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ON THE QUESTION OF THE POLYMORPHIC TRANSFORMATION IN AgCl AT HIGH PRESSURE

Reversible phase transformations in silver chloride and silver bromide at pressures of 88 and 84 kbar, respectively, were first discovered by Bridgman (1) at room temperature from a jump in volume. According to later differential-thermal-analysis data (2, 3), the polymorphic transition in AgCl occurs at 76 ± 2 kbar, if the transition pressure in bismuth V–VI is taken to be 88-89 kbar. Using the method of x-ray diffraction at high pressure, R. N. Schock and J. C. Jamieson (4) investigated the crystal structure of the high-pressure phases AgCl II and AgBr II and suggested that these modifications have the cinnabar-type structure (B9). The parameters of the hexagonal unit cell of AgCl II at 70–90 kbar are: $a = 4.06$ Å, $c = 7.02$ Å; the volume jump is 7.8%. The x-ray data for AgCl II given in (4) agree with the proposed structural model. At the same time, there is a noticeable discrepancy with the volume data of Bridgman (1), according to which the volume jump in phase transitions in AgCl and AgBr is 1.6 and 1.1%, respectively. The authors of (4) attribute this discrepancy to the sluggishness of the processes studied and suggest that the volume jumps recorded by Bridgman refer to incomplete polymorphic transformations. The work of V. A. Kirkinskii and B. A. Fursenko (5) contains x-ray data obtained from Debye-Scherrer patterns for the high-pressure phases AgCl II and AgBr II; no assumptions concerning the crystal structure of these modifications are given.

Table 1

Comparison of x-ray data for AgCl II obtained by different authors

(4), 70-90 kbar	(4), 70-90 kbar	(5), 110 ± 10 kbar	(5), 110 ± 10 kbar	Our data, 100 kbar	Our data, 100 kbar
d, Å	I	d, Å	I	d, Å	I
3.145	med.	3.16	8	3.167	strong
2.832	weak	2.78	2	2.852	weak

(4), 70-90 kbar	(4), 70-90 kbar	(5), 110 ± 10 kbar	(5), 110 ± 10 kbar	Our data, 100 kbar	Our data, 100 kbar
		2.59	5		
2.482	strong	2.49	10	2.540	strong
2.288	med. weak	2.27	2	2.293	weak
		2.16	2	2.137	very weak
2.030	med. strong	2.02	10	2.034	med.
		1.91	3	1.878	very weak
				1.782	very very weak
1.702	med. weak	1.71	4	1.719	med.
		1.68	2		
				1.649	very weak
1.568	weak	1.58	4	1.582	weak
				1.524	very weak
1.410	med.	1.39	4	1.413	very weak
		1.32	4	1.340	very weak
1.300	med.			1.305	very weak
1.240	very weak	1.24	4	1.264	very weak
				1.185	very very weak

We carried out an x-ray study of the influence of high pressure on the crystal structure of AgCl with the aid of apparatus similar in type to that used in (4), and obtained a considerable number of x-ray patterns in the pressure interval 40-115 kbar. The diffraction pattern of the high-pressure phase AgCl II obtained by us agrees in the main with the results of previous investigators (4, 5) (Table 1). V. A. Kirkinskii and B. A. Fursenko (5) additionally recorded a number of weak reflections which were also observed in our photographs but are absent from the table in (4). The line with $d = 2.59$ Å, obna-

apparently should be assigned to the initial phase AgCl.

As was already shown (4), the diffraction pattern of the new modification AgCl II can be indexed on the basis of a structure of the HgS type, if very weak reflections are not taken into account. Along with this, it proved possible to index the data obtained for the same phase on the basis of an orthorhombic unit cell, to which there should correspond a crystal structure less dense than B9. The parameters of the orthorhombic unit cell are: $a = 6.90$ Å, $b = 5.08$ Å, $c = 4.05$ Å. Table 2 gives the results of indexing the experimental data for AgCl II on the basis of hexagonal (B9) and orthorhombic cells.

