PHYSICAL REVIEW B VOLUME 29, NUMBER 2 15 JANUARY 1984

Pressure-induced successive phase transitions in CsI and its equation of state in relation to metallization

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(Received 10 November 1983)

A high-pressure x-ray diffraction study has been performed in CsI up to 65 GPa at room temperature by using a diamond-anvil cell. Pressure-induced successive phase transitions, apparently of second-order nature, from cubic to tetragonal and from tetragonal to orthorhombic, have been observed at 40 ±1 and 56 ±1 GPa, respectively. On the basis of the present and previous work, pressure-induced metallization in CsI is expected to take place at the volume ratio $V/V_0=0.50$, which corresponds to the pressure 70 GPa determined by the optical-absorption data reported previously. In the present work, the volume ratio $V/V_0=0.51$ was achieved.

The properties of solids in an extremely high pressure region are of great physical interest from two points of view: the transition from insulator to metal at very high pressure and the change of crystal structure when the crystal volume is highly compressed, such as to half or one-third of the initial volume. Recently we have reported the optical-absorption measurements in three alkali iodides—CsI (Ref. 1), RbI, and KI (Ref. 2)—under very high pressure with the aim at metallization. The metallization pressures of CsI, RbI, and KI were estimated to be 70, 85, and 115 GPa, respectively. Since CsI had the lowest metallization pressure, it is very important to perform the x-ray diffraction study of this material to obtain the metallization volume and to confirm the crystal structure at very high pressure.

The present paper deals with the result of the high-pressure x-ray diffraction study in CsI up to 65 GPa by using a diamond-anvil cell. Successive phase transitions, of second-order nature, from cubic to tetragonal and from tetragonal to orthorhombic are reported at 40 ±1 and 56 ±1 GPa, respectively. From the combined results of this x-ray diffraction and the optical-absorption studies, the possible metallization transition of CsI at very high pressure is discussed.

High-pressure x-ray diffraction patterns were obtained by using a diamond-anvil cell devised by the author.[2] Diamond anvils were 0.23 carat with 0.5-mm cross-sectional-diameter truncated faces. An x-ray beam generated by a 1.2-kW sealed-off Mo tube was focused onto the sample with a 0.1-mm cross-sectional-diameter pinhole collimator. The diffraction pattern was recorded on a flat film located 45.0 mm from the sample. Typical exposure time was 20–40 h. Sampling procedure was as described in Ref. 2. The sample was obtained from Harshaw chemical company. Pressures were calibrated by the ruby R_1 fluorescence scale.[3] All measurements were performed at room temperature.

Although CsI has the symmetry of simple cubic, only those diffraction lines with $h+k+l=even$ were observed because the scattering powers of Cs^+ and I^- are equal. Thus (110), (200), and (211) lines were observed below 10 GPa. Two lines, (110) and (211), were observed up to 20 GPa and only the (110) line was observed above 20 GPa. At 40 ±1 GPa the (110) line began to split gradually into two lines (011) = (101) and (110) with the intensity ratio 2:1. This suggested a second-order phase transition from cubic to tetragonal. At 56 ±1 GPa the (011) = (101) line split into two lines (011) and (101). This suggested another second-order phase transition from tetragonal to orthorhombic. In the high-pressure x-ray diffraction study of RbI and KI,[2] no such line splitting was observed up to 70 GPa. So the present result is peculiar to CsI.

The theory of the second-order phase transition predicts that a crystal passes from a group to a subgroup by an infinitesimal distortion of the lattice. From the relation of holohedral groups and their subgroups,[4] we can see that cubic O_h crystal passes either D_{4h}, T_h, O, T_d, or D_{3d}. Among them T_h, O, and T_d belong to the cubic group and so cannot yield the (110) line splitting. D_{3d} can yield the (110) line splitting, but with intensity ratio 1:1. Consequently D_{4h} is the only possible group to give the (110) line splitting with the intensity ratio 2:1. A similar argument is applied to the transition at 56 GPa and the final group is determined to be D_{2h}. Thus we can interpret these two second-order transitions as a sequence from cubic (O_h) to tetragonal (D_{4h}) and finally to orthorhombic (D_{2h}).

