Observation of Molecular Dissociation of Iodine at High Pressure by X-Ray Diffraction

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Metallic iodine in the high-pressure phase above $P_t = 21$ GPa is found to form a body-centered orthorhombic Bravais lattice. Hence, pressure-induced molecular dissociation takes place at P_t.

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Solid iodine is one of a small number of elemental molecular crystals which show pressure-induced metallization under conditions accessible in the laboratory. Measurements of electrical conductivity[1] and optical energy gap[2] showed that gradual metallization takes place over a wide pressure range from 5 through 18 GPa at room temperature. At about 18 GPa, the conductivity reaches the metallic limiting value and the energy gap becomes zero. Roughly speaking, the mechanism of this metallic conduction can be explained by either of the following two models: (1) overlap between the full valence band and the empty conduction band present in diatomic molecular iodine, or (2) the unfilled conduction band (5*p* band) present in monatomic iodine, which presumably forms a simple Bravais lattice. While it is very interesting and important to clarify the metallization mechanism of iodine, which resembles that of metallic hydrogen under extremely high pressure,[3] various experiments such as shock compression[4,5] and x-ray diffraction[6] carried out beyond the metallization pressure have produced no conclusive result. These experiments measured only the unit cell volume, and did not provide information about the microscopic atomic arrangement. In 1978, Shimomura *et al.*[7] succeeded in determining the precise crystal structure of metallic iodine at 20.6 GPa by the use of a sophisticated high-pressure x-ray diffraction method, which employed a position-sensitive detector and a diamond-anvil pressure cell. According to their results, the space group at 20.6 GPa is the same as that at atmospheric pressure (D_{2h}^{18}-$Cmca$),[8] and iodine still retains its molecular character. It was therefore concluded that the continuous increase of the band overlap causes gradual metallization and no molecular dissociation takes place during the metallization process. Using a further developed x-ray diffraction technique,[9] Takemura *et al.*[10] recently discovered a new phase transition for iodine at $P_t = 21$ GPa, where x-ray diffraction patterns showed a drastic change and became simpler. This experimental fact suggested a simple crystal structure for the high-pressure phase.

In the present Letter, we report the crystal structure in this new phase, which provides direct evidence for the onset of the molecular dissociation of iodine at 21 GPa.

The high-pressure x-ray diffraction experiment was performed with the Institute for Solid State Physics computer-controlled high-pressure x-ray diffractometer system ISSP-XPSD, which consisted of a diamond-anvil cell[11] and a one-dimensional position-sensitive detector (PSD) which was highly efficient for Mo-$K\alpha$ radiation.[9] The experimental setup was identical with that used in the previous study.[10]

The measurement was carried out at several points above the transition pressure P_t. Figures 1(a)–1(c) display diffraction patterns observed at 21, 25, and 30 GPa, respectively. The diffraction pattern at 21 GPa contains spectra of both the low-pressure (LP) and the high-pressure (HP) phases, as a result of the rather large pressure distribution in the sample estimated to be ± 2 GPa. The diffraction peaks belonging to the LP phase, marked with small triangles in Fig. 1(a), were very well explained by the space group D_{2h}^{18}-

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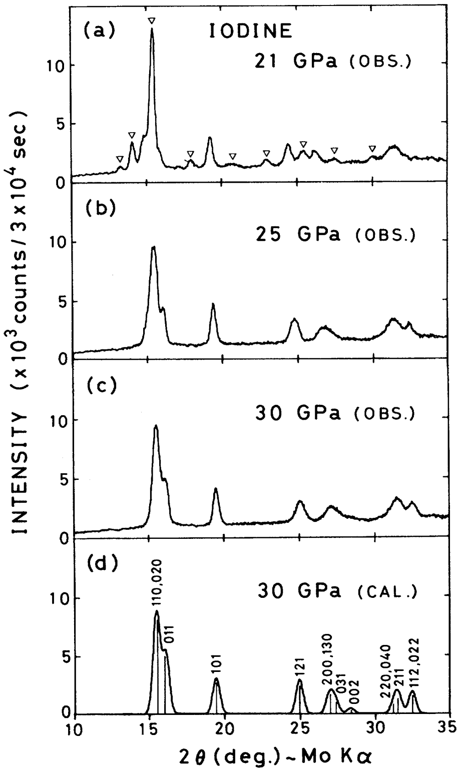

FIG. 1. Diffraction patterns of iodine observed at (a) 21, (b) 25, and (c) 30 GPa. The peaks belonging to the LP phase are marked with small triangles in (a). The pattern in (d) shows the calculated intensity for the body-centered orthorhombic Bravais lattice convoluted with the instrumental resolution.

