

Structure analysis of high-pressure metallic state of iodine

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The crystal structure of the high-pressure metallic state of iodine has been determined by x-ray diffraction technique utilizing a diamond-anvil high-pressure cell combined with a position-sensitive proportional counter. Diffraction intensities measured at 206 kbar were very well interpreted by assuming the space group D_{2h}^{18} which is the same as that at atmospheric pressure. With further increase in applied pressure, the structure will approach to a face-centered orthorhombic lattice formed by monoatomic iodine.

I. INTRODUCTION

Metallization of molecular crystals with pressure is one of the interesting physical problems in condensed matter. Crystalline iodine has been known as a prototype material belonging to this category. The electrical resistance of iodine shows a logarithmic decrease with pressure and saturates at 160 kbar when measured along the *a* axis,¹ while it saturates at 180 kbar in the *b-c* plane.^{2,3} The resistance measured in both directions changes smoothly through 160–180 kbar. The energy gap between the valence band and the conduction band decreases with pressure and becomes zero at about 160 kbar.³ The resistance changes almost linearly with temperature at about 200 kbar, which indicates the metallic behavior.⁴ The *P-V* relation was determined by shock-wave com-

pression. McMahan *et al.*⁵ observed no kink in the volume compression up to 2 Mbar and concluded that iodine molecules continuously dissociate to iodine atoms with pressure.

The crystal structure of the metallic state of iodine has attracted much attention from the viewpoint of whether the molecular character still remains or turns into atomic character in the course of metallization. A structure analysis of the metallic state by x-ray diffraction was made by Lynch *et al.*⁶ and by Kabalkina *et al.*,⁷ but the definitive structure has not been obtained as yet. At atmospheric pressure, molecular iodine crystallizes into a base-centered orthorhombic structure with the space group $D_{2h}^{18}-Cmca$ and with four molecules per unit cell.⁸ Figure 1(a) shows the projection of the atomic positions onto the (100) and (001) planes, and the crystal structure data are listed in Table I. Iodine molecules lie

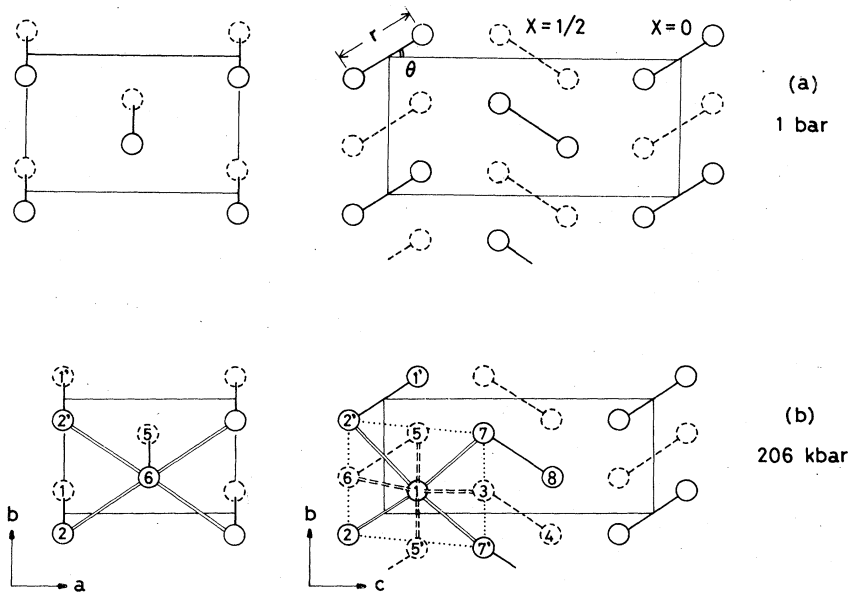


FIG. 1. Projection of the atomic positions onto the (001) and (100) planes (a) at 1 bar and (b) at 206 kbar.

TABLE I. Comparison between the crystal-structure data of solid iodine at 1 bar and those at 206 kbar. The standard deviations are given in parentheses.