Figure 1 shows the pressure dependence of the lattice

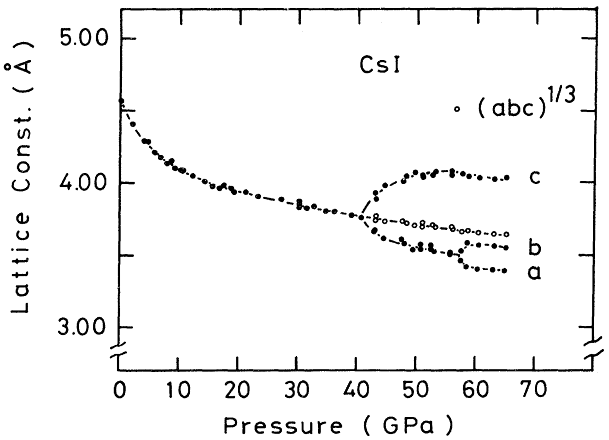

FIG. 1. The lattice constants of CsI at very high pressures. Solid circles represent the lattice constants *a*, *b*, and *c*. Open circles above 40 GPa represent their geometric means. Second-order successive phase transitions from cubic to tetragonal and from tetragonal to orthorhombic have been observed at 40 ±1 GPa and at 56 ±1 GPa, respectively.

constants of CsI. Solid circles are the lattice constants *a*, *b*, and *c*. Open circles above 40 GPa are their geometric means. As shown in this figure, no volume discontinuity is observed at the phase transitions within the experimental error. In Fig. 2 the pressure dependence of the relative volume of CsI is shown. Solid circles represent the present experimental result. Open circles are calculated values by Barsch and Chang.[5] These agree fairly well with the present experiment. Crosses are the experimental results by Hammond.[6] The solid line in this figure is a least-squares fit obtained by using an equation of state of second-order Birch-Murnaghan (BM) type;

$$P=\frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{7/3}-\left(\frac{V_0}{V}\right)^{5/3}\right]\times\left\{1+\frac{3}{4}(B_0'-4)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\} .$$

Though the experimental data points in this figure include those for three phases of CsI, the overall feature of this volume change is reproduced fairly well with the "single" second-order BM equation of state. Initial bulk modulus (B_0) and its pressure derivative (B_0') are determined as $B_0 = 11.1 \pm 0.8$ GPa and $B_0' = 6.9 \pm 0.4$.

The effects of very high pressure on the optical-absorption edge in CsI up to 46 GPa have been reported previously.[1] In that paper, the pressure-induced metallization was predicted to occur at 70 GPa from the pressure versus optical-absorption edge curve. In Fig. 3 the threshold energy (E_{th}) was replotted as a function of volume ratio.[7] E_{th} first increased to the high-energy side (blue shift) and formed a peak at the volume ratio 0.90. Then E_{th} decreased monotonically.

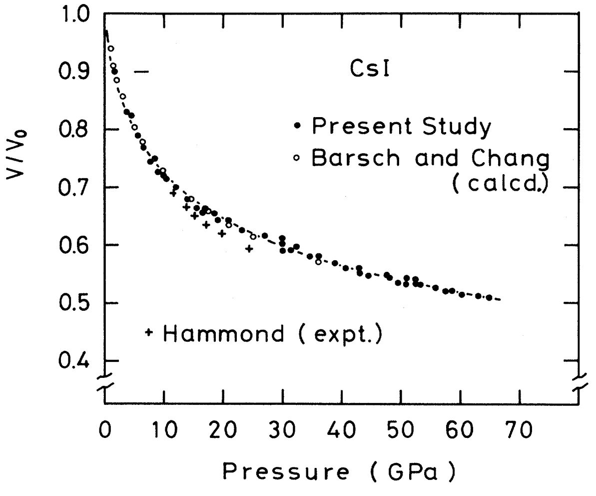

FIG. 2. Volume compression of CsI at high pressure. Solid circles represent the present experimental result. Open circles represent the calculated values by Barsch and Chang. Crosses are the experimental results by Hammond. Solid lines represent the least-squares fit to the data points using an equation of state of second-order Birch-Murnaghan type. The initial bulk modulus and its pressure derivative are obtained as 11.1 ±0.8 GPa and 6.9 ±0.4, respectively.

