Band-Overlap Metallization of Cesium Iodide

Yogesh K. Vohra, Samuel T. Weir, Keith E. Brister, and Arthur L. Ruoff
Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

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X-ray diffraction studies to 73 GPa show that CsI becomes orthorhombic at about 56 GPa. Infrared absorption studies show the band gap dropping from 6.4 to 0.36 eV at 62 GPa. At 65 ±5 GPa, CsI becomes metallic and reflects in the red, which we attribute to the plasma edge being in the visible. The interatomic distances of the nearest like neighbors are reduced from the zero-pressure value by 28% at metallization where CsI has a pseudo tenfold coordination.

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Recently CsI has been studied extensively because it is considered the most likely candidate among the alkali halides to be metallized at high pressure. Recent studies include finding a phase transition from the cubic to a tetragonal phase,[1-4] studies on the equation of state,[1-5] and optical absorption studies.[1,4,6-8] Theoretical studies include predictions of the cubic to tetragonal phase transition[9,10] and of band-gap variation with pressure and the metallization pressure.[11,12] Asaumi also observed a tetragonal to orthorhombic phase transition at 56 GPa on the basis of the splitting of the (110) diffraction peak.[3]

There is a wide experimental range of about 65–110 GPa for the extrapolated pressure of metallization (from optical absorption studies).[1,4,6-8] At the same time augmented-plane-wave calculations[11] predict direct-band-gap closure at 55 GPa with use of the Hedin-Lundquist model for exchange correlation and at 100 GPa with use of the Slater potential, under the assumption in both cases that the structure remains cubic. Both Satpathy[10] and Carlsson[12] have shown that the direct band gap drops more rapidly with pressure for the tetragonal structure than for the cubic structure and still more rapidly for the orthorhombic structure.[10]

We therefore undertook detailed experimental x-ray diffraction studies to look for the orthorhombic structure in the extended pressure range and to obtain the best equation of state that we could. In addition we made absorption studies to a much smaller energy band gap (0.36 eV) than previously. Furthermore, microscopic observation of CsI in reflection in the metallic phase shows interesting color changes representative of the movement of the plasma edge.

The energy-dispersive x-ray diffraction studies at high pressures were carried out in a diamond anvil cell at the Cornell High Energy Synchrotron Source. A new collimator system was used to collimate the polychromatic x-ray beam to the sample whereby a pin hole of 30-μm diameter was located close to the diamond and adjusted with motor-driven motion in two directions normal to the beam in steps of 0.5 μm (diamond flats of 200- and 300-μm diameter and samples of 50-μm diameter were used in the x-ray experiments). This represents a substantial improvement over the slit system of Baublitz, Arnold, and Ruoff.[13] In x-ray experiments, platinum (Pt) was employed as an internal pressure marker and the equation of state for Pt as found by Jamieson, Fritz, and Manghnani was used.[14] For optical absorption studies, a He-Ne laser with 1.2 mW output at 3.4 μm was incident on a sample of 75-μm diameter in the diamond anvil cell, and transmission was detected with a pyroelectric detector. In the optical absorption measurements, the ruby-fluorescence technique was used for pressure measurements.[15] We purposely placed our ruby at the edge of the gasket hole to measure the lowest pressure in the sample, as the outer region of the sample contributes mostly to transmission when the center of the sample (at higher pressures) becomes opaque to the infrared photons.

The phase transition in CsI around 38 GPa from the cubic to the tetragonal phase is well established,[1-4] but the tetragonal to orthorhombic phase transition around 56 GPa was not established as most of the observations[3,4] were based on the splitting of only the (110) diffraction line of the cubic phase. In Fig. 1 we show the first clear evidence of the occurrence of the orthorhombic phase where both the (110) and the (211) diffraction peaks of the cubic phase are shown to have split into three peaks of the orthorhombic phase at a pressure of 73.3 GPa. In Fig. 2 we show the equation-of-state data up to 73.3 GPa ($V/V_0=0.493$) based on a total of thirty-five data points. Table I contains equation-of-state parameters. Figure 3 shows the pressure variation of c/a (tetragonal phase) and of c/a and b/a (orthorhombic phase). It is interesting to note that in experiment C where pressure was raised rapidly the tetragonal phase was seen at a pressure of only 33 GPa.

