High-Pressure Phase Transition and Equation of State of CsI

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Structural properties of CsI at high pressure have been investigated by the use of synchrotron x-ray-diffraction techniques with the diamond-anvil cell at 300 K. The results indicate that the material undergoes a continuous distortion from $B2$ to an hcp-like phase, which is stable to at least 302 GPa. The intermediate orthorhombic phase is geometrically different from previous assignments and $\sim 10\%$ denser. With the new structure, the p-V results of static pressure experiments, shock-wave studies, and theoretical calculations are now in good agreement.

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CsI has become a prototype material for both static and dynamic high-pressure investigations as a result of the wide variety of phenomena exhibited by the material on compression. Despite the large number of high-pressure studies of this material,[1-14] several inconsistencies concerning its structural and thermodynamic properties remain. Previous static compression experiments[1-4] indicated that the cubic CsI ($B2$ structure) undergoes tetragonal and orthorhombic distortions[2] at approximately 25 and 65 GPa, respectively. The 300-K p-V isotherm of CsI obtained in Refs. 1-3 on the basis of these structures, however, is significantly higher than the 300-K isotherm reduced from the high-temperature shock-wave Hugoniot obtained at 3440-10800 K.[9,10] The latter is in good agreement with theoretical studies.[11-13] The discrepancies between static and shock measurements have been ascribed[14] to disproportionation of CsI at the high temperatures of the shock-wave experiments. This interpretation has not been fully accepted by the shock-wave community, and does not explain the discrepancy between static results and theoretical calculations. An attempt[10] has been made to attribute the discrepancy to errors in static experiments due to stress inhomogeneity or uniaxial strain, because of the apparently higher compressibility reported for static experiments performed with rare-gas media.[4] The required differential stress, however, appear to be greater than those permitted by the strength of CsI at high pressure.

In a recent ultrahigh-pressure study,[5] we showed that CsI has a hexagonal-close-packed- (hcp-) like structure above 200 GPa. This structure contrasts with the previously proposed high-pressure form,[1-4] which maintains the topology and the orthogonality of the three crystallographic axes of the cubic $B2$ cell but allows for variable axial lengths. The difference in the two structure types has suggested the need to reinvestigate the x-ray diffraction of CsI below 100 GPa. In the present study we demonstrate that the phase-transition sequence in CsI is actually a new type of transition that can be described as a continuous distortion from $B2$ to an hcp-like structure, instead of the previously proposed tetragonal and orthorhombic phases. Even though the intermediate phase also has orthorhombic symmetry, it is geometrically different from the previously proposed assignment and has significantly lower volume.

Four samples of powdered mixtures of CsI and Pt, pure-powdered CsI, and a single crystal of CsI were studied in diamond-anvil cells.[15] X-ray diffraction of Pt were used for pressure calibration.[16] Pure-powdered CsI was used for detailed examination of phase transitions. In order to avoid contamination, no pressure-transmitting medium was used. Because of the low strength of CsI, the effect of nonhydrostatic stress on the p-V results is less than 2%. Data were obtained at the National Synchrotron Light Source (NSLS) by energy-dispersive x-ray-diffraction techniques[17] with diffraction angle varying from 16° to 23°. A total of 54 diffraction patterns were measured to 100 GPa.

All diffraction patterns can be indexed with an orthorhombic unit cell consistent with a structure intermediate between $B2$ and hcp. The relationship between the new structure to $B2$ and hcp is shown in Fig. 1. In the undistorted $B2$ structure, the unit cell is simply related to the $B2$ subcell with $a_o = a_c$, $b_o = c_o = \sqrt{2} a_c$, and $x = 0$; for the other boundary condition (hcp): $a_o = a_h$, $b_o = \sqrt{3} \times a_h$, $c_o = c_h (c_h / a_h = 1.633$ for ideal close packing), and $x = b/6$, where the subscripts o, c, and h denote the lattice parameters of the new orthorhombic structure, cubic $B2$, and hcp-like, respectively. The parameter x, which defines the gliding of the $c/2$ plane in the b direction, does not affect the lattice parameter directly, but affects the extinction rules and intensities of diffraction lines. The space group is $Pm2m$ with Cs^+ at 0,0,0 and $0, \frac{1}{2}+x, \frac{1}{2}$, and I^- at $\frac{1}{2}, \frac{1}{2}, 0$ and $\frac{1}{2}, x, \frac{1}{2}$. This orientation, instead of that of $Pmm2$, is chosen to keep the correspondence between the a and c axes of the orthorhombic and hcp-like phases. Because the difference in scattering between Cs^+ and I^- is small, the x-ray sym-