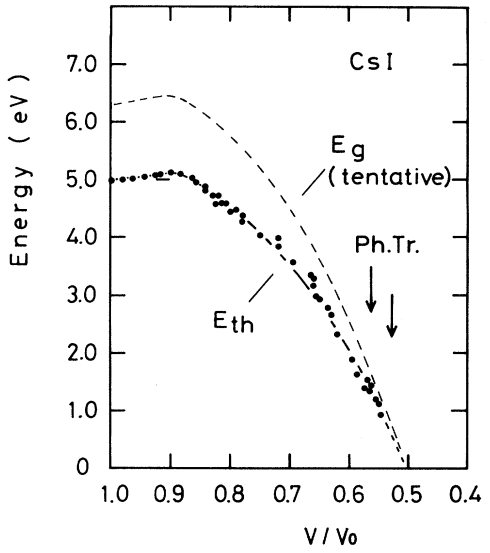

FIG. 3. Threshold energies (E_{th}) for the rising of optical absorptions and tentative band-gap energies (E_g) plotted as a function of volume ratio. Two arrows indicate the phase transitions. By extrapolating E_g vs volume-ratio curve, metallization transition in CsI is expected to occur at the volume ratio 0.50 and the corresponding pressure 70 GPa.

The ultraviolet absorption spectra of alkali-halide crystals of 0 GPa have been obtained by Eby, Teegarden, and Dutton,[8] and later by Teegarden and Baldini.[9] According to their results, optical absorption due to the direct exciton is observed from about 5 eV for CsI. The band-gap energy of CsI at 0 GPa and at room temperature was determined to be 6.3 eV. In our optical-absorption measurement the sharp rising of optical absorption due to excitons was observed from 5.0 eV at 0 GPa. At present, there is no possible way to know the band-gap character of CsI at very high pressures. Such being the case, E_{th} in CsI at high pressure is assumed to represent the onset energy of exciton absorption. In order to estimate the band-gap energy (E_g) at high pressure, the ratio of E_g to E_{th} is assumed to be kept constant, namely,

$$\frac{E_g(p)}{E_{\text{th}}(p)}=\frac{E_g(0)}{E_{\text{th}}(0)}=1.26 .$$

Thus we can obtain the band-gap energy of CsI at high pressure tentatively as illustrated in Fig. 3. Two arrows at the volume ratio 0.56 and 0.52 indicate those at the phase transitions.

From the extrapolated curve of E_g versus volume ratio, the pressure-induced metallization transition in CsI is expected to occur at the volume ratio $V/V_0 = 0.50$ and the corresponding pressure 70 GPa. Present metallization volume is somewhat larger than 0.42 obtained by classical Herzfeld theory.[10]

Though the overall feature of the compression curve is reproduced fairly well with the "single" second-order BM equation of state, there remain minute anomalies at the phase transitions when viewed in detail. When the experimental data points below 40 GPa (cubic phase only) are fitted to the second-order BM equation of state $B_0 = 9.2 \pm 1.2$ GPa and $B_0' = 8.1 \pm 0.9$ are obtained. When the data points below 56 GPa (cubic and tetragonal phases) are fitted $B_0 = 10.5 \pm 0.9$ GPa and $B_0' = 7.2 \pm 0.5$ are obtained. When all the data points are included (cubic, tetragonal, and orthorhombic phases) $B_0=11.1\pm0.8$ GPa and $B_0'=6.9\pm0.4$ are obtained. This systematic decrease of B_0' suggests that CsI softens at every phase transition. Thus CsI at very high pressure contracts by lowering the crystal symmetry from cubic to tetragonal and further from tetragonal to orthorhombic. This softening may also be observed at the beginning of metallization as a result of electron transfer from valence to conduction band. In this sense it would be quite interesting to extend the present high-pressure x-ray study to the 100-GPa region.

