

Equation of state and high-pressure phase transition of CsI

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High-pressure x-ray diffraction patterns of CsI were obtained to 660 kbar. Diffraction peaks of a new phase appear between 370 and 385 kbar. The pressure-volume relationship of the low-pressure cubic phase was fitted to Keane's second-order equation of state with $B_0=118.9$ kbar, $B'_0=5.93$, and $B''_0=-0.131$ kbar $^{-1}$ with B_0 and B'_0 values forced to fit the isothermal values obtained from ultrasonic data. The d spacings of the new high-pressure phase are consistent with tetragonal indexing.

There has been substantial recent interest in the metallization pressures of the isoelectronic series Xe (Refs. 1-3), CsI (Refs. 4-7), and BaTe (Refs. 8 and 9). It is expected that the metallization pressure will be highest for xenon (1.3 to 2.0 Mbar),^{2,3} which is above the current routine capability of the diamond anvil cell. From theoretical considerations it is predicted that CsI will exhibit band overlap at 800 kbar (Ref. 4) to 1 Mbar.⁵ The Herzfeld criterion¹⁰ predicts metallization of CsI at a reduced volume, V/V_0 , of 0.42. Asami and Kondo⁶ carried out studies on the optical energy gap of CsI up to 460 kbar. They extrapolated their curve and estimated that the pressure at which the band gap went to zero was 700 kbar. A pressure-volume relation to this pressure is necessary in order to compare with the Herzfeld criterion. Huang and Ruoff⁷ made absorption edge measurements versus pressure and versus lattice parameter to 420 kbar. Their plot of absorption edge versus volume extrapolates to zero at $V/V_0=0.47$.

Hammond¹¹ carried out experiments to determine the equation of state of CsI up to 230 kbar using a conventional x-ray source and Debye-Scherrer camera method and fitted his results with Birch's second-order equation of state.¹² Barsch and Chang¹³ proposed an equation of state for CsI based on Birch's second-order equation of state and the zero pressure value of the bulk modulus and its first two pressure derivatives which they obtained from ultrasonic experiments. Disagreement exists between these two equations. Lattice parameter data versus pressure to pressures substantially above those used by Hammond (230 kbar) was expected to clarify this discrepancy, to provide calibrant data for CsI, and to provide equation-of-state data necessary to test the theoretical description of CsI.

We undertook studies using energy dispersive x-ray diffraction with the Cornell High Energy Synchrotron Source to study the compression curve of CsI and have obtained data to 660 kbar. A detailed description of the experiments is given by Baublitz, Arnold, and Ruoff.¹⁴ In our experiments an intrinsic Ge detector was used. The temperature was $(28 \pm 1)^\circ\text{C}$. The data collecting time for a diffraction spectrum was typically one hour. Diamond tips of 320- μm diameter were used. A 250- μm -thick stainless-steel sheet was first preindented to a thickness of about 40 μm and a 75- μm gasket hole was drilled. CsI powder was mixed with 8% in weight Pt powder in order to get a good diffraction peak ratio between the sample and the calibrant. The Pt was used as a pressure calibrant based on the equation of state obtained by Jamieson, Fritz, and Manghnani.¹⁵ Because CsI is hygroscopic, the sample preparation process

was carried out under an argon atmosphere. No pressure transmitting medium was used in this experiment. A computer program was used to deconvolute overlapping peaks.

The fractional volume ratio was calculated by averaging the lattice parameter obtained from the available diffraction peaks with energy lower than the first iodine fluorescence peak. We have chosen Keane's second-order equation of state¹⁶ to compare Hammond's and our value of B''_0 ; we obtained $B''_0=-0.153$ kbar $^{-1}$ by fitting Hammond's data and $B''_0=-0.131$ kbar $^{-1}$ for our data. In both cases the isothermal values, obtained by converting the ultrasonic data, of $B_0=118.9$ kbar and $B'_0=5.93$ were used.¹³ These two values of B''_0 are in close agreement with each other but differ significantly from the ultrasonic value given by Barsch and Chang¹³ which is $B''_0=-0.07$ kbar $^{-1}$. At high pressures, Barsch and Chang's equation of state¹³ gives higher volumes than we obtain for the corresponding pressures.