1 bar, 110 K Ref. 8		206 kbar, 293 K Present work	
Space group	$D_{2h}^{18} - Cmca$	$D_{2h}^{18} - Cmca$	
Lattice constants and volume			Relative change
a (Å)	7.136(10)	5.779(8)	0.81
b (Å)	4.686(7)	3.943(14)	0.84
c (Å)	9.784(15)	9.076(10)	0.93
v (Å ³)	335.4(15)	206.8(12)	0.61
Atomic coordinates			
x	0	0	
y	0.15434(36)	0.194(4)	
z	0.11741(13)	0.128(3)	
r (Å)	2.715	2.78	
θ (deg)	32.2	33.4	
Interatomic distances (Å)		r_{1j}/r_{12}	r_{1j}/r_{12}
1-2	2.715(6)	1	1
1-3	4.412(7)	1.62	1.31
1-5	4.269(6)	1.57	1.26
1-6	4.337(7)	1.60	1.34
1-7	3.496(6)	1.29	1.06
1-2'	3.972(6)	1.46	1.20
Temperature factor			
B (Å ²)	Anisotropic	Isotropic	0.3(3)

nearly perpendicularly to each other in the b - c plane and form a layer structure stacked along the a axis. The intermolecular distance between the layers is comparable to twice the Van der Waals radius (4.30 Å), while the distance in the b - c plane is significantly smaller than that. This fact means the existence of covalency between neighboring molecules in the b - c plane.

Lynch *et al.*⁶ determined the lattice constants under pressure by two reflection lines [(200) and (112)] instead of the necessary three peaks assuming the compressibility relation of the b and c axes $\Delta b/b = \Delta c/c$ or $2\Delta b/b = \Delta c/c$. They proposed two possible model structures for the metallic state; the "square-lattice" model and the "rigid-molecule" model. In the square-lattice model, the molecule dissociates into atoms and they form a body-centered tetragonal structure with a square lattice in the b - c plane. In the rigid-molecule model, it is assumed that the molecule does not lengthen nor rotate with pressure. Based on the latter model, they estimated the critical intermolecular distance for an onset of metallic conduction as 3 Å. On the other hand, Kabalkina *et al.*⁷ proposed the "tilting model" in which the

molecules tilt from the b - c plane. However, these previous data were not sufficient to prove these model structures owing to the low S/N ratio of their x-ray powder photographs.

In order to make a precise determination of the high-pressure structure, we developed a new system of x-ray diffraction. The system consists of a diamond-anvil high-pressure cell incorporated with a one-dimensional position-sensitive proportional counter (PSPC). We improved a diamond-anvil cell which can stably generate a pressure of more than 200 kbar. In comparison with other types of high-pressure apparatus, the diamond-anvil cell, when used as attachment to an x-ray diffractometer, has the advantage that the background scattering is much lower and is nearly independent of the scattering angle. The use of the PSPC enables us to reduce largely both the exposure time and the natural background by a factor of more than 10.

In the present study to clarify the structure of the metallic state of iodine, the atomic coordinates as well as the lattice constants were precisely determined making use of the above advantages of the system.

II. EXPERIMENTAL DETAILS

The iodine sample was sublimated onto a glass plate at a slow rate to make a fine powder. To prevent any contamination with water, the sample was treated in an Ar atmosphere.

Figure 2 shows a cutaway drawing of a diamond-anvil cell designed by three of the present authors (O.S., K.T., and S.M.).⁹ High pressure is obtained by applying opposing forces to a pair of diamond anvils of about 0.25 carats each. The flat center of the anvils was 0.6 mm across. A Udimet 700 gasket was put between the diamonds. A hole in the gasket, drilled by spark erosion, was used as a sample cell. The dimensions of the sample cell were 0.15-mm diameter and 0.15-mm thickness. The diameter became 0.10 mm after precompression. The x rays impinged on the sample through a collimator (0.1-mm diam with divergence of 0.2°) set just behind the anvil. The pressure was calibrated by the shift of the ruby R_1 line using the relation $d\lambda/dp = 0.365 \text{ \AA}/\text{kbar}$.¹⁰ A small piece of crystalline ruby ($50 \mu\text{m} \times 50 \mu\text{m} \times 50 \mu\text{m}$) was glued on one side of the diamond with a very small amount of silicone grease. The pressure was measured before and after the x-ray measurement, and the change of pressure was found to be within 2 kbar in the 200-kbar range.

