The Influence of High Hydrostatic Pressure on the Crystal Structure of Cesium Gold Chloride (Cs$_2$Au^{I}Au^{III}Cl$_6$) in the Pressure Range up to 52 × 10^8 Pa

By W. Denner, Heinz Schulz and H. d'Amour

Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80 (Büsnau), Federal Republic of Germany

Abstract

Using a gasketed diamond-anvil high-pressure cell, which has been adapted to the automatic four-circle diffractometer, we have studied the structural changes of single crystals of the mixed-valence compound Cs$_2$Au^{I}Au^{III}Cl$_6$ under high hydrostatic pressure. Measurements with a modified measuring procedure at different pressures show a continuous decrease in the lattice constants. The changes in the relative volume are about 19% in the pressure range up to 52 × 10^8 Pa while the *a/c* ratio remains constant. The Cl atoms, which coordinate with the different gold atoms in the form of strongly distorted octahedra, move towards the symmetrical position between the Au^I and Au^{III} atoms as the pressure increases. At about 52 × 10^8 Pa the gold atoms become indistinguishable, this means only formal Au^{2+} atoms are present.

Introduction

The crystal structure of the mixed-valence compound Cs$_2$Au^{I}Au^{III}Cl$_6$ was first determined in 1938 by Elliott and Pauling from powder photographic data (Elliott & Pauling, 1938). The structure was redetermined using single-crystal data by Tindemans v. Eijndhoven & Verschoor (1974) and independently in 1975 by the authors. Cs$_2$Au^{I}Au^{III}Cl$_6$ crystallizes in the space group *I4/mmm* with lattice constants $a = 7.495$ (1) and $c = 10.880$ (2) Å. The two different gold atoms, valency +1 (Au^I) and +3 (Au^{III}), in this compound show typical coordination. The Au^I are linearly, the Au^{III} quadratic planar coordinated with the Cl atoms. In this way chains of strongly distorted AuCl$_6$ octahedra are produced, which are parallel to the *c* axis (Fig. 1). Within such a chain, there are alternately elongated octahedra with Au^{III} and compressed octahedra with Au^I in the centres. The different Au–Cl distances are given in Table 1. Neighbouring chains along [110] are translated by *c*/2 and connected by the Cl atoms of the planar Au^{III} coordination.

Table 1. Au–Cl *distances in the coordination octahedra at different pressures*

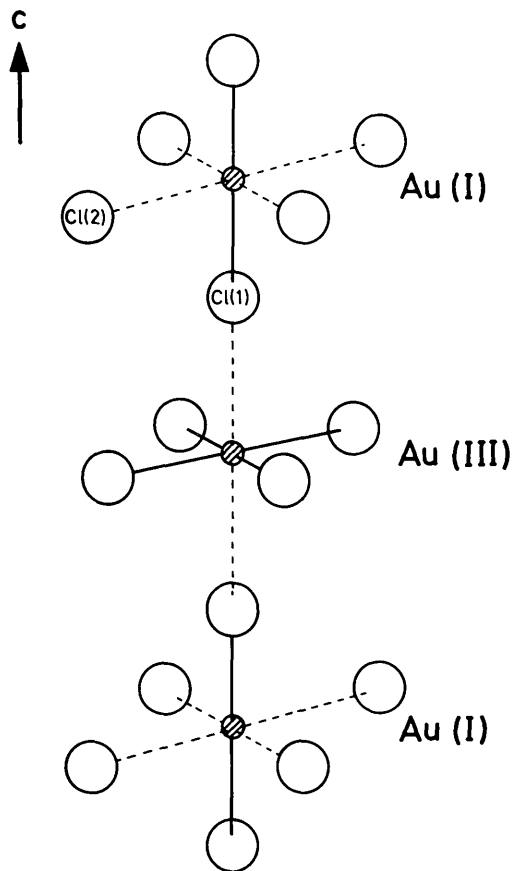| P (Pa × 10^{-8})	Au^I–Cl (1) (Å)	Au^I–Cl (2) (Å)	Au^{III}–Cl (1) (Å)	Au^{III}Cl (2) (Å)
10^{-3}	2·28 (003)	3·01 (003)	3·15 (003)	2·29 (003)
1·5	2·23 (09)	2·97 (03)	3·11 (09)	2·31 (03)
11·5	2·42 (09)	2·85 (03)	2·91 (09)	2·33 (03)
33·1	2·40 (10)	2·77 (03)	2·80 (10)	2·28 (03)
43·1	2·39 (17)	3·01 (12)	2·62 (17)	2·07 (12)
51·7	2·56 (13)	2·49 (11)	2·56 (13)	2·49 (11)

Fig. 1. Chain of distorted AuCl$_6$ octahedra.