In our experiments we find for the cubic phase just prior to the transformation the following peaks: 110, strong; 200, very weak; 211, very strong; and 220, strong. As the phase transformation occurs we find that both the original 110 peak and the original 211 peak split into two peaks; the 200 peak or the possible pair of peaks which emerge from it are not observed; while these could be obscured by the Pt 200 peaks, they were also not observed in subsequent experiments made without platinum. Results at 515 kbar are shown in Fig. 1; peaks 1 and 2 emerged from the 110 peak of the cubic phase while 3 and 4 have emerged from the 211 peak of the cubic phase. The data in Fig. 1 are shown in Table I, fitted to two possible tetragonal cells, A and B, as noted. (A third cell, indexed with the first and second

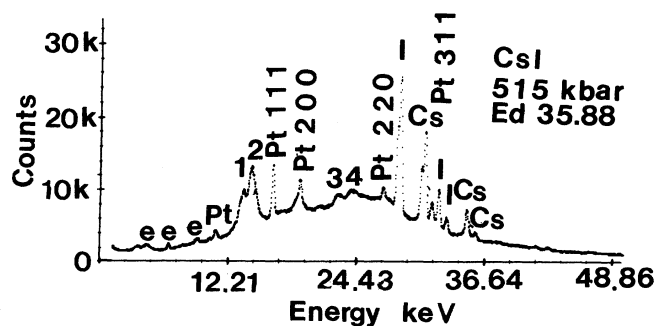


FIG. 1. CsI with platinum at 515 kbar. Peaks 1, 2, 3, and 4 are due to the high-pressure polymorph of CsI. $E_d=35.88$ keV. $T=(28 \pm 1)^\circ\text{C}$. $\theta=9.499^\circ$.

TABLE I. Diffraction pattern of CsI at 515 kbar, $T=(28 \pm 1)^\circ\text{C}$, $\theta=9.499^\circ$, $Ed=35.88 \text{ keV}\text{\AA}$.

d_{obs} (\AA)	Index	Cell A	d_{calc} (\AA)	Index	Cell B
		(First order) $a=2.800 \text{\AA}^a$ $c=5.272 \text{\AA}$			(Possible second order) $a=3.497 \text{\AA}$ $c=4.012 \text{\AA}$
2.636	002		2.636	101	2.636
2.473	101		2.473	110	2.473
1.579	112		1.583	112	1.558
1.494	103		1.488	211	1.457

^aThe a and c are calculated based on the first two diffraction peaks and the remaining peaks are used to test the assumed indexing.

peaks fitted to 110 and 011, respectively, can be ruled out since this indexing does not lead to a peak in the vicinity of peak 3 (a peak which is emphatically present in the experiment.) As can be seen, the calculated peaks for cell A fit remarkably well; the calculated peaks for cell B do not fit nearly as well (this is true at all the pressures studied). Because the stress state is not hydrostatic, such disparities may be possible and we must conclude, in spite of the poorer fit, that we cannot exclude cell B. However, we note that when a new phase appears in a nonhydrostatic situation, the peaks of the new phase are sharper inasmuch as stress relaxation occurs during the transition.¹⁷ Figure 2 shows the lattice

parameters versus pressure for cells A and B. Figure 3 shows the corresponding volume ratio versus pressure. If the new phase corresponds to cell A, the transition is first order, while if the new phase is described by cell B, the transition is possibly second order.

The band gap does not appear to show a discontinuous change at the transition.⁷ However, these band-gap measurements were carried out in the presence of pressure gradients and it is possible that at the highest apparent pressure of 420 kbar, a fraction of the sample being observed may still have been below the transition. If improved band-gap studies to substantial higher pressures do not show a discontinuity in the band gap, this would indicate that cell B is preferred to cell A. Cell B could involve a second-order transition. A second-order transition could occur due to a macroscopic elastic instability, an example being the transition

