	0	0.031(4)
Cl3	0.029(6)	0.037(3)	0.044(5)	− 0.011(3)	− 0.002(2)	0.003(2)	0.037(3)
(c) Parameters at 35.9 kbar							
Atom	x	y	z				
Cs1	0.1309(5)	0.25	0.1075(3)				
Cs2	− 0.0043(4)	0.75	0.3342(4)				
Cu	0.2292(10)	0.25	0.4204(6)				
Cl1	0.3513(18)	0.25	0.5810(12)				
Cl2	− 0.0094(18)	0.25	0.3792(16)				
Cl3	0.3023(15)	− 0.0177(18)	0.3528(9)				
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{23}	U_{eq}
Cs1	0.039(4)	0.042(3)	0.017(3)	0	0.003(1)	0	0.033(2)
Cs2	0.044(4)	0.050(3)	0.006(3)	0	0.005(1)	0	0.033(2)
Cu	0.040(9)	0.033(5)	0.017(6)	0	− 0.001(3)	0	0.030(4)
Cl1	0.033(15)	0.049(9)	0.014(12)	0	0.002(5)	0	0.032(7)
Cl2	0.038(17)	0.047(10)	0.024(13)	0	− 0.005(6)	0	0.037(6)
Cl3	0.051(13)	0.061(10)	0.026(10)	− 0.006(6)	0.001(4)	− 0.001(8)	0.046(6)

Note. The parameters U_{eq} are the equivalent isotropic thermal displacement parameters estimated for each atom as $\frac{1}{3}\text{trace}(\mathbf{U})$.

scan technique. The data collection was restricted to reflections with $2\theta < 80^\circ$, which, from the crystal orientation, could be expected to allow a transmission of the incident and scattered beams through the DAC. Azimuthal angles were selected to minimize the absorption and shadowing of the beams, by utilizing computer programs developed by one of the authors (R.N.) to generate optimal setting angles (ω_ψ , θ_ψ , ϕ_ψ , χ_ψ) directly from the orientation matrix. Lorenz, polarization, and absorption corrections were applied to the diffraction data.

The 41 parameters of a structural model derived from the published data by McGinnety (1) were refined against ≈ 400 unique reflections. The model allowed all atoms to vibrate anisotropically with constraints imposed by the site symmetries of the space group (see Table 3). Structure refinements were made with the SHELXTL PC software package (3), using neutral atomic scattering factors collected from the *International Tables of Crystallography* (4). Various geometric calculations were performed with the programs PLATON (5) and VOLCAL (6). The structure packing diagrams were obtained with the program ATOMS (7).

DISCUSSION

The structure of Cs_2CuCl_4 at ambient pressure (Fig. 1) has been previously determined by Morosin and Lingafelter (8), McGinnety (1), and Bailleul *et al.* (9). In the present paper the results obtained by McGinnety, who refined the ambient structure to $R = 0.055$ using anisotropic displacement parameters for all atoms, were used. In Cs_2CuCl_4 , the Cu^{2+} ions are four-coordinated by the Cl^- ions, with Cu–Cl distances ranging from 2.22 to 2.24 Å (see Table 4). The coordinations around the Cu^{2+} ions can be described as significantly flattened tetrahedra, with two Cl–Cu–Cl angles of $\approx 130^\circ$ and four of $\approx 100^\circ$. As mentioned above, the CuCl_4 tetrahedra are “isolated” from each other in the structure by not sharing any common coordination elements, with a shortest Cu...Cu distance of ≈ 6.2 Å. The bond distribution in the ambient structure is rather normal as is indicated by estimated values of the bond valence sums (bvs), using the parameters given by Brese and O’Keeffe (10). The bvs values at Cu and at the two Cs positions are 2.15, 0.81, and 1.13.

There are two symmetry-independent Cs positions, Cs1 and Cs2. Within the range up to 4.5 Å, the Cs2 atom is nine-coordinated by Cl atoms with a coordination geometry that can be regarded as a distorted monocapped quadratic antiprism. The Cs1 atom has a more regular 11-coordination, with the geometry of an Edshammar polyhedron (Edshammar (11) and Lidin *et al.* (12)). Within 4.5 Å all three symmetry-independent Cl atoms are six-coordinated, by five Cs atoms (3.1 to 4.0 Å) and one Cu atom (≈ 2.2 Å). The coordination geometries around the Cl atoms are all distorted octahedra.