The geometrical differences in the coordination octahedra of the gold atoms produce very weak superstructure reflections in the diffraction pattern. These reflections are characterized by hkl values with $l = 2n + 1$. If one considers the coordination octahedra to be metrically equal, the structure can be described as a distorted perovskite structure with the Cs atoms on the lattice sites of Ca, the Au atoms on the sites of Ti and the Cl atoms on the sites of O in perovskite. To get the unit cell of the cubic perovskite structure, the unit cell (a_1, a_2, c) of $Cs_2Au^IAu^{III}Cl_6$ has to be transformed according to

$$a' = \tfrac{1}{2}(a_1 - a_2); \quad b' = \tfrac{1}{2}(a_1 + a_2); \quad c' = \tfrac{1}{2}c.$$

Effect of pressure on the properties of $Cs_2Au^IAu^{III}Cl_6$

It is known that increase in pressure can produce substantial changes in structure and physical properties (Chiu & Drickamer, 1973; Interante, Browall & Bundy, 1974). Resistivity measurements on polycrystalline $Cs_2Au^IAu^{III}Cl_6$ at different quasi-hydrostatic pressures and different temperatures showed a drastic decrease of resistivity with increasing pressure (Keller, Fenner & Holzapfel, 1974). The decrease in resistivity is about nine decades in the pressure range $0–80 \times 10^8$ Pa. At about 80×10^8 Pa a value of about 10^{-5} Ω m^{-1} is reached.

The structure of $Cs_2Au^IAu^{III}Cl_6$ at 10^5 Pa may be changed in two different ways with increasing pressure, either of which allow us to explain the observed semiconductor-metal transition.

(1) With increasing pressure the interatomic distances decrease but the geometrical differences in the coordination octahedra of Au^I and Au^{III} do not change very much. In this case the increase in the conductivity could be explained by an overlap of the empty $5d_{x^2-y^2}$ band of Au^{III} and the filled $5d_z$ band of Au^I. This overlap can be caused by a broadening of the energy band as the potential in the crystal is changed.

(2) Not only the interatomic distances decreases with increasing pressure, but also the coordination octahedra of the gold atoms become more and more similar, i.e. the gold atoms become more and more indistinguishable and at the end of this process, they have a formal valency +2. In this case, two electrons per Au^I–Au^{III} pair cannot be coordinated uniquely to Au^I or Au^{III}. These electrons may contribute to the conductivity.

There are two ways to decide which of these two structural changes is the dominant one. The simpler method is to measure only exact intensities of a few superstructure reflections at different pressures, because these reflections are produced by the geometrical differences in the coordination octahedra of gold. The more general method is to determine the atomic parameters of the Cl atoms at different

pressures from complete data sets. For both possibilities the best results can be obtained from intensity measurements on single crystals with a four-circle diffractometer. For that reason we have adapted the high pressure cell described by Keller & Holzapfel (1977) to a Philips diffractometer PW 1100. To ensure that the crystals included in the high pressure cell are kept exactly in the centre of the four circles, the high pressure device is fixed in the χ circle not only at $\chi = 0°$ but also at $\chi = 180°$. Nevertheless, all degrees of freedom of a diffractometer are preserved and the crystals can be centred as exactly as crystals on a glass fibre. Details of the adaptation and the centering procedure are given elsewhere. (Denner, 1977; Denner, Dieterich, Schulz, Keller & Holzapfel, 1978).

