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Abstract

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S. S. KABALKINA, T. N. KOLOBYANINA, Academician L. F. VERESHCHAGIN

X-RAY DIFFRACTION STUDY OF THE CRYSTALLINE STRUCTURE OF IODINE AT HIGH PRESSURE

The study of the physical properties of iodine under conditions of strong compression has been carried out by many investigators ($^{1-6}$) over a number of years. These works had as their aim the detection of the presumed transition of iodine from the semiconducting state to the metallic state by means of measurements of electrical conductivity and of the energy gap. Studying the dependence of the resistance of iodine on temperature, Riggleman and Drickamer (^{5}) showed that at pressures above 235 kbar iodine is a metal. However, the very first attempt to investigate the behavior of iodine under high-pressure conditions was made by Bridgman (^{7}), who, by the volumetric method, recorded a phase transition at a relatively low pressure of $\sim$ 13 kbar; the transition pressure and the volume jump found by him (0.0045 cm^3/g, which is approximately 2% of the initial volume) did not depend on temperature and were the same at -80 and $+40°$. He observed no other phase transformations up to 52 kbar.

From the crystallochemical point of view, the study of iodine under high-pressure conditions is of interest in connection with the fact that iodine is one of the few elements having a molecular structure and, perhaps, it alone among them permits structural investigations at room temperature.

Fig. 1. Projection of the iodine structure onto the *ac* face

Iodine crystals have a rhombic cell with parameters $a = 4.792$ Å, $b = 7.271$ Å, $c = 9.803$ Å, $z = 8$ (^{8}), and belong to the space group D_{2h}^{18} ($Ccmb$). The centers of the J_2 dumbbells are located at the nodes of the unit cell and at the centers of the faces, while the dumbbells themselves are situated in the symmetry planes $y = 0$ and $y = 1/2$, grouping into layers parallel to the plane ac (Fig. 1). The length of the covalent bond in the molecule is 2.68 Å; the remaining distances

Fig. 2. Schemes of X-ray diffraction patterns of iodine with successive increase of pressure

Figure 2: Fig. 2. Schemes of X-ray diffraction patterns of iodine with successive increase of pressure

are substantially larger (Table 2), since they are due mainly to weak van der Waals attraction between molecules.

We have carried out an X-ray diffraction study of the structure of iodine at room temperature and at pressures up to 60 kbar, using the method described earlier ($^{9-11}$). Usually the main part of the high-pressure X-ray camera is a pellet of amorphous boron with a channel for the sample, placed between two anvils of hard alloy VK-6. However, since amorphous boron gives a number of diffuse lines on the X-ray pattern, it is desirable in some cases, in order to reveal the diffraction pattern of the sample under study, to replace boron with another suitable material. Therefore, in our work, along with boron, polystyrene was used. The initial dimensions of the pellets were: height $1.0 \div 1.3$ mm, diameter 2 mm, channel diameter 0.2 mm. Calibration of the chamber for pressure was carried out by recording the jumps in the electrical resistance of bismuth during phase transitions at 25.4, 27, and 90 kbar (^{12}), and also by X-ray diffraction from the compressibility of NaCl using Bridgman' s data (^{13}). The error in determining the pressure is ± 5 kbar. The photography was carried out with molybdenum radiation.

In the work, crystalline iodine of chemically pure grade was used. To improve the quality of the diffraction pattern, the starting material was ground in a mortar and then subjected to high pressure of ~ 60 kbar for several hours.* The iodine powder obtained in this way was packed, with the aid of a kapron fiber, into the channel of the tablet; the latter was sealed with paraffin or molten polystyrene to prevent evaporation of iodine at atmospheric pressure.

Schemes of the X-ray diffraction patterns of iodine with successive increase of pressure are presented in Fig. 2. The positions and intensities of the lines shown are the result of averaging the data from 18 photographs; the line indices correspond to the initial rhombic cell. Measurements showed that at pressure $p \simeq 10$ kbar there occurs a merging of the lines (113) with (004) and (132) with (203), and at $p \simeq 20$ kbar—of (131) with (024). Along with this, even at low pressures (~ 10 kbar) two new very weak lines appear, to which one can assign only indices forbidden by the extinction rules of the space group $D_{2h}^{18}(Ccmb)$:

Fig. 2. Schemes of X-ray diffraction patterns of iodine with successive increase of pressure