Table 2

Indexing of the experimental data for AgCl II (on the basis of hexagonal B9 and orthorhombic cells)

Type B9 $a = 4.07$ Å, $c = 7.2$ Å d_{calc}, Å	Type B9 $a = 4.07$ Å, $c = 7.2$ Å $h.l$	Experimental data d_{obs}, Å	Experimental data I	Orthorhombic cell $a = 6.90$ Å, $b = 5.08$ Å, $c = 4.05$ Å d_{calc}, Å	Orthorhombic cell $a = 6.90$ Å, $b = 5.08$ Å, $c = 4.05$ Å hkl
3.167	101	3.1672.852	strongweak	3.1672.8482.875	011210111
2.5232.415	102003	2.5402.293	strongweak	2.5402.3292.292	020211300
		2.137	very weak	2.152	021
2.034	110	2.034	medium	2.0261.995	002301
1.9591.9891.772	111103112	1.8781.781	very weakvery, very weak	1.8571.8151.745	211112202
1.7121.608	201104	1.7191.649	mediumvery weak	1.7191.6291.654	400410212
1.584	202	1.582	weak	1.5841.569	022321
1.555	113	1.521	very weak	1.5191.523	230131
1.4221.3511.3[illegible]	203114105211	1.4131.3401.305	very weakvery weakvery weak	1.4221.3251.305[illegible]	[illegible]402
1.261	204	1.264	very weak	1.2701.257	040203
1.1741.179	300115	1.185	very, very weak	1.175	123

It is known that there exist two polymorphic modifications of HgO (^{6}): a denser one, isostructural with HgS (type B9), and a less dense orthorhombic one with unit-cell parameters $a = 6.068$ Å; $b = 5.518$ Å; $c = 3.519$ Å; $z = 4$. The space group is D_{2h}^{16} ($Pnma$); the atoms are located on mirror planes m in the positions $\pm(x\ 1/4\ z,\ 1/2 + x\ 1/4\ 1/2 - z)$, with coordinates $x_{Hg} \simeq 0.115$; $z_{Hg} \simeq 0.245$; $x_0 \simeq 0.365$; $z_0 \simeq 0.585$. The crystal structure of each of these phases can be obtained from NaCl by distorting it. As a result, infinite Hg–O chains appear, extending helically along the c axis in the B9 phase, and planar zigzag Hg–O chains along the a axis in the orthorhombic modification. The relation between the structural types HgS and NaCl was considered by N. V. Belov (^{7}). Figure 1 schematically presents a possible mode of transformation of the NaCl structure into the structure of the orthorhombic HgO phase.

It is natural to assume that the "orthorhombic" cell for AgCl II presented above should correspond to a crystal structure close to the structure of the orthorhombic HgO phase. Such an assumption is supported by the closeness

Fig. 1. Scheme of the reconstruction of the NaCl structure into a rhombic structure of the HgO type. 1 —Na atoms; 2 —Cl atoms. The arrows show the direction of displacement of anions

Figure 1: Fig. 1. Scheme of the reconstruction of the NaCl structure into a rhombic structure of the HgO type. 1 —Na atoms; 2 —Cl atoms. The arrows show the direction of displacement of anions

of the axial ratios $a : b : c$ in both cases, which are equal to $1 : 0.83 : 0.53$ for HgO and $1 : 0.76 : 0.58$ for AgCl II. In addition, the parameters of the cubic cell of the AgCl I phase and of the "orthorhombic" AgCl II are related to one another by a ratio corresponding to the structural rearrangement of NaCl into the orthorhombic HgO type presented in Fig. 1: $a_{\text{orth}} \sim a_{\text{cub}}\sqrt{2}$; $b_{\text{orth}} \sim a_{\text{cub}}$; $c_{\text{orth}} \sim a_{\text{cub}}/\sqrt{2}$.

What, then, is the true crystal structure of the high-pressure phase AgCl II: B9, orthorhombic HgO, or some other? In order to attemp—

to try to answer this question, it was necessary to obtain reliable data on $V(p)$ for AgCl before and after the polymorphic transition, to compare them with Bridgman' s results (1), and to attempt to establish the true magnitude of the volume jump.