Figure 4 shows the infrared transmission for CsI in the diamond anvil cell for 3.4-μm laser radiation from a He-Ne laser as a function of pressure. No transmission was detected at pressures at the sample edge greater than 62 GPa. This indicates that the band gap of CsI drops below 0.36 eV at these pressures. This effect is not due to infrared absorption in diamonds, because large-band-gap materials such as CsCl and LiF in the same cell show no drop in transmitted intensity at the same pressures.

It is well established that CsI, which is transparent to visible light at low pressures, becomes opaque at pressures above 50 GPa. On increase of pressure beyond 62 GPa, the appearance of CsI in reflection with white light changes from black to dark red (red metal). This indicates that the plasma frequency of CsI lies in the visible. On further loading the color becomes red, orange, yellow, and finally a dull silver. A theoretical calculation[10] appears to rule out the possibility of this reflecting behavior being due to an interband transition. Thus these color changes can be attributed to an increase in the plasma frequency with an increase in the free-electron concentration.

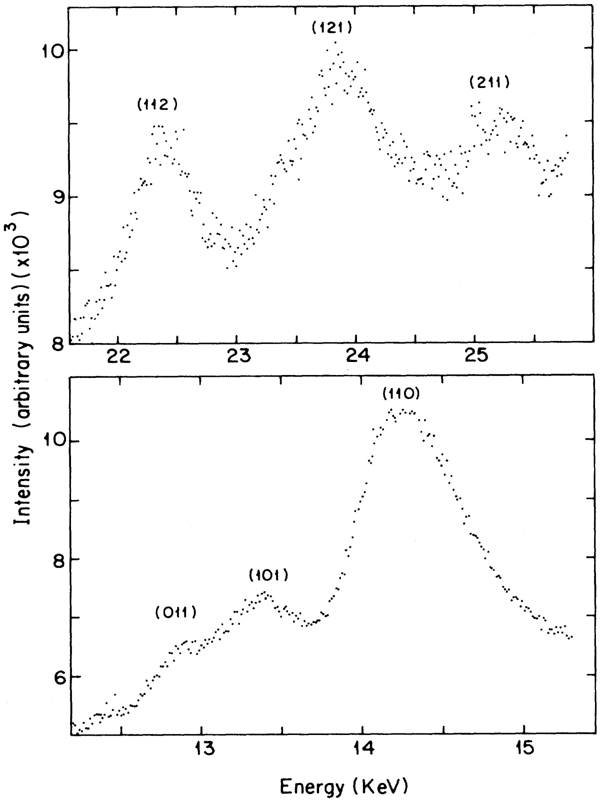

FIG. 1. Energy-dispersive x-ray diffraction from CsI at a pressure of 73.3 GPa taken with the synchrotron source (diffraction angle $\theta = 10.38°$). The (110) and (211) diffraction peaks from the cubic phase split into three peaks in the orthorhombic phase. The relative intensities of the diffraction peaks are affected by preferred orientation effects in the diamond anvil cell.

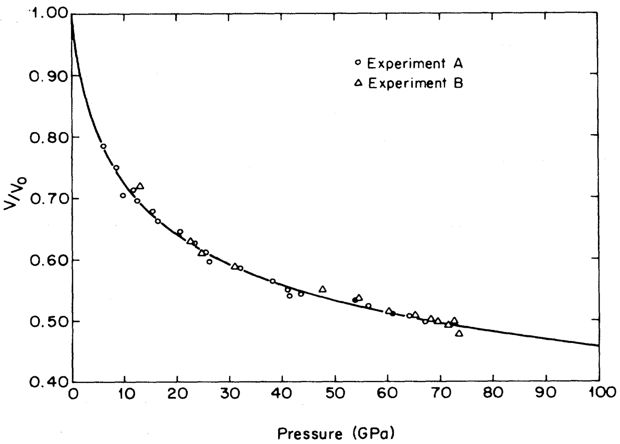

FIG. 2. The equation of state of CsI. Experiments A and B correspond to two different samples (CsI–20 wt.% Pt). The solid curve is Keane's fit to the combined data with the parameters listed in Table I.

TABLE I. Equation-of-state parameters.

Data	Fit	B_0 (GPa)	B_0'	B_0'' (GPa^{-1})
Expt. A	Keane[a,c]	11.89	5.93	−0.83
Expt. B	Keane[a,c]	11.89	5.93	−0.76
Expt. A+B	Keane[a,c]	11.89	5.93	−0.80
Expt. A+B	Birch II[b,c]	11.89	5.93	−0.67
Expt. A+B	Birch I[b,d]	11.89	6.38	
Ultrasonic[e]		11.89	5.93	−0.73

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[b] F. Birch, Geophys. Res. **83**, 1257 (1978).