The PSPC with a high-resistance wire was used as a detector. The resolution in position of the counter was 200 μm , and then the detectable range of 50 mm was divided into 250 channels. The distance between the PSPC and the sample was 250 mm, so that the resolution of the scattering angle was 0.04°/channel, while the vertical divergence was 2.3°. The detectable angle of the

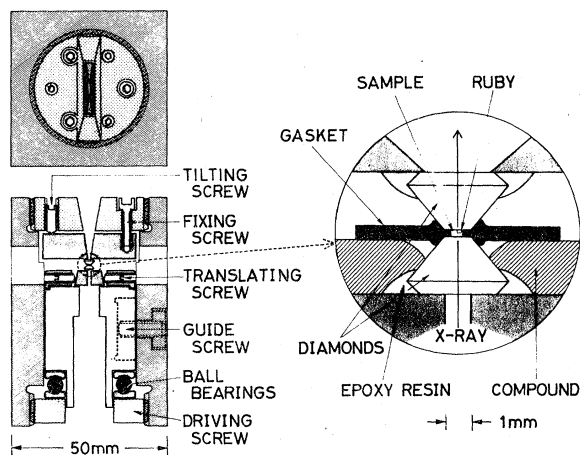


FIG. 2. Cutaway drawing of the diamond-anvil high-pressure cell. Sample assembly is shown in the right-hand circle.

counter in this configuration was 10°. The Mo $K\alpha$ line was monochromatized with pyrolytic graphite. For this radiation, a 9:1 mixture of krypton and methane was selected as filling gas. The gas pressure was 1.5 bar and the counting efficiency was estimated to be about 15%. With this PSPC system, the measuring time was reduced by a factor of about 10 compared to the step-by-step measurement using a conventional counter or a photographic method. The PSPC system supplied data of better quality than the conventional method because the natural background of the PSPC was about 1/10 that of the conventional method.

In order to eliminate the effect of a preferred orientation of crystallites, an x-ray powder photograph was taken prior to the PSPC measurement. As the diamond-anvil cell allowed a rotation within $\pm 10^\circ$ around the axis of the incident beam, the PSPC data were taken in the directions which were least affected by the preferred orientation.

III. EXPERIMENTAL RESULTS AND ANALYSIS

Diffraction patterns were taken at several pressures. Figure 3 shows the diffraction pattern at 206 kbar. In the lower-pressure region, the photographic method was also employed. On increasing the pressure step by step, neither appearance of extra peaks nor disappearance of existing peaks occurred throughout the process. From this fact, it is inferred that the space group D_{2h}^{18} does not change up to 206 kbar. This was confirmed by the more detailed intensity analysis mentioned later.

Figure 4 shows the relative lattice-constant change versus the relative volume change. The compressibilities of the a and b axes are almost the same as those obtained by Kabalkina *et al.*,⁷ but that of the c axis is smaller than theirs. In the higher-pressure region, the c axis becomes less compressible while the a and b axes seem to show the opposite tendency.

At 206 kbar, where the electrical resistance is fully saturated, 12 sets of intensity data were taken to ascertain the reliability and the reproducibility of the results. As seen in Fig. 3, the several diffraction peaks are not separable in the high-scattering-angle region. Since it was impossible to deconvolute them into individual peaks, the whole pattern was divided into 13 groups including three peaks with zero intensity. The atomic coordinates y and z of the $8f$ site of the space group D_{2h}^{18} and the isotropic temperature factor B were determined by the least-squares fit so as to minimize the χ^2 factor defined by $\chi^2 = \sum [(I_{\text{obs}}^2 - I_{\text{cal}}^2) / 2I_{\text{obs}} \sigma_{\text{obs}}]^2 / (N - P)$, where I_{obs} and I_{cal} are the observed and calculated intensities,