In some runs, when the sample was compressed very rapidly, the cubic-tetragonal transition was observed at a pressure as low as 35 GPa. This was an example of shear-induced accelerated transition frequently observed in high-pressure experiments when the free-energy difference between the two phases is small. But the volume of this tetragonal phase remained identical with that of the cubic phase between 35 and 40 GPa.

The cubic-tetragonal transition mechanism is readily understandable as follows. Figure 4 shows the atomic arrangement in the (110) plane of $B2$-type and tetragonal CsI. At 40 ± 1 GPa, I^- (Cs^+) ions begin to move toward the Cs^+ (I^-) ion in the directions shown (arrows). This movement shows a continuous decrease of volume (second-order transition). The resultant tetragonal structure is equivalent to the ordered phase of CuAu I ($L1_0$) type.[11] Since $L1_0$-type structure is considered to be a pseudo-fcc structure (coordination number ~12), this cubic-tetragonal transition indicates a process of increasing the coordination number from 8 ($B2$) to ~12 ($L1_0$) with increasing pressure. The tetragonal-orthorhombic transition is not interpreted in such a simple way. In this transition the ions must distort gradually; ions along the *a* axis get near and those along the *b* axis go away while the *c* axis remains almost constant.

Since the CsCl-type structure is a high-pressure form between the two [NaCl-type ($B1$) and CsCl-type ($B2$)] crystal structures of alkali halides, the present result is highly suggestive of the structural sequences in other alkali halides at extremely high pressure. On this line, x-ray–diffraction and optical-absorption studies of other heavy alkali halides are now in progress to obtain the systematic knowledge of metallization transition and of the structural behaviors in these materials at a half volume region.

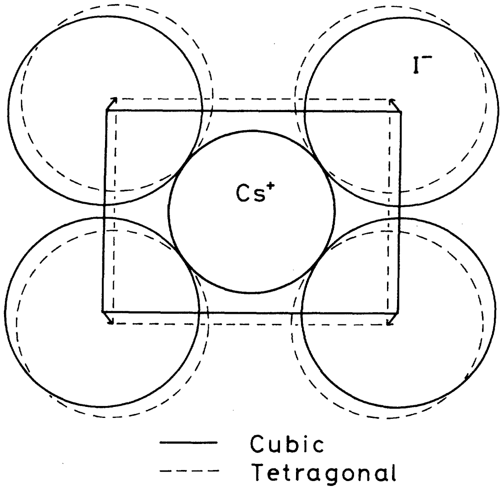

FIG. 4. The (110) cross section of the cubic-$B2$-type and tetragonal-type CsI with Cs^+ ion at the center and four I^- ions at the corner. At 40 ± 1 GPa, I^- ions start to shift toward the Cs^+ ion in the directions indicated, thus reducing the unit-cell volume. The resultant crystal structure is simple tetragonal [CuAu I ($L1_0$) type].

Note added. By a recent communication from Professor Jeanloz, the author was made aware of an independent study that CsI undergoes the second-order phase transition from cubic to tetragonal at 40 ± 1 GPa [E. Knittle and R. Jeanloz, Science (in press)]. Their work corroborates the present study.

ACKNOWLEDGMENTS

The author is grateful to Professor Y. Kondo of Tohoku University for his continuous encouragement in performing this work and to Dr. T. Suzuki of the Institute for Solid State Physics (Tokyo) for help in computer calculation.

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[7] Though optical-absorption measurements below 5 GPa were not included in Ref. 1, the threshold energies (E_{th}) below 5 GPa obtained by sapphire window cell are added in Fig. 3. E_{th} is determined as the energy where optical density is 0.10. For experimental details see Refs. 1 and 2.

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[11] H. Sato and R. S. Toth, Phys. Rev. 124, 1833 (1961). Though the unit cell of this CuAu I ($L1_0$) structure is chosen in fcc-like, its true Bravais lattice is simple tetragonal [$P4/mmm$ (D_{4h}^1)].