Fig. 3. Relative change in the volume of iodine as a function of pressure (different point symbols correspond to different experiments)

indices: (124) and (213) of one line and (140) and (231) of the other. The

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diffraction pattern becomes more distinct at a pressure of 20 kbar and remains unchanged up to 60 kbar. In parallel with the strengthening of the two new lines, the increase in pressure leads to some redistribution of the intensities of the old ones, as a result of which the line (131)–(024) is weakened and the line with indices (132)–(203) is considerably strengthened, becoming the strongest in this group of lines. In addition, at $p \geq 20$ kbar the β-line (132)–(203) is strengthened to such an extent that the normal intensity ratio for α- and β-reflections is disturbed. Simultaneously, a deviation is observed of the ratio $k = \sin\vartheta_\alpha / \sin\vartheta_\beta$ from the value 1.125, characteristic of molybdenum radiation. Both of these facts can be explained by the appearance of a new line with indices (211)—(123)—(032), which is also forbidden by the extinction rules. The presence of forbidden lines in the diffraction pattern makes it possible to suppose that, in the pressure range $10 \div 20$ kbar, we observe in iodine a phase transition discovered by Bridgman (^{6}). Unfortunately, the accuracy of the present experiment does not make it possible to record the small jump in volume established by him ($\sim 2\%$). Our data on the change in volume and in the unit-cell parameters with increasing pressure are presented in Figs. 3 and 4.

Successful indexing of the iodine radiograph at high pressure on the basis of the old rhombic cell apparently may mean that the structure of the new phase does not differ greatly from the initial one. The indices assigned to the new lines indicate the absence of centering of the ab face in the cell of the new phase. The disappearance of centering during the phase transition could occur as a result of the molecules leaving the symmetry planes $y = 0$ and $y = 1/2$. If the J_2 molecules "lose" in the crystal only the symmetry plane, while preserving the inversion center and the general motif of arrangement in the cell (in the structure of the new phase the glide-reflection planes b and c are preserved), then the atoms, instead of the positions

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* After such treatment, a Debyegram taken in the RKU-114 chamber with copper radiation gave lattice parameters $a = 4.77$ Å, $b = 7.26$ Å, and $c = 9.78$ Å, space group $D_{2h}^{18}(Ccmb)$, which agrees well with the literature data (^{8}) cited above.

Fig. 4

Figure 4: Fig. 4

$$\begin{array}{cc}
x\,0\,z, & \frac{1}{2}+x\,0\,\frac{1}{2}-z, \\
\frac{1}{2}+x\,\frac{1}{2}\,z, & x\,\frac{1}{2}\,\frac{1}{2}-z, \\
-x\,\frac{1}{2}\,\bar{z}, & \bar{x}\,\frac{1}{2}\,\frac{1}{2}+z, \\
\frac{1}{2}\,\bar{x}\,0\,\bar{z}, & \frac{1}{2}-x\,0\,\frac{1}{2}+z,
\end{array}$$

which they occupied in the initial phase, will be arranged according to the law

$$\begin{array}{cc}
x\,y\,z, & \frac{1}{2}+x\,\bar{y}\,\frac{1}{2}-z, \\
\frac{1}{2}+x\,\frac{1}{2}-y\,z, & x\,\frac{1}{2}+y\,\frac{1}{2}-z, \\
\bar{x}\,\bar{y}\,\bar{z}, & \frac{1}{2}-x\,y\,\frac{1}{2}+z, \\
\frac{1}{2}-x\,\frac{1}{2}+y\,\bar{z}, & \bar{x}\,\frac{1}{2}-y\,\frac{1}{2}+z,
\end{array}$$

corresponding to the space group $D_{2h}^{15}(Pcab)$.

Fig. 4. Relative change in the cell parameters of J_2 as a function of the relative change in volume

The assumption of such a rotation of the molecules under the action of strong compression is quite natural from the standpoint of the basic rules of organic crystal chemistry (^{14}), according to which the "loss" by a molecule of a symmetry plane and the associated increase in the number of its degrees of freedom in the crystal lead to an increase in the packing density*. As is known, the space group D_{2h}^{15} is among the densest for molecular crystals.

The proposed structure of the high-pressure phase of J_2 may be regarded as a rhombically distorted variant of the $CO_2(Pa3)$ type, since the arrangement of the dumbbells is the same in both cases.