[c] Assuming the isothermal values obtained from the ultrasonic data of Barsch and Chang (Ref. 16) for the bulk modulus $B_0 = 11.89$ GPa and its pressure derivative $B_0' = 5.93$.

[d] B_0 is fixed to the ultrasonic value.

[e] Reference 16.

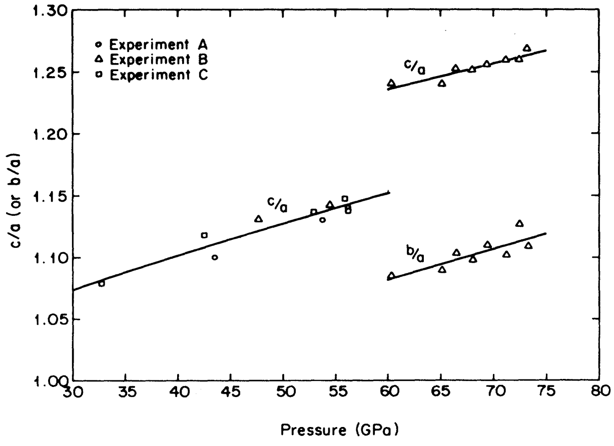

FIG. 3. Axial ratios for various phases of CsI as a function of pressure. The solid lines are straight-line fits to the data points. Experiment C corresponds to the case in which no platinum marker was present and CsI itself served as a pressure scale; rapid loading in this case effected the tetragonal transition at a lower pressure than usual.

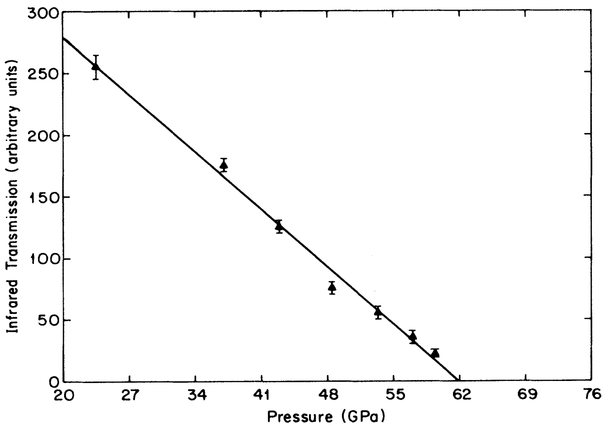

FIG. 4. Infrared transmission for 3.4-μm radiation as a function of pressure. The sample is opaque to this radiation at pressures greater than 62 GPa. The continuous drop in transmitted intensity is due to the pressure gradient across the 75–100-μm-diam sample.

The separation between the nearest like ions (Cs^+-Cs^+ and I^--I^-) decreases at the successive phase transitions. This decrease is further accelerated with increasing pressure as c/a and b/a increase. This increases the wave-function overlap between the $5d$ states of adjacent Cs^+ ions and the $5p$ states of adjacent I^- ions and hence decreases the band gap. In this way these new structures push CsI to metallization at a much lower pressure than one would find with a cubic phase at the same volume.

In conclusion, (1) CsI is the first alkali halide to be metallized under pressure. The metallization pressure is 65 ±5 GPa; this corresponds to a volume ratio of $V/V_0 = 0.506$ and to a reduction in the distance between the nearest like ions of 28% from the zero-pressure value. This metallization pressure is based on the visual observation of the onset of reflection of the dark red at 65 GPa. Quantitative reflectivity studies are need to pinpoint the metallization pressure more precisely. The infrared absorption studies show the band gap of the orthorhombic phase dropping below 0.36 eV at pressures above 62 GPa. (2) CsI undergoes two structural phase transitions in the pressure range 0 to 73 GPa: cubic to tetragonal at 38 GPa and tetragonal to orthorhombic at 56 GPa. These transitions have no associated volume change within experimental errors, though axial ratios tend to show discontinuous changes at the phase transition (Fig. 3). These considerations along with the theoretical total-energy calculations[9,10] indicate that these transitions may be of first order. (3) The color changes in the CsI samples above 65 GPa in reflection are highly suggestive of the movement of the plasma edge with pressure. Quantitative studies of reflectivity versus photon energy are needed to further elucidate the details.

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