Preparation of the high pressure cell

The high pressure chamber of a gasketed diamond-anvil device usually consists of two diamond anvils and a hole in a metal gasket (Fig. 2). As the gasket we used a thin foil of Inconel. The initial thickness of the foil was 0·3 mm. This foil was hardened at a temperature of about 873 K for some hours. Afterwards, the foil was compressed between the two diamond anvils to a thickness of about 0·15 mm and a hole was drilled in the centre of the diamond imprints. To make sure that the crystals could not slip under the gasket when the pressure transmitting fluid was added, the gasket was oriented on one diamond such that it fitted exactly in its own imprint. Care had to be taken that the crystals were placed in the centre of the hole. The crystals chosen had to be so small that there was enough space left for a reference crystal which was used for the pressure determination. The height of the crystals should be less than 0·07 mm because the thickness of the gasket usually is less than 0·08 mm at about 60×10^8 Pa. Contrary to the black colour of $Cs_2Au^IAu^{III}Cl_6$ reported in previous papers, the single crystals of this size are dark red.
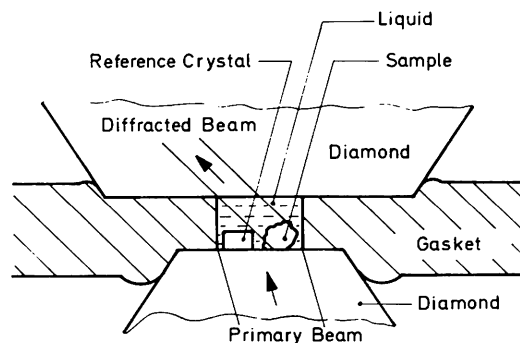

Fig. 2. High pressure chamber with crystals and the path of the X-ray beam for an arbitrary reflection.

As the pressure transmitting medium a mixture of pentane and isopentane (1 : 1) was used. According to Piermarini, Block & Barnett (1973) this fluid guarantees hydrostatic pressure up to about 65×10^8 Pa. Because of the low boiling point of the fluid (~ 300 K) it was difficult to get the fluid into the tiny hole, and the crystals were strongly displaced on adding the fluid. All attempts to fix the crystals failed, for all the fixatives were partly dissolved by the pentane–isopentane mixture. The properties of the fluid were then changed so drastically that the crystals were destroyed by shear stresses below 25×10^8 Pa. Test measurements showed that it was not necessary to fix the crystals because the viscosity of the liquid mixture was, even in the lower pressure range, high enough to keep the crystals in the same orientation for at least three days. This was checked by comparing the angular positions of several reflections and the orientation matrices.

A mixture of methanol : ethanol (4 : 1) which guarantees hydrostatic pressure up to about 100×10^8 Pa (Piermarini, Block & Barnett, 1973) and which was easier to handle could not be used, because this fluid decomposed the $Cs_2Au^IAu^{III}Cl_6$ crystals.

Pressure calibration

The pressure inside the high pressure cell was determined using a single crystal of CsCl as reference crystal. As the equation of state of CsCl is known at high pressures (Decker, 1971), it was possible to determine the pressure directly on the diffractometer by measuring the changes in the lattice constants of CsCl. In contrast to this, it would have been necessary to take the high pressure cell from the diffractometer for each pressure determination if, as usual, a splinter of ruby had been used as the reference crystal. The accuracy of the pressure determination is limited by the accuracy of the lattice constants measured with a diffractometer. The relative error in the lattice constants $\Delta a/a$ usually is less than 10^{-3} and so the pressure can be determined with an accuracy better than 10^8 Pa relative to the CsCl scale. The time necessary for the determination of the pressure using CsCl as reference crystal usually is less than 1 h.

Measurements

Because of the free movements of the high pressure cell in the Eulerian cradle it is possible to determine the orientation matrices of all single crystals in the high pressure device using the standard peak-hunting program of the Philips diffractometer PW 1100 (Hornstra & Vossers, 1973/74). The only restriction $|\varphi| \leq 35°$ or $145° \leq |\varphi| \leq 180°$ is caused by the geometry of the high pressure device (Denner, Schulz & d'Amour, 1978a).

During the peak-hunting procedure, reflections of all four single crystals of the high pressure device are usually found. These crystals are the sample, the reference crystal and the two diamond anvils. If at least three linearly independent reflections of each crystal are found, their orientation matrices can be determined and refined in the usual way. Then the lattice constants of the different crystals can be calculated and in this way the pressure can be determined from the CsCl lattice constants.