To estimate the possible angle by which the molecule leaves the *ac* plane, a very rough analysis of the intensities was carried out. It was assumed that pressure does not affect the length of the intramolecular bond, 2.68 Å, and that the plane passing through $\bar{b}$ and the axis of the molecule retains its initial position in cell. From Table 1, which gives calculated and measured data for the diffraction pattern of iodine at $p = 27$ kbar, it is seen that satisfactory agreement of the intensities occurs for $10^\circ < \varphi < 20^\circ$,

Table 1

* Loss of symmetry by a molecule means that the molecule occupies in the crystal a position whose symmetry is lower than its own (^{14}).

hkl	d/n calc., Å	I/I_0 calc., %, $\varphi =$ 0	I/I_0 calc., %, $\varphi =$ 10°	I/I_0 calc., %, $\varphi =$ 20°	d/n meas., Å	I/I_0 meas., %	*hkl*	d/n calc., Å	I/I_0 calc., %, $\varphi =$ 0	I/I_0 calc., %, $\varphi =$ 10°	I/I_0 calc., %, $\varphi =$ 20°	d/n meas., Å	I/I_0 meas., %
111	3.44_2	31	33	44	3.42	weak-medium	124	1.76_5	–	4	16	1.76	weak
020	3.30_2	46	38	25	3.28	weak-medium	213	1.74_8	–	<1	2		
112	2.90_4	100	100	100	2.91	strong	222	1.71_5	<1	<1	<1		
022	2.71_2	<1	<1	1			115	1.68_4	5	6	9	1.70	very weak
200	2.68_8	5	5	4			133	1.67_3	3	2	<1		
120	2.65_1	–	10	30			040	1.65_1	6	2	1	1.65	very weak
121	2.54_7	–	4	12			204	1.61_6	2	2	1		
113	2.39_8	11	10	10	2.39	medium	034	1.61_1	–	<1	1		
004	2.36_8	22	23	27	2.39	medium	232	1.60_3	–	2	3		
122	2.31_0	–	<1	1			223	1.58_9	11	10	8	1.59	weak
014	2.22_7	–	<1	1			006	1.57_8	<1	<1	1		
200	2.21_4	3	3	2			214	1.57_0	–	<1	<1		
201	2.15_6	13	14	18	2.17	weak	042	1.55_9	<1	<1	<1		
211	2.05_0	–	2	7			140	1.54_7	–	5	9	1.53	weak
123	2.03_0	–	3	11	2.(2	medium	125	1.54_0	–	<1	1	1.53	weak
202	2.00_7	<1	<1	<1	2.(2	medium	231	1.54_0	–	4	13	1.53	weak
032	1.99_8	–	13	32			016	1.53_5	–	<1	2		
114	1.99_1	<1	1	3			141	1.52_6	–	2	3		
1?1	1.92_9	7	4	<1	1.92	weak	134	1.51_5	<1	<1	<1		
024	1.92_3	22	18	11	1.92	weak	142	1.47_0	–	<1	<1		
212	1.92_0	–	<1	1			224	1.45_2	3	2	1		
220	1.83_9	3	3	1			116	1.45_0	10	10	9	1.45	weak
132	1.82_0	26	15	2	1.82	medium-strong							
203	1.81_2	9	11	16	1.82	medium-strong							
221	1.80_6	14	12	8									

where φ is the angle between the molecular axis and the *ac* face. Table 2 gives intermolecular distances in the iodine crystal at atmospheric pressure and at $p = 30$ kbar, calculated under the same assumptions as the intensities. It is interesting to note that when the molecule moves 20° out of the *ac* plane, the shortest intermolecular distance R_{15} (Fig. 1) is restored to its original value, 3.56 Å.

Table 2

R	$p = 1$ atm, initial structure	$p = 30$ kbar, $\varphi = 0$	$p = 30$ kbar, $\varphi = 20°$	R	$p = 1$ atm, initial structure	$p = 30$ kbar, $\varphi = 0$	$p = 30$ kbar, $\varphi = 20°$
$R_{13'}$	4.04 Å	3.77 Å	3.87 Å	R_{45}	4.35	3.94	4.73
R_{15}	3.56	3.31	3.55	$R_{56'}$	4.38	4.06	3.99
R_{25}	4.40	4.10	4.18				

It is well known that the powder method is not unambiguous in determining nontrivial structures. In the present case the matter is complicated by the comparative paucity of the diffraction pattern. Therefore our assumptions concerning the structure of the high-pressure phase of iodine require additional investigations on a single crystal.

Institute of High-Pressure Physics
Academy of Sciences of the USSR

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