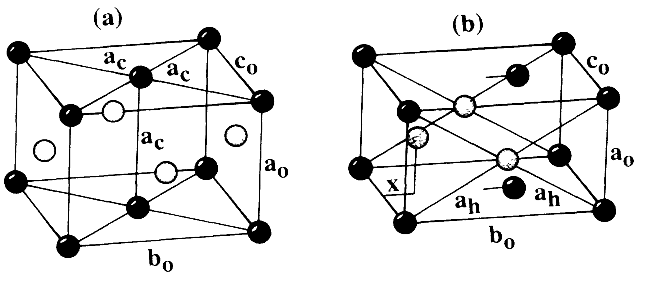

FIG. 1. Structure drawings indicating the nature of phase transitions in CsI. The solid and shaded spheres represent Cs and I. (a) The cubic $B2$ structure has the three equal and orthogonal axes a_c. The orthorhombic structure is chosen with $a_o = a_c$, and b_o and c_o corresponding to two face diagonals of $B2$. As the three axes vary in length, the original cubic axes are no longer orthogonal. In (b), the orthorhombic intermediate structure is shown by varying the axial lengths and by displacing the plane of atoms at $z = 0.5$ by an amount x. This change finally leads to an "hcp-like" structure with an angle of 120° between the two a_h axes. In this transition, the arrangement of Cs^+ and I^- continuously approaches a close-packed configuration.

metry is close to $Pb2_1m$; therefore, the $0kl$ diffractions with k odd are essentially extinct. The observed phase transition is consistent with the orthorhombic structure with the b/a ratio increasing continuously with pressure from $\sqrt{2}$ to $\sqrt{3}$, c/a from $\sqrt{2}$ to 1.633, and $0 < x < b/6$. All thirteen diffraction lines up to 202 predicted for this structure were observed (Table I). No diffraction lines are left unidentified.

The positions of major diffraction peaks of CsI at high pressures are basically in agreement with those in previous static experiments.[1-3] However, we observed additional peaks that could not be indexed with the previously assigned structures. The most characteristic difference is in the multiplet corresponding to the 110 diffraction of the original $B2$ phase. Because of the small hkl number and large-d spacing, this region is also most diagnostic for structure assignment. According to previous reports, the 110 diffraction of the cubic $B2$ phase splits into a doublet in the tetragonal phase and a triplet in the orthorhombic phase. An example of a diffraction pattern measured at 77.5 GPa in the present study is shown in Fig. 2; this portion of the diffraction pattern is not just a triplet, as reported earlier (e.g., Ref. 2), but a quintuplet. The two outside peaks (marked as 110 and 021) do not fit the previously assigned orthorhombic unit cell. In fact, these two peaks do not originate from the splitting of 110 of $B2$. They were first observed at 45 GPa, with the energies of 110 and 021 far below and above, respectively, those of the central triplet

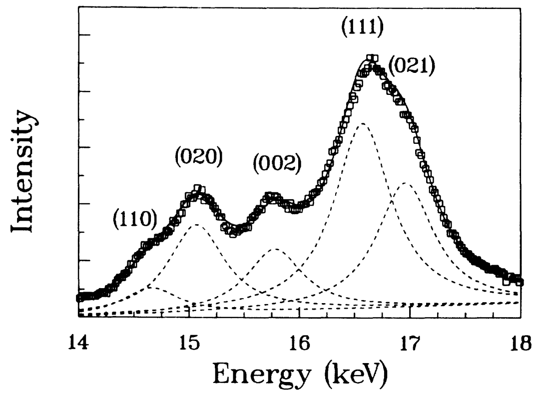

FIG. 2. Energy-dispersive x-ray-diffraction pattern of CsI at 77.5 GPa showing deconvolution of the quintuplet. $E(\mathrm{keV}) \times d(\text{Å}) = 39.62$.

TABLE I. Observed and calculated lattice spacings for orthorhombic CsI at two pressures.