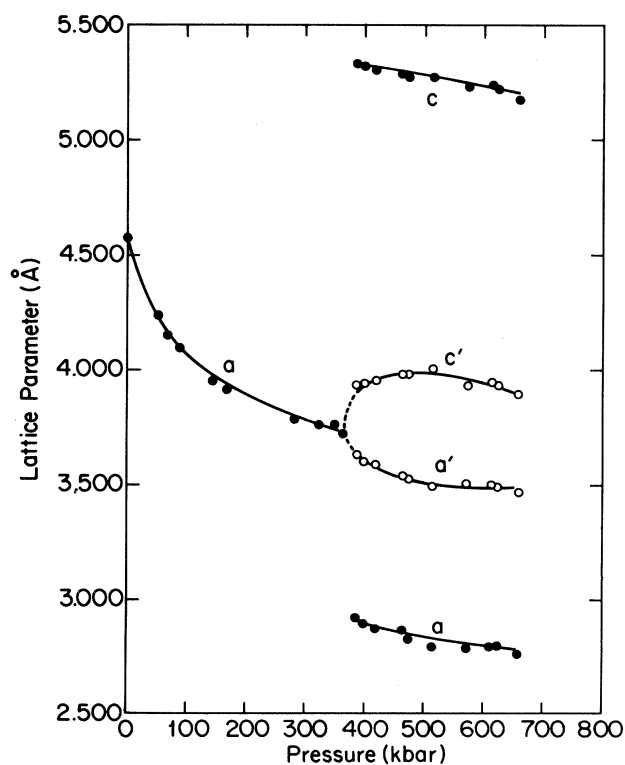


FIG. 2. Lattice parameters vs pressures for CsI at $T=(28 \pm 1)^\circ\text{C}$. Above the transitions a and c refer to cell A, and a' and c' refer to cell B (open circles).

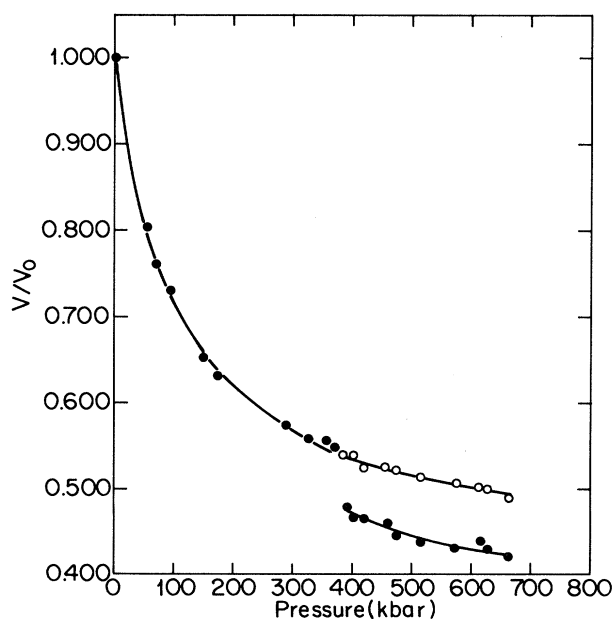


FIG. 3. Reduced volume ratio vs pressure for CsI at $T=(28 \pm 1)^\circ\text{C}$. Above the transition solid circles refer to cell A and open circles to cell B. The solid line for the cubic phase represents our fit to the Keane equation.

found by Batterman and Barrett¹⁸ in V_3Si as $c_s = (c_{11} - c_{12})/2$ approaches zero.¹⁹ Anderson and Demarest²⁰ have analyzed the behavior of c_s for CsCl-type crystals when they are described by a central force model with a repulsive potential b/r^n . From their results it is easy to show that c_s goes to zero when the curve, $V/V_0 = 34.63p^{-3/4}$ (values of B_0 and B'_0 from Ref. 13 were used), intersects the equation-of-state curve. This intersection (with the curve of Fig. 3) occurs at 218 kbar, substantially below the transition pressure; of course, we do not expect that such a simple theory should give quantitative results.

At 660 kbar, with cell A, the volume ratio is 0.42, while with cell B the ratio is 0.49, compared to the value of 0.42 obtained from the Herzfeld criteria for metallization. In summary, there is a phase transition. The tetragonal cell A, corresponding to a first-order transition, is in excellent agreement with our experimental x-ray data while cell B,

corresponding to a possible second-order transition, fits less well. Recent theoretical calculations (for the CsCl structure) predict metallization for $V/V_0 = 0.40$ to 0.48 .^{5,21} Had there been no phase transition, the preferred value⁵ of $V/V_0 = 0.40$ would correspond to a pressure in excess of 1.1 Mbar according to our equation of state. The presence of the phase transition requires a completely new theoretical consideration of the possible tetragonal phases and the possible volumes (and pressures) at which these become metallic.

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