Although all degrees of freedom of a diffractometer are preserved, only intensities in a severely restricted range of reciprocal space can be measured due to restrictions of the high pressure device (Merrill & Bassett, 1974). In addition, many of the intensities measured in this range may be influenced by systematic errors due to the high pressure cell (Denner, 1977; Denner, Schulz & d'Amour, 1978a). Therefore, in our first test measurements with the high pressure device, we only studied the pressure dependence of the lattice constants and of the intensities of some selected main and superstructure reflections. For these test measurements only those reflections were selected whose intensities could not be influenced by the systematic errors, i.e. only reflections with small ω and φ values and with symmetrical background were used. For small values of ω and φ the shadowing effects are negligible and the symmetrical background indicates that no reflections of the other crystals are partly overlapped. After these test measurements had been taken, complete data sets at five different pressures in the range up to 52×10^8 Pa were measured using the high pressure measuring procedure described by Denner (1977) and Denner, Schulz & d'Amour (1978a). At each pressure 300–400 reflections could be measured in the θ-range $0 \leq \sin \theta/\lambda \leq 0.48$ using Mo $K\alpha$ radiation. Thus about 40% of all reflections in that range could be measured. The intensity measurements were made in the ω-scan mode. In this scan mode the influence on the intensity due to the X-ray scattering of the polycrystalline Be half-spheres of the high pressure cell is cancelled. The

Table 2. *Parameters for the measurement of the complete data sets at different pressures*

P (Pa $\times 10^{-8}$)	1·5	11·5	33·1	43·1	51·7
Scan speed (° s^{-1})					
Main reflections	0·02	0·01	0·01	0·02	0·03
Superstructure reflections	0·001	0·001	0·001	0·002	0·003
Scan-width (°)	1·0	1·0	1·0	1·8	3·6
Background measuring time (s)					
Main reflections	50	40	40	40	40
Superstructure reflections	240	240	240	240	240
Θ range (°)	0–20	0–20	0–20	0–20	0–20
Total number of measured reflections	419	389	359	270	258
Number of symmetrically independent reflections	79	76	67	59	57

parameters for the measurements at the different pressures are given in Table 2.

Before starting an intensity measurement, the single crystal quality was checked by looking at different reflection profiles. Fig. 3 shows the profiles of a main and a superstructure reflection at different pressures. These profiles were obtained during the test measurements.

Results and discussion

(a) Lattice constants

The test measurements showed a continuous decrease in the lattice constants with increasing pressure as illustrated by the crosses in Figs. 4 and 5. However, they decrease in such a way that the ratio a/c remains constant in the measured pressure range (Denner, Schulz & d'Amour, 1978b). In Fig. 5 the ratio $a\sqrt{2}/c$ is shown, for this should approach the value one as the structure of $Cs_2Au^IAu^{III}Cl_6$ approaches the cubic

perovskite structure with increasing pressure. The decrease of the relative volume V/V_0 is about 19% in the pressure range up to 50×10^8 Pa. The open circles in Figs. 4 and 5 represent the results obtained from the measurements of complete data sets using the procedure described by Denner, Schulz & d'Amour (1978a).

The deviation of the continuity in the lattice constants at 43.1×10^8 Pa (Fig. 4) was caused by shear stresses. At this pressure the orientation matrix showed a deviation from tetragonal symmetry and the reflection profiles showed a shoulder. After increasing the pressure to about 52×10^8 Pa, the tetragonal symmetry could be observed again, but the reflection profiles showed that the crystal had broken. The misorientation of the two individual crystals, however, was so small that the reflection intensities could still be measured by increasing the scan width.