	$p = 47$ GPa[a]		$p = 78$ GPa[b]	
Index	d_{obs} (Å)	d_{calc} (Å)	d_{obs} (Å)	d_{calc} (Å)
(110)	2.863(2)	2.898	2.686(2)	2.682
(020)	2.717(6)	2.699	2.651(2)	2.651
(002)	2.663(1)	2.683	2.527(1)	2.514
(111)	2.544(1)	2.550	2.387(1)	2.367
(021)	2.440(1)	2.411	2.332(1)	2.339
(112)	1.979(1)	1.969	1.871[c]	1.834
(022)	1.897(1)	1.903	1.820(1)	1.821
(200)	1.715[c]	1.718		
(130)	1.588(1)	1.588	1.530(1)	1.533
(131)	1.523(3)[c]	1.528		1.467
(113)		1.522	1.436[c]	1.421
(023)	1.493(3)[c]	1.491		1.415
(220)	1.454(3)[c]	1.449	1.345(1)	1.341
(202)	1.434[c]	1.446	1.318(2)	1.323

[a] $a = 3435(13)$ Å, $b = 5.398(21)$ Å, $c = 5.366(24)$ Å, $b/a = 1.571$, $c/a = 1.562$.

[b] $a = 3.113(9)$ Å, $\mathrm{b} = 5.285(18)$ Å, $c = 5.049(25)$ Å, $b/a = 1.697$, $c/a = 1.615$.

[c] These lines were not used in the least-squares fits due to insufficient statistics in multiplet deconvolution.

(020, 002, and 111). Their intensities increase and the separation between them decreases with pressure. At the highest pressure the two peaks merge into shoulders of the two side peaks of the triplet.

The behavior is entirely consistent with the new orthorhombic structure. The 020, 002, and 111 of the orthorhombic phase arise from the splitting of the 110 of $B2$. As the x parameter increases with pressure, the 110 and 021 lines of the orthorhombic form, which originate from the forbidden diffractions of $\frac{1}{2}\,\frac{1}{2}\,1$ and $\frac{3}{2}\,\frac{1}{2}\,0$ of $B2$, become allowed, and gain intensity. As the b/a and c/a ratios increase with pressure, 110 and 021 converge while the splitting of the 020 and 111 increases. Eventually, the 110 and 020 lines of the orthorhombic structure merge into the single 100 line of hcp, and 111 and 021 merge to form 101 of hcp. On the other hand, the structures previously proposed follow the same extinction rules as $B2$ and cannot account for lines originating from the half-numbered *hkl*.

Although all 54 diffraction patterns can be indexed with the new orthorhombic structure, there is some variability in the relative intensities. In extreme cases, certain diffraction peaks are weak or even missing in some patterns. To examine whether these variations are related to preferred orientations of CsI under uniaxial compression or due to initial orientation, in one experiment, we started with a single crystal of CsI. The crystal was crushed under compression, but a strong preferred orientation remained. After transforming to the high-pressure phase, the relative intensities in this experiment were still markedly different from those of other experiments started with well-randomized polycrystalline CsI samples. We also observed strong diffraction lines in $B2$ transforming preferentially into one branch of a multiplet in the high-pressure phase instead of splitting into a multiplet. This behavior gives additional support that the phase transition is largely displacive.

The variability in relative intensities can explain the apparent differences between previously measured diffraction patterns, in which all possible peaks were not observed.[1-4] A characteristic feature previously reported at the "$B2$-tetragonal" transition, for example, is the weakening and disappearance of the 200 diffraction of $B2$. Such an observation, however, is not consistent with intensity calculations for the assigned structures. In the present experiment we have observed a moderately intense 022 diffraction of the orthorhombic phase, which is derived from the 200 of $B2$. Another branch of the 200 line of $B2$ which transforms into the 200 of the orthorhombic cell, however, is absent in three of the four samples. The observation is consistent with the proposed orthorhombic distortion, which is characterized by a preferential reduction of the a axis. Thus, the orthorhombic (200) plane would have a preferred orientation normal to the load axis, the direction of maximum stress, and would be far from the diffraction position.