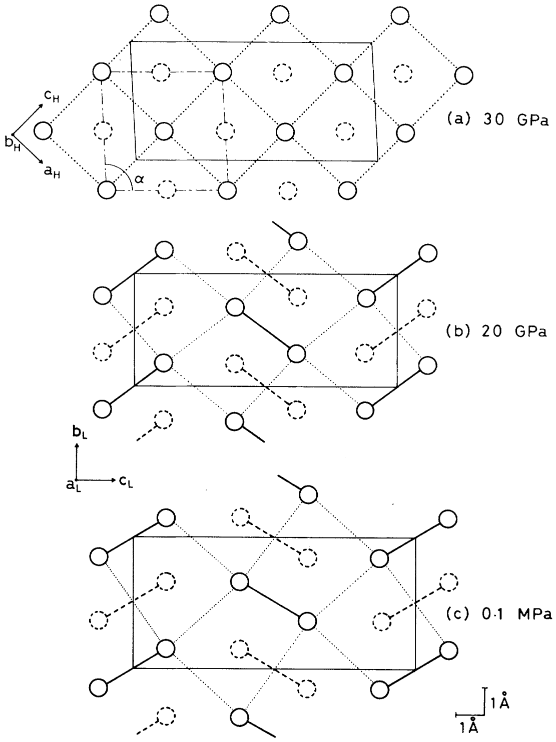

FIG. 2. Crystal structures projected onto the b_H plane of the HP phase [(a) present work] and the a_L plane of the LP phase [(b) Ref. 14, (c) Ref. 8]. The atoms drawn with the solid and dashed lines are located, respectively, at the basal plane and the half-height plane perpendicular to the paper surface. The crystallographic unit cell of the HP phase is shown by the dotted rectangle in (a) while that of the LP phase is shown by the solid one in (b) or (c).

Cmca, which had been previously assigned to the structure at 20.6 GPa.[7]

There is no systematic method for determining a general crystal structure only from powder diffraction data. In the present analysis, the following procedure was used. The profile of each peak in the observed diffraction pattern was fitted by a Gaussian function in order to obtain the peak position and integrated intensity. The peak position was determined to an accuracy of about 1%. Attempts were made to index these peaks in cubic, tetragonal, orthorhombic, and hexagonal systems. Other lower symmetry systems were not considered since the diffraction pattern of the HP phase was simpler than that of the LP orthorhombic phase. Bunn's method[12] for the hexagonal system failed to index the observed peaks. For the other three systems, the indexing method recently developed by Aoki *et al.*[13] was used to search a suitable set of lattice constants. Only the orthorhombic system with $a = 3.031$, $b = 5.252$, and $c = 2.904$ Å was found to give an excellent agreement between the observed peak positions and the calculated ones, under the condition that $h + k + l =$ even. This extinction rule indicates a body-centered lattice. It turned out that the body-centered orthorhombic lattice shown with the dotted lines in Fig. 2(a) is formed by monatomic iodine. The intensity calculated for this Bravais lattice with the space group D_{2h}^{25}-*Immm* is shown with vertical bars in Fig. 1(d). The only adjustable parameters used in fitting the intensity were the scale factor and the isotropic temperature factor. The latter had the final value $B = 0.2 \pm 1.3$ Å^2. The solid curve in Fig. 1(d) gives the resolution-convoluted intensity profile, which agrees very well with the observed diffraction pattern in Fig. 1(c). The reliability factor, defined by $R = \sum |I_{\mathrm{obs}} - I_{\mathrm{cal}}| / \sum I_{\mathrm{obs}}$, was 17%. The new orthorhombic axes, $\vec{a}_H$, $\vec{b}_H$, and $\vec{c}_H$, are taken to be $\vec{a}_H = -\vec{b}_L/2 + \vec{c}_L/4$, $\vec{b}_H = \vec{a}_L$, and $\vec{c}_H = \vec{b}_L + \vec{c}_L/4$, where $\vec{a}_L$, $\vec{b}_L$, and $\vec{c}_L$ are the axes of the LP phase shown in Fig. 2(b). The near-neighbor interatomic distances at 30 GPa are found to be 2.904 ± 0.010 Å (c_H), 3.031 ± 0.004 Å (a_H), 3.362 ± 0.004 Å (corner to body center), 4.198 ± 0.007 Å (face diagonal in the b_H plane), and 5.252 ± 0.009 Å (b_H).