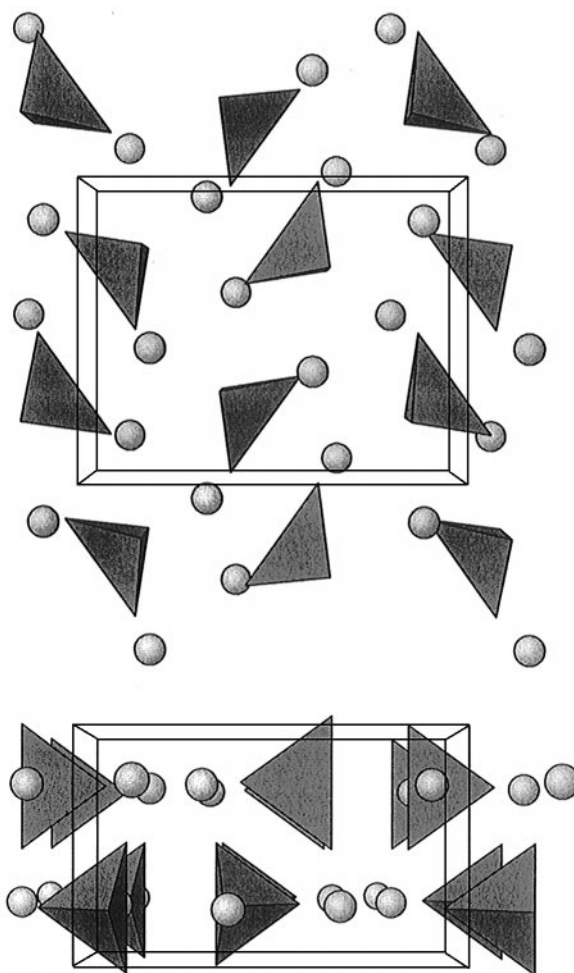


FIG. 1. Packing of Cs^+ and CuCl_4^{2-} ions in the structure of Cs_2CuCl_4 . The origins are at the lower left corner and the $[001]$ directions are horizontal. The upper projection is along $[010]$ and the lower along $[100]$.

The Cu atoms are coordinated by four Cl atoms to form a flattened CuCl_4^{2-} tetrahedron. The effects observed on the conformation of the CuCl_4 tetrahedra, when the hydrostatic pressure is increased, are very limited (Table 4) and cannot be expected to be of relevance for the observed color change at the phase transition. The major changes of the CuCl_4 geometry involve the two Cl3 atoms. Packing reasons for this can be anticipated from an inspection of the different distributions of short adjacent Cs–Cl bonds around each Cl atom. A comparison of the geometries determined at ambient and at 33.2 kbar shows that the Cu–Cl3 bond and the Cl3–Cu–Cl3 angle decrease by 0.037 Å and 4.1° , respectively. At the same time the Cl1–Cu–Cl2 angle increases by 1.9° , and the changes in Cu–Cl1 and Cu–Cl2 bonds are less than 0.02 Å.

If it is assumed that the sizes of the Cu^{2+} ions are comparatively unaffected by moderate pressures, the ionic

TABLE 4
Bond Distances (Å), Bond Valence Sums for Cu²⁺, and Bond Angles (°) with esds (in Parentheses) Obtained for the CuCl₄²⁻ Ion in Cs₂CuCl₄ at Different Pressures

	Pressure			
	Ambient	27.7 kbar	33.2 kbar	35.9 kbar
Distance Cu-Cl1	2.235(4)	2.224(9)	2.230(9)	2.205(17)
Cu-Cl2	2.244(4)	2.238(9)	2.231(9)	2.260(19)
Cu-Cl3	2 × 2.220(2)	2 × 2.191(6)	2 × 2.191(6)	2 × 2.179(13)
Average distance	2.230	2.211	2.211	2.206
Angle Cl1-Cu-Cl2	131.2(2)	132.4(4)	133.0(4)	133.2(7)
Cl3-Cu-Cl3	127.0(1)	123.7(4)	123.1(4)	122.7(7)
Cl1-Cu-Cl3	99.6(1)	99.5(2)	99.2(2)	98.9(4)
Cl2-Cu-Cl3	101.7(1)	102.4(2)	102.7(2)	103.0(5)