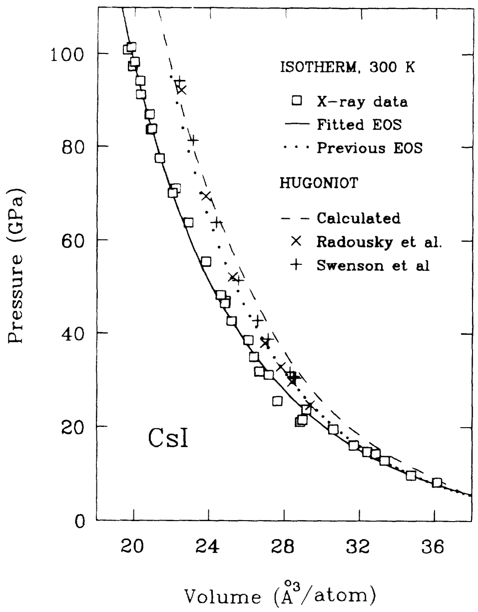

FIG. 3. Pressure-volume relation for CsI. The solid line is a universal equation-of-state (Ref. 19) fit through all of the present data (squares). The parameters are $V_0 = 47.66$ Å^3, $K_0 = 13.5 \pm 0.2$ GPa, and $K_0' = 5.45 \pm 0.06$. The dotted line gives the result of previous static equation-of-state studies (Refs. 1-3). The shock-wave data of Radousky *et al.* (Ref. 9) and Swenson, Shaner, and Brown (Ref. 10) are at Hugoniot temperatures (3440-10800 K). The dashed line is the Hugoniot predicted from the present static data with the thermal pressure by Aidun, Bukowinski, and Ross (Ref. 12).

The starting point of the phase transition, characterized by broadening and then splitting of the $B2$ diffraction lines with increasing pressure, is observed at pressures as low as 15 GPa. Below 45 GPa, the splitting is not large enough to permit unequivocal identification of the orthorhombic structure. Since the observed splittings and intensities of multiplet peaks evolve continuously from 15 to 100 GPa, a single orthorhombic phase with variable distortion parameters from $B2$ to hcp is assigned for the equation-of-state calculation for the entire range. However, first-order transitions with small distortions within the experimental resolution cannot be ruled out.

The pressure-volume data of CsI obtained in the present study are compared with previous static and dynamic compression results in Fig. 3. There is a significant difference in volume between that calculated on the basis of the previous structural assignment and the present result (10% and 80 GPa), and the difference increases with increasing orthorhombic distortion. An analysis of the previous raw data on the basis of the new structure gives an equation of state that agrees with the present results within the previously quoted uncertainties, with the exception[18] of Ref. 4. To investigate the compatibility of the present data with the shock-wave results, we use the theoretical calculation of the thermal pressure $p_{\text{th}}(V,T)$ along the Hugoniot by Aidun, Bukowinski, and Ross.[12] In the spirit of a Mie-Gruneisen model, we calculate the Hugoniot pressure $p_H(V,T) = p_S(V,300\text{ K}) + p_{\text{th}}(V,T)$, where $p_S(V,300\text{ K})$ is the static equation of state determined by the present measurements. The Hugoniot predicted with $p_{\text{th}}(V,T)$ calculated assuming a linear dependence of the band gap on pressure[12] is shown in Fig. 3. The result is in excellent agreement with the shock-wave points, particularly at higher pressure. The new static equation of state is close to theoretical predictions,[12,13] although further calculations should be performed using the newly identified crystal structures.

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[1] K. Asaumi, Phys. Rev. B **29**, 1118 (1984).

[2] T.-L. Huang and A. L. Ruoff, Phys. Rev. B **29**, 1112 (1984); Y. K. Vohra, S. J. Duclos, and A. L. Ruoff, Phys. Rev. Lett. **54**, 570 (1985); Y. K. Vohra, K. E. Brister, S. T. Weir, S. J. Duclos, and A. L. Ruoff, Science **231**, 1136 (1986).

[3] E. Knittle and R. Jeanloz, Science **223**, 53 (1984); J. Phys. Chem. Solid **46**, 1179 (1985).

[4] A. N. Zisman, I. V. Aleksandrov, and S. M. Stishov, Phys. Rev. B **32**, 484 (1985); I. V. Aleksandrov, A. N. Zisman, and S. M. Stishov, Zh. Eksp. Teor. Fiz. **92**, 657 (1987) [Sov. Phys. JETP **65**, 371 (1987)].