As the thickness of the gasket was still about 0·08 mm after the measurement while the height of the crystal at the beginning of the measurement was only 0·07 mm, the shear stresses could only be caused by the very high viscosity of the pressure-transmitting medium.
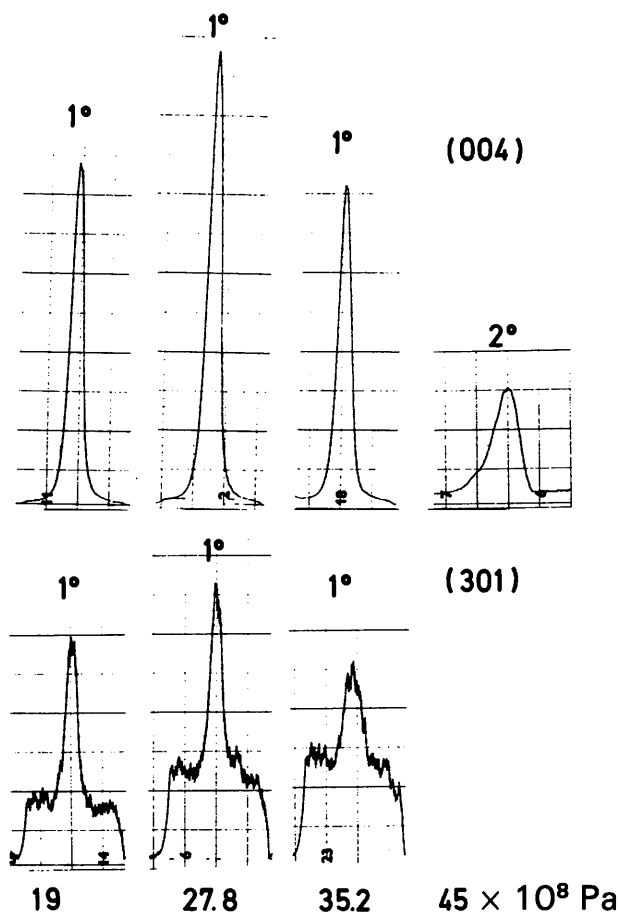

Fig. 3. Peak profiles of a main and a superstructure reflection at different pressures (obtained during the test-measurements). The numbers at the top of the profiles indicate the scan width in ω.
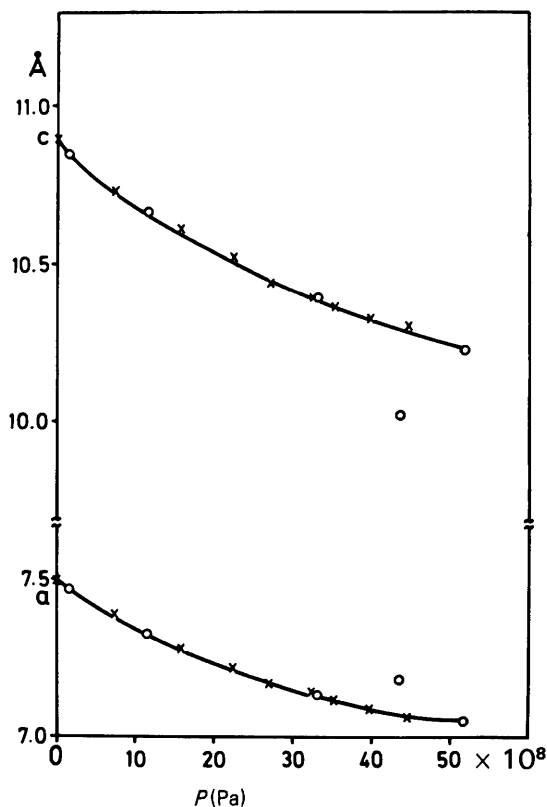

Fig. 4. Lattice constants as a function of the pressure. The standard deviations of the lattice constants are 0·002 Å. × represents results of test measurements; ○ represents results of the complete data set measurements.

(b) Intensities

During the test measurements only the superstructure reflections showed peculiar behaviour. The intensities of all measured superstructure reflections showed a strong decrease at pressures above 30×10^8 Pa. In Fig. 6 the pressure dependence of the intensity of two arbitrarily chosen superstructure reflections is shown (obtained in the test measurements). The strong decrease in the intensity at higher pressures indicates that the coordination octahedra of Au^I and Au^{III} become more and more similar with increasing pressure. This means the Cl atoms move towards the symmetrical position between the gold atoms (Denner,
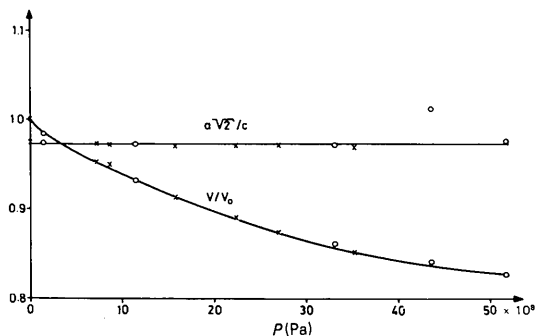