The diffraction patterns measured at other pressures above P_t were also analyzed, based on this structure. The volume compression V/V_0, where V_0 is the volume at atmospheric pressure, can be calculated from the lattice constants so determined. In the HP phase, V/V_0 changes from 0.572 ± 0.004 at 21 GPa to 0.541 ± 0.002 at 30 GPa. These values agree well with the previous data obtained from shock-compression measurements.[4,5] Our recent structure analysis of iodine in the LP phase[14] shows $V/V_0 = 0.597 \pm 0.002$ at 21 GPa. Therefore, the phase transition at P_t is accompanied by a volume change of about 4%.

The present x-ray diffraction study revealed pressure-induced molecular dissociation of solid iodine, which takes place at about 21 GPa at room temperature. The crystal structure in the HP phase is a body-centered orthorhombic Bravais lattice, which is very rare. This simple lattice has a close structural relationship with that of the LP phase [Figs. 2(b) or 2(c)], which has molecular character. The compression of iodine in the LP phase causes the nearest-neighbor intermolecular distance (between the molecule at the corner and that at the face center in the a_L plane) to approach the intramolecular one (i.e., bond length), and the angle between the molecular axes of these adjacent molecules to approach 90°. Therefore, the transition to the HP structure can be simply understood as the culmination of these trends.

In the pressure range from P_t through 30 GPa, the ratio of the lattice constants a_H to c_H changes linearly with pressure as plotted in Fig. 3. The slight difference between a_H and c_H gives $\alpha = 94.5°$ and 92.5° at 21 and 30 GPa, respectively, where α is the unique angle of the "face-centered monoclinic" lattice defined as in Fig. 2(a). This monoclinic lattice is expected to become face-centered tetragonal at about 45 GPa, where the linear extrapolation of the observed a_H/c_H crosses $a_H/c_H = 1$ ($\alpha = 90°$). If b_H furthermore becomes equal to $\sqrt{2}a_H$ beyond this pressure, the ideal face-centered-cubic lattice is realized. The linear extrapolation of the data of $b_H/(a_H^2 + c_H^2)^{1/2}$ suggests an onset of the fcc lattice at an extremely high pressure.

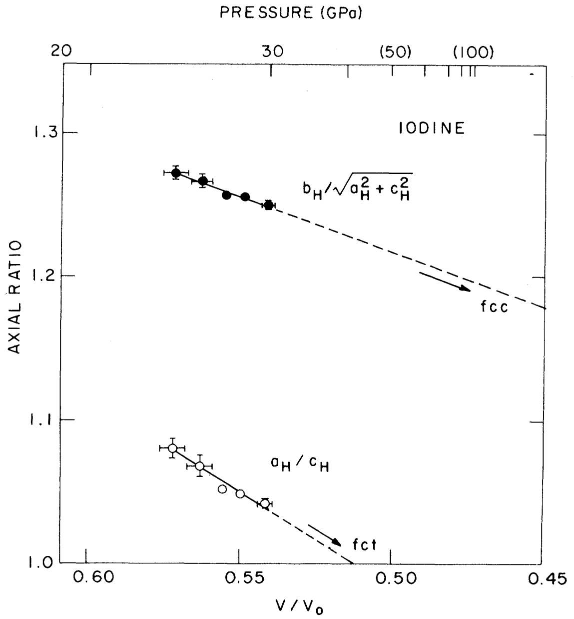

FIG. 3. The ratio of the lattice constants observed in the HP phase as a function of the volume compression V/V_0 or pressure.