radii of the Cl⁻ ions must decrease by only 0.02 Å to explain the change in the Cu-Cl distances. The Cl⁻ ionic radius (see Shannon (13)) of 1.67 Å at ambient pressure thus decreases to about 1.65 Å at pressures of around 30 kbar. The effect on the ionic size can be expected to be much larger for the Cs⁺ ions. Due to the very uneven distribution of bond lengths around the Cs⁺ ions, root harmonic mean square (rhms) estimates of the Cs⁺ radii were used rather than root mean square or average values. Values of the latter have been shown (Norrestam (14)) to be highly dependent on the magnitudes of the distortions of coordination polyhedra. With the Cl⁻ radii given above the rhms estimates of the Cs⁺ radii at the 11-coordinated Cs1 positions became 2.10, 1.95, 1.92, and 1.90 Å for ambient, 27.7, 33.2, and 35.9 kbar pressures, respectively. The corresponding coordination radii at the Cs2 positions became 2.10, 1.93, 1.91, and 1.90 Å, respectively. The latter values were obtained by multiplying rhms estimates for the nine-coordinated Cs2 by the factor $\sqrt{11/9}$, as discussed elsewhere (Norrestam (14)). From these eight observations the decrease of the ionic radius R with pressure p (kbar) for 11-coordinated Cs⁺ can be described by the linear relation $R = 2.10 - p \cdot 0.0056$ Å with a correlation coefficient $r^2 = 0.994$.

The compressibilities of the structures of Cs₂CuCl₄ and Cs₂CoCl₄ are high and rather isotropic (see Figs. 2 and 3). The observed changes in unit cell volumes are well described by a Birch-Murnaghan type of equation of state (EOS),

$$P[x] = \frac{3}{2}K_0(x^{-7/3} - x^{-5/3}),$$

where P is the pressure, $x = V/V_0$ the relative volume change, and K_0 the isothermal bulk modulus at ambient pressure. With the EOS used it is implicit that the first pressure derivative (K_0') of the bulk modulus has a value of 4.00 in the pressure interval. A least-squares fitting of the observed P versus x Cs₂CuCl₄ data to the EOS, using the

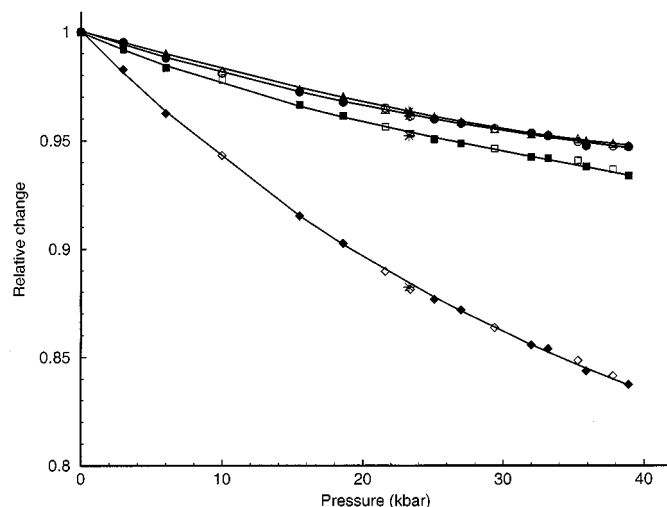


FIG. 2. Relative changes in unit cell parameters versus pressure for Cs₂CuCl₄. The open symbols denote measurements with argon as pressure medium, the filled ones denote glycerol, and the stars denote the pentane:isopentane mixture. Changes for the a axis, b axis, c axis, and volume are given as circles, squares, triangles, and diamonds, respectively.

volume V_0 obtained at ambient pressure, gave the value of the bulk modulus $K_0 = 15.0(2)$ GPa. The corresponding value for Cs₂CoCl₄ is very similar, viz., 17(1) GPa. The values of the bulk moduli K_0 are remarkably low and reflect the high compressibility of the two related structures. This is obviously due to the presence of the large, relatively soft, monocharged ions Cs⁺ (see discussion above). As a comparison, CsCl, CsBr, and CsI have bulk moduli K_0 of 18.2(9), 15.5(8), and 12.9(6) GPa, respectively (Hazen and

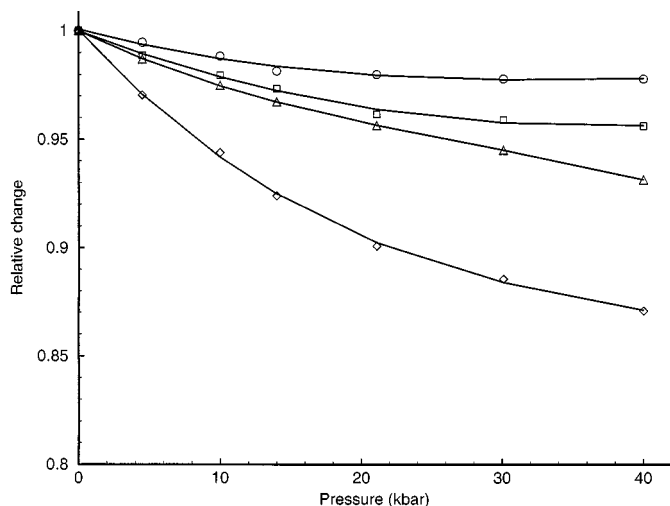


FIG. 3. Relative changes in unit cell parameters versus pressure for Cs₂CoCl₄ measured with glycerol as pressure medium. Changes for the a axis, b axis, c axis, and volume are given as circles, square, triangles, and diamonds, respectively.