For this purpose, a series of X-ray diffraction patterns was obtained for a mixture of AgCl—NaCl in the pressure range 40–120 kbar, sodium chloride serving as an internal standard for estimating the pressure in each experiment by means of Decker' s semiempirical equation of state (8). In this way, values of $V(p)$ were obtained for the initial cubic modification AgCl I at 45–65 kbar. At pressures > 74 kbar, only reflections of the high-pressure phase were observed on the X-ray diffraction patterns; its volume was calculated on the assumption of a rhombic structure*. In determining the values of $V(p)$ for the cubic phase AgCl I, it turned out that in the pressure interval 45–65 kbar the diffraction patterns of AgCl I and NaCl merge**. Under ordinary conditions no such merging is observed. The fact of merging can be proved as follows: neglecting the contribution of NaCl to the intensity of the (111), (311) lines—since on NaCl X-ray diffraction patterns they are practically absent (because of the different scattering power of the Ag and Na atoms)—one can compare the parameter of the cubic cell for pure AgCl I and for the "mixture" NaCl and AgCl I***.

Fig. 1. Scheme of the reconstruction of the NaCl structure into a rhombic structure of the HgO type. 1 —Na atoms; 2 —Cl atoms. The arrows show the direction of displacement of anions.

Fig. 2. Change in volume compressibility of AgCl with pressure. 1 —Bridgman' s data (1), 2 —data of work (4); 3 —our data.

* The accuracy of determining the pressure is up to the transition ±1 kbar, after the transition ±2–3 kbar.

Fig. 2. Change in volume compressibility of AgCl with pressure. 1 — Bridgman' s data (1), 2 —data of work (4); 3 —our data

Figure 2: Fig. 2. Change in volume compressibility of AgCl with pressure. 1 — Bridgman' s data (1), 2 —data of work (4); 3 —our data

** The recording was carried out with molybdenum radiation. Cassette diameter 114 mm, sample diameter ~ 0.12 mm.

*** In calculating a_0, the reflections (111) and (311) were used for AgCl I; for the mixture AgCl I + NaCl, (200), (220), (222), and (400).

In both cases, within the limits of experimental error ($\pm 0.1\%$), a_0 has one and the same value. The volume compressibilities obtained from the X-ray data for both modifications of AgCl at different p are presented in Fig. 2. The data of Bridgman ([1]) are also given there, with allowance for the correlation between the NaCl pressure scale and Bridgman' s volume scale, carried out on the basis of the results of work ([9]).

As is seen from Fig. 2, there is good agreement of our data with the volumetric data ([1]) for the AgCl I phase (45-65 kbar). The results of the X-ray and volumetric studies at $p > 74$ kbar agree completely if a "rhombic" cell is adopted for AgCl II, and diverge considerably if the volume of the same phase is calculated according to the B9 model. Since the results of the present work show that the polymorphic transition in AgCl at $p \simeq 74$ kbar on the NaCl scale ([8]) (88 kbar on Bridgman' s volume scale ([1])) is completed, the observed discrepancy cannot be explained by incompleteness of the transformation process in Bridgman' s experiments.

Thus, the "rhombic"structure is closer to experiment than B9. It would therefore be natural to assign to the AgCl II phase the structure of the rhombic modification of HgO. Experiment has shown, however, that there is no complete analogy in the present case: 1) The diffraction patterns differ; strong reflections on the HgO X-ray patterns (210), (201), and (221) are either not observed at all on the AgCl II photographs or are very weak. 2) From an analysis of interatomic distances it follows that the positions of the atoms in the two structures cannot be identical; otherwise the distances between neighboring Ag and Cl atoms in AgCl II would be 2.25 Å in a chain, and 2.7 and 3.4 Å in different chains. The corresponding values between Hg and O atoms in HgO are 2.03, 2.86, and 2.86 Å (the first is characteristic of a covalent bond, the other two of a van der Waals bond). With complete structural similarity, one should expect in AgCl II one distance of 2.3 Å and two others of 3.1-3.3 Å. If the Ag atom is assigned the coordinates $x = 0$; $z = 0.25$, then an analysis of intensities and interatomic distances (2.3, 3.1, and 3.2 Å) gives a picture closer to the experimental data and to the character of the bonding in the model of rhombic HgO. The structural motif of rhombic HgO can be represented in monoclinic variants, for example in the space groups C_{2h}^4 and C_{2h}^2. In this case the model proposed by us will be still closer to the experimental data.

Thus, the crystal structure of the high-pressure phase AgCl II is most likely a distorted variant of the rhombic structure of the HgO type. But in view of the limited number of X-ray data, there is as yet no possibility of determining the true character of the distortion.

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Note: Figure translations are in progress. See original paper for figures.