Shimomura *et al.*[7] already showed that the crystal structure in the metallic state below P_t (i.e., ca. 18 GPa $< P < P_t$) still has diatomic molecular character. It has been concluded from this that the gradual metallization in the LP phase is caused by the continuous increase of the band overlap without molecular dissociation. In fact, a recent band calculation by Natsume[15] shows the semimetallic character of iodine in this pressure region. In the metallic state in the HP phase above P_t, on the other hand, iodine completely loses its molecular character because of the formation of a monatomic lattice. The electronic conduction mechanism in this phase, however, is not obvious because each iodine atom has a nearly isotropic environment in the b_H plane while a significant anisotropy still exists in the direction perpendicular to it. It is very interesting to investigate the mechanism of this phase transition accompanied by molecular dissociation from electronic and structural points of view. The present structural data, which have important implications for the band structure, are being incorporated into a band calculation by Natsume.[15]

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[1] A. S. Balchan and H. G. Drickamer, J. Chem. Phys. 34, 1948 (1961).

[2] B. M. Riggleman and H. G. Drickamer, J. Chem. Phys. 38, 2721 (1963).

[3] A. K. McMahan, *High-Pressure and Low-Temperature Physics* (Plenum, New York, 1978), p. 21.

[4] B. J. Alder and R. H. Christian, Phys. Rev. Lett. 4, 450 (1960).

[5] A. K. McMahan, B. L. Hord, and M. Ross, Phys. Rev. B 15, 726 (1977).

[6] R. W. Lynch and H. G. Drickamer, J. Chem. Phys. 45, 1020 (1966).

[7] O. Shimomura, K. Takemura, Y. Fujii, S. Minomura, M. Mori, Y. Noda, and Y. Yamada, Phys. Rev. B 18, 715 (1978).

[8] F. van Bolhuis, P. B. Koster, and T. Migchelsen, Acta Crystallogr. 23, 90 (1967).

[9] Y. Fujii, O. Shimomura, K. Takemura, S. Hoshino, and S. Minomura, J. Appl. Cryst. 13, 284 (1980).

[10] K. Takemura, Y. Fujii, S. Minomura, and O. Shimomura, Solid State Commun. 30, 137 (1979).

[11] K. Takemura, O. Shimomura, K. Tsuji, and S. Minomura, High Temp.-High Pressures 11, 311 (1979).

[12] C. W. Bunn, *Chemical Crystallography* (Oxford Univ. Press, London, 1945).

[13] K. Aoki, O. Shimomura, and S. Minomura, J. Phys. Soc. Jpn. 48, 551 (1980).

[14] K. Takemura, S. Minomura, O. Shimomura, and Y. Fujii, private communication.

[15] Y. Natsume, private communication.

Condensation of Random-Site Electric Dipoles: Li in $KTaO_3$

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Nuclear magnetic resonance and dielectric susceptibility data are reported in $KTaO_3$:Li which show, for the first time, ordering of random-site electric dipoles in a nonpolar lattice.

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Intensive research has been recently conducted on randomly interacting (or random-site) dipoles with the aim of understanding the nature of their condensed state. The question still appears to be open even as to its very existence, both from an experimental and theoretical point of view.[1] Most of the work has been on magnetic systems whose condensed state (if it exists) is called spin glass. It has been less appreciated that randomly interacting electric dipoles have also been predicted to condense.[2] Such condensation, i.e., the presence of an electric-dipole glass has also been hypothesized on the basis of observed electret polarization.[3] The close analogy of the two systems and the availability of a well-behaved random electric-dipole system led us to search for the analog of a spin glass.

Thus, for the first time, we provide experimental evidence for condensation of random-site interacting electric dipoles. To this end, we study the dipole moment arising from the off-center position of Li^+ replacing K^+ in $KTaO_3$. The local sites of Li^+ in the lattice are determined by nuclear magnetic resonance (NMR), whereas the global behavior of interacting dipoles is probed by dielectric measurements.

$KTaO_3$ turns out to be a most suitable lattice to host an electric dipole, Li^+, whose infrared properties have been explored[4] and whose giant single-particle response[5] had been related to the large susceptibility of the lattice.[6] Furthermore, the relevant Li relaxation and the concommittant

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