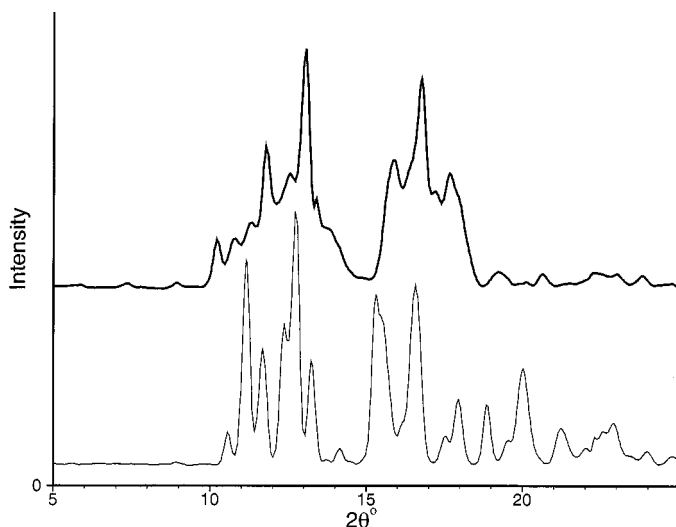


FIG. 4. Powder patterns for Cs₂CuCl₄ collected with $\lambda \approx 0.85 \text{ \AA}$ at the MAX II synchrotron source in Lund, Sweden. The lower pattern was collected at 29 kbar and the upper one at 47 kbar (crystal collapse pressure ≈ 40 kbar).

Finger (15)). Least-squares determination of both zero pressure bulk modulus K_0 and unit cell volume V_0 , from the EOS equation, gave the V_0 values 921(2) and 926(10) \AA^3 for Cs₂CuCl₄ and Cs₂CoCl₄, respectively. The rather large esds of the V_0 values reflect the high correlation (and consequently the numeric instability) between K_0 and V_0 . However, the estimated V_0 values agree with those observed at ambient conditions (920.1(2) and 937.67(5) \AA^3 for Cs₂CuCl₄ and Cs₂CoCl₄, respectively) within 1–2 esds.

As discussed above, the qualities of the Cs₂CuCl₄ single crystals deteriorated significantly a few kilobars above ≈ 36 kbar. The single crystals, which at lower pressures are seen through the diamonds of the DAC as yellow to orange, simultaneously turn deep red. The observed color change is reversible when the pressure is lowered by a few kilobars. Above 40 kbar the reflection profiles became so poor and the intensities of the reflections so low that further studies by single-crystal methods could not be carried out. This collapse of monocrystalline specimens at about 40 kbar was observed for several different crystals. Lowering the pressure from just above the transition to below the transition indicates a partial “reconstruction” of the crystallinity yielding a discrete diffraction pattern. This pattern could be indexed with the same unit cell as observed before. Thus, the transition is at least partly reversible.

To obtain some further information on the observed crystal collapse at ≈ 40 kbar, powder patterns for Cs₂CuCl₄ were collected with $\lambda \approx 0.85 \text{ \AA}$ at the crystallography beamline of the synchrotron source MAX II in

Lund, Sweden. Although the diffractometer equipment used was far from optimal for collecting accurate powder data, the collected patterns clearly show that the transition involves a substantial reduction of the crystallinity (cf. Fig. 4). The poor resolution of the low-angle peaks and the complete lack of resolvable peaks above about $2\theta = 25^\circ$ indicate, as could be expected from the single-crystal studies, that the specimen becomes largely amorphous after the transition. Increasing the pressure far above the transition pressure (< 70 kbar) gave no indications of the formation of a new more crystalline phase. The lack of indications for any phase transition of Cs₂CoCl₄ in the investigated pressure range suggests that the transition depends on the presence of the highly distorted coordination tetrahedra in Cs₂CuCl₄.

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Note added in proof. A collaborator (Dr. G. Svensson) at our Department made us aware of a previous paper by P. J. Wang and H. G. Drickamer (*J. Chem. Phys.* **59**, 559–560 (1973)), reporting an investigation of Cs₂CuCl₄ by high pressure optical absorption techniques. Their results indicate pressure dependent color shifts, and also a reversible transition from tetrahedral to planar CuCl₄²⁻ geometry to occur above 60–70 kbar.

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