Fig. 5. Pressure dependence of the ratio $a\sqrt{2}/c$ and of the relative volume V/V_0; ×, results of the test measurements; O, results of the complete data set measurements.
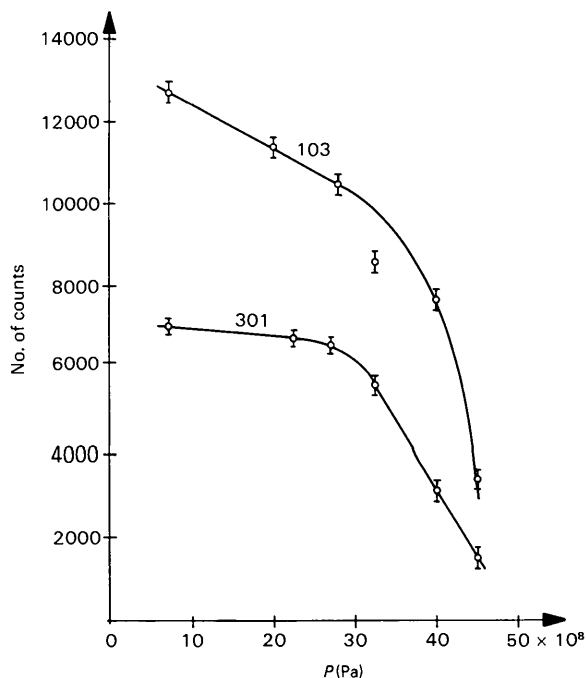

Fig. 6. Pressure dependence of the intensities of two arbitrarily chosen superstructure reflections. The error bars equal the counting statistics.

Schulz & d'Amour, 1978b). This tendency is confirmed by the behaviour of the atomic parameters of the Cl atoms, which were obtained from the structure refinements with the complete data sets at different pressures. The results of these refinements are given in Table 3.

Fig. 7 shows the pressure dependence of the atomic parameters x of the Cl atom in planar coordination [Cl (2)] and z of the Cl atom in linear coordination [Cl (1)]. Both x and z approach the value 0·25. This indicates that both Cl (1) and Cl (2) move towards the symmetrical position between the two different gold atoms. At a pressure of 52×10^8 Pa we fixed the values of x and z at 0·25. At this pressure no superstructure reflection could be observed with an intensity greater than three times the standard deviation $[I > 3\sigma(I)]$. However, it is quite possible that the atomic parameters still deviate slightly from the value 0·25 at 52×10^8 Pa, but these deviations would be within experimental error.

Conclusions

The high-pressure measurements on $Cs_2Au^IAu^{III}Cl_6$ represented in this paper are the first investigations of the behaviour of a superstructure under high pressure. They show that the structure of $Cs_2Au^IAu^{III}Cl_6$ does not approach the cubic perovskite structure in the pressure range up to 52×10^8 Pa. The Cl atoms move towards the symmetrical position between the Au atoms and at about 52×10^8 Pa the Au atoms have identical coordinations although the octahedra are still slightly elongated along the c axis. The Au—Cl distances in these octahedra now are 2·49 (4×) and 2·56 Å (2×) while the initial values at 1×10^8 Pa were (Table 1)

$$\text{and} \quad \begin{array}{l} Au^I\text{—}Cl \quad 2\cdot28 \ (2\times) \text{ and } 3\cdot01 \text{ Å } (4\times) \\ Au^{III}\text{—}Cl \ 3\cdot15 \ (2\times) \text{ and } 2\cdot29 \text{ Å } (4\times). \end{array}$$
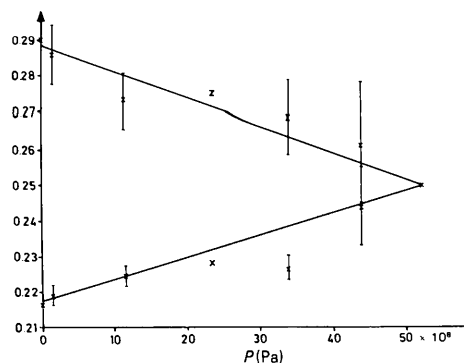

Fig. 7. Atomic parameters of the Cl atoms as a function of pressure. The error bars equal one standard deviation.