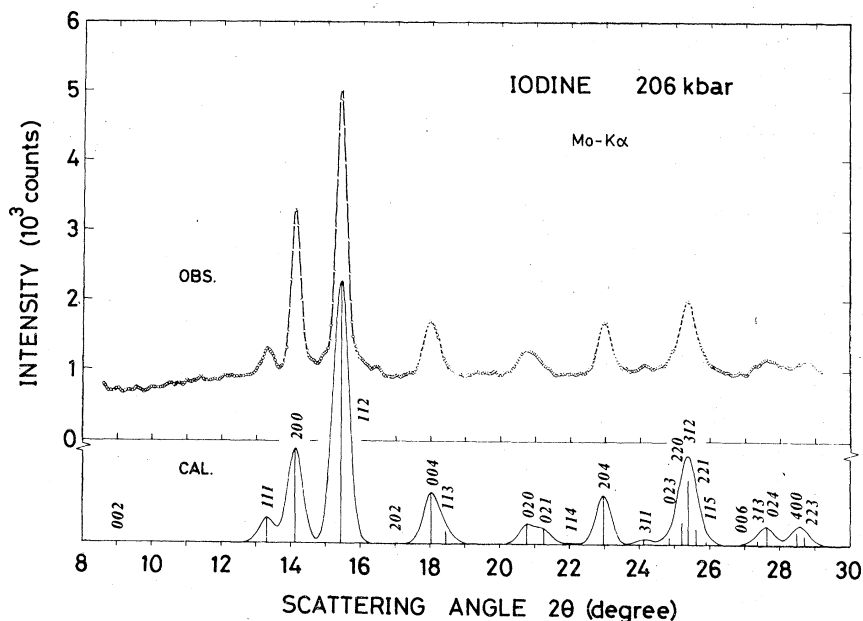


FIG. 3. Diffraction profile of metallic iodine at 206 kbar. Open circles show the observed intensities and the smooth curve at the bottom gives the calculated intensity profile based on the space group D_{2h}^{18} . The numbers indicate the indices of the Bragg reflections.

respectively, σ_{obs} is the uncertainty of I_{obs} and $N - P$ is the number of intensity data minus the number of parameters. The peak of the (200) reflection was eliminated from the fit because this peak was severely affected by the preferred orientation. The χ^2 factor finally obtained was 2.1. The solid curve at the bottom of Fig. 3 shows the

calculated intensity convoluted with the instrumental-resolution function. Agreement between observation and calculation is excellent. The resultant parameters and the interatomic distances of metallic iodine at 206 kbar are summarized in Table I together with those at atmospheric pressure and 110K reported by Bolhuis *et al.*⁸ It is

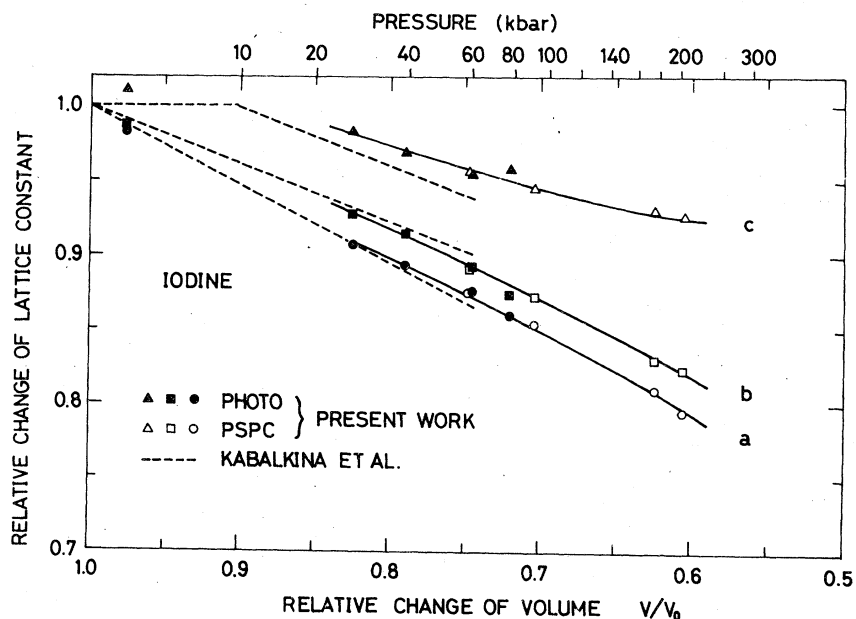


FIG. 4. Relative change of lattice constants vs relative change of volume. Open marks show the result by the PSPC method and black ones show the result by the photographic method. The broken lines are from Kabalkina *et al.*, Ref. 7.