[5] H. K. Mao, Y. Wu, R. J. Hemley, L. C. Chen, J. F. Shu, and L. W. Finger, Science **246**, 649 (1989).

[6] K. Asaumi and Y. Kondo, Solid State Commun. **40**, 715 (1981); I. N. Makarenko, A. F. Goncharov, and S. M. Stishov, Phys. Rev. B **29**, 6018 (1984); J. P. Itie, A. Polian, and J. M. Besson, Phys. Rev. B **30**, 2309 (1984); Y. K. Vohra, S. T. Weir, K. E. Brister, and A. L. Ruoff, Phys. Rev. Lett. **55**, 977 (1985); Q. Williams and R. Jeanloz, Phys. Rev. Lett. **56**, 163 (1986).

[7] R. Reichlin, M. Ross, S. Martin, and K. A. Goettel, Phys. Rev. Lett. **56**, 2858 (1986).

[8] L. V. Al'tshuler, M. M. Pavovskii, L. V. Kuleshova, and G. V. Simakov, Fiz. Tverd. Tela (Leningrad) **5**, 279 (1962) [Sov. Phys. Solid State **5**, 203 (1963)]; V. Ya. Vashchenko and G. V. Simakov, Fiz. Tverd. Tela (Leningrad) **7**, 972 (1965) [Sov. Phys. Solid State **7**, 972 (1965)].

[9] H. B. Radousky, M. Ross, A. C. Mitchell, and W. J. Nellis, Phys. Rev. B **31**, 1457 (1985).

[10] C. A. Swenson, J. W. Shaner, and J. M. Brown, Phys. Rev. B **34**, 7924 (1986).

[11] M. Ross and F. J. Rogers, Phys. Rev. B **31**, 1463 (1985).

[12] J. Aidun, M. S. T. Bukowinski, and M. Ross, Phys. Rev. B **29**, 2611 (1984).

[13] N. E. Christensen and S. Satpathy, Phys. Rev. Lett. **55**, 600 (1985); S. Satpathy, N. E. Christensen, and O. Jepsen, Phys. Rev. B **32**, 6793 (1985).

[14] Q. Williams and R. Jeanloz, Phys. Rev. Lett. **59**, 1132 (1987).

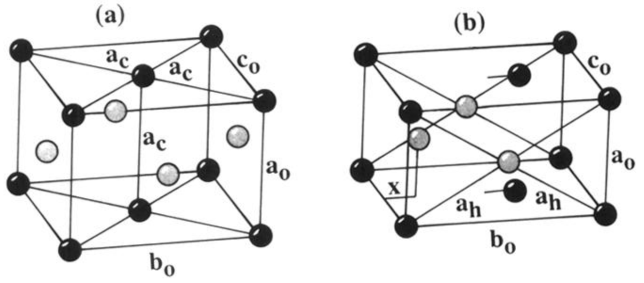
[15] H. K. Mao, in *Simple Molecular Systems at Very High Densities*, edited by P. Loubeyre, A. Polian, and N. Boccara (Plenum, New York, 1989), pp. 221–236.

[16] N. C. Holmes, J. A. Moriarty, G. R. Gathers, and W. J. Nellis, J. Appl. Phys. **66**, 2962 (1989).

[17] A. P. Jephcoat, H. K. Mao, C. S. Zha, P. M. Bell, L. W. Finger, and D. E. Cox, National Synchrotron Light Source Annual Report 1986 (unpublished), p. 323.

[18] If the present structure assignment is used in the analysis of the Zisman *et al.* (Ref. 4) data, considerably smaller volumes are obtained. The discrepancy could be the result of bridging of CsI single crystal between the diamond anvils [a serious problem when hydrostatic media are used above 20 GPa (Ref. 15)], sample contamination by the noble-gas pressure medium, or complications arising from diffraction from the medium itself (see Ref. 5). In addition, their single crystal of CsI broke down into several crystallites at the phase transition, and only a limited portion of the complicated polycrystalline diffraction pattern was measured, thereby making peak assignments difficult.

[19] P. Vinet, J. Ferrante, J. H. Rose, and J. R. Smith, J. Geophys. Res. **92**, 9319 (1987).



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