Table 3. *Results of the structure refinement*

Values in parentheses indicate one standard deviation.

$P (\times 10^{-8}$ Pa)	1·5	11·5	33·1	43·1	51·7
a (Å)	7·47	7·33	7·14	7·18	7·05
c (Å)	10·85	10·66	10·40	10·02	10·23
x [Cl(2)]	0·219 (0·003)	0·225 (0·003)	0·226 (0·004)	0·204 (0·012)	0·250 (0·011)
z [Cl(1)]	0·286 (0·009)	0·273 (0·008)	0·269 (0·010)	0·261 (0·017)	0·250 (0·013)
Temp. factors					
Cs^+	2·22 (0·47)	5·09 (0·61)	2·48 (0·57)	2·58 (0·84)	3·72 (0·65)
Au^I	1·09 (0·58)	3·70 (0·72)	1·02 (0·67)	3·33 (0·02)	3·89 (0·75)
Au^{III}	0·90 (0·57)	3·44 (0·70)	1·26 (0·67)	4·31 (1·12)	3·89 (0·75)
Cl(1)	6·24 (2·27)	5·42 (1·77)	6·60 (2·42)	1·20 (2·47)	1·33 (1·91)
Cl(2)	3·70 (1·26)	4·68 (1·77)	3·56 (1·37)	5·83 (2·84)	9·73 (3·28)
Extinction factor (10^{-3})	5·2 (1·2)	5·1 (0·9)	1·6 (0·4)	–	–
R %	10·4	7·4	8·2	14·9	7·9

These structural changes cause an increase in the translational symmetry and a change in the space group from $I4/mmm$ to $P4/mmm$. The lattice constants in the new space group are $a = 4·99$ and $c = 5·14$ Å.

The formal valency of the gold atoms in this case is +2 which means that there are delocalized electrons which contribute to the conductivity.

References

CHIU, V. C. K. & DRICKHAMER, H. G. (1973). *Proc. Natl Acad. Sci. USA*, **70**, 3065.

DECKER, D. L. (1971). *J. Appl. Phys.* **42**, 3239–3244.

DENNER, W. (1977). *Strukturanalyse an Einkristallen unter hydrostatischem Druck*. Thesis, Univ. Karlsruhe.

DENNER, W., DIETERICH, W., SCHULZ, H., KELLER, R. & HOLZAPFEL, W. B. (1978). *Rev. Sci. Instrum.* **49**, 775–777.

DENNER, W., SCHULZ, H., & D'AMOUR, H. (1978*a*). *J. Appl. Cryst.* **11**, 260–264.

DENNER, W., SCHULZ, H., & D'AMOUR, H. (1978*b*). *Naturwissenschaften*, **65**, 257.

ELLIOTT, N. & PAULING, S. L. (1938). *J. Am. Chem. Soc.* **60**, 1846–1850.

HORNSTRA, J. & VOSSERS, H. (1973/74). *Philips Tech. Rundsch.* **33**, 65–78.

INTERANTE, L. V., BROWALL, K. W. & BUNDY, F. B. (1974). *Inorg. Chem.* **13**, 1158–1162.

KELLER, R., FENNER, J. & HOLZAPFEL, W. B. (1974). *Mater. Res. Bull.* **9**, 1363–1370.

KELLER, R. & HOLZAPFEL, W. B. (1977). *Rev. Sci. Instrum.* **48**, 517–523.

MERRILL, L. & BASSETT, W. A. (1974). *Rev. Sci. Instrum.* **45**, 290–294.

PIERMARINI, G. J., BLOCK, S. & BARNETT, J. D. (1973). *J. Appl. Phys.* **44**, 5377–5382.

TINDEMANNS V. EIJNDHOVEN, J. C. M. & VERSCHOOR, S. G. C. (1974). *Mater. Res. Bull.* **9**, 1667–1670.