convenient to express the atomic coordinates in terms of the polar coordinates r and θ , where r represents the intramolecular distance and θ the angle between the molecular axis and the c axis. These parameters at 206 kbar and at atmospheric pressure are also tabulated in Table I. In Fig. 1, the projection of the atomic positions so obtained at 206 kbar onto the (001) and (100) planes is shown together with those at atmospheric pressure.

IV. DISCUSSION

The previous tilting model with the space group D_{2h}^{15} - $Pbca$ proposed by Kabalkina *et al.*⁷ was carefully examined. The break of the base-center symmetry with respect to the a - b plane results in the appearance of extra reflections such as (102) at $2\theta = 11.5^\circ$ and (210) at $2\theta = 17.5^\circ$. In the present measurement, however, these peaks were not observable within the experimental error. Therefore, we can finally establish the space group D_{2h}^{18} for the crystal structure of the metallic state.

As seen in Table I, the changes in the parameters r and θ at 206 kbar are only 2% relative to the values at atmospheric pressure, in the course of a relative volume change of 40%. This fact together with the compressibility data of Fig. 4 shows that crystalline iodine is compressed approximately along the [110] axis without a rotation or an elongation of the molecule. That is, the iodine molecule behaves like a rigid molecule in the pressure range less than 206 kbar.

The square-lattice model proposed by Lynch *et al.*⁶ can be ruled out. To construct a square

lattice in the b - c plane, a relation $b = \frac{1}{2}c$ must hold, which is not attained in the observed pressure range. Not only that, the linear compressibility of the b axis is larger than that of the c axis, whence the deviation of b from $\frac{1}{2}c$ becomes even larger as the pressure is increased.

When extrapolated to higher pressure, it seems that interatomic distances in the b - c plane tend to be equal to one another. This suggests that the structure finally becomes a "face-centered orthorhombic" structure, in which a unit cell is drawn by the dotted lines connecting 2-2'-7-7' in Fig. 1(b). In this structure, the following relations must hold: $r_{1-2} = r_{1-2'} = r_{1-7}$ (in the b - c plane) and $r_{1-3} = r_{1-6}$ (out of the plane). A rough extrapolation of the lattice-constant and atomic-coordinate changes indicates that such a structure would be realized in the pressure range of 1-2 Mbar.

From the results obtained, it is clear that there is no discrete change in crystal symmetry in the course of metallization. Therefore, metallic conduction is caused by continuous increase of overlapping of the wave functions.

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¹The pressure values of Refs. 2-4 were recalibrated with the pressure scale revised by Drickamer [H. G. Drickamer, *Rev. Sci. Instrum.* **41**, 1667 (1974)].

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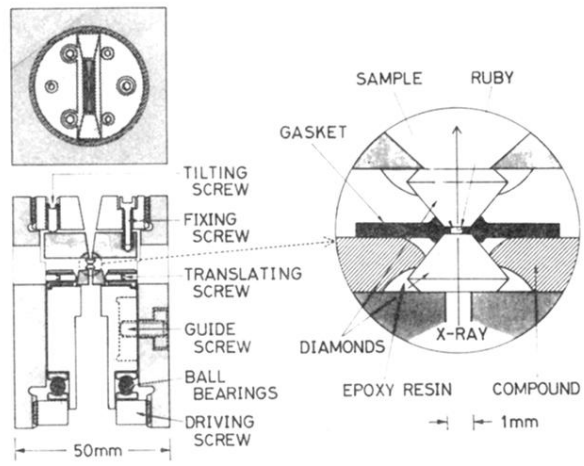


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