Polymorphism of CsI

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Abstract. *Ab initio* total energy calculations based on density functional theory and the generalized gradient approximation in conjunction with a constant-pressure minimization algorithm have been used to investigate the pressure-induced structural phase transitions in CsI. According to the calculations, increasing the pressure above ≈ 20 GPa causes a small continuous distortion of the ambient pressure B2 structure. At higher pressures, a weakly first-order isosymmetric transition occurs at ≈ 47 GPa. The high-pressure polymorph has an orthorhombic 'hcp-like' structure with space group *Pmma*.

1. Introduction

The high-pressure behaviour of CsI has been studied extensively, both experimentally and theoretically. However, despite the apparent simplicity of the structure, there is no consensus yet with regard to the structure of the high-pressure polymorphs and their physical properties. Knittle and Jeanloz (1984) and Huang and Ruoff (1984) interpreted their high-pressure x-ray data in terms of a structural phase transition at 37–40 GPa, in which the structure of the room pressure phase, where CsI has the CsCl or B2 structure, is tetragonally distorted. Huang and Ruoff (1984) proposed two structural models, which have molar volumes of 41.03 and 49.06 $\text{\AA}^3$ at 51 GPa. The latter value agrees with the findings of Knittle and Jeanloz (1984) and Zisman *et al* (1985), who obtained a molar volume of ≈ 50 $\text{\AA}^3$ at 50 GPa. Asaumi (1984), Asaumi *et al* (1985) and Vohra *et al* (1985b, 1986) concluded that their data implied two structural phase transitions at ≈ 39 and ≈ 56 GPa. The structural phase transition at 56 GPa was thought to lead to an orthorhombic distortion of the previously tetragonally distorted B2 structure. The existence of the orthorhombically distorted B2 structure was rejected by Knittle and Jeanloz (1985). In contrast to this, Aleksandrov *et al* (1987) remarked that, according to unpublished experiments, CsI would transform directly into an orthorhombic structure. All of these propositions where questioned by Mao *et al* (1990), who demonstrated a good agreement between observed energy-dispersive x-ray patterns and those derived from a structural model based on 'hcp-like' distortion, which they thought would begin to appear at 15 GPa. At very high pressures, the atoms would then be packed in a hcp arrangement. Due to experimental difficulties, Mao *et al* (1990) could not establish whether the phase transition from B2 to the orthorhombic phase was of first or second order. Mao *et al* (1990) thought that the symmetry of the high-pressure polymorph corresponded to space group *Pmm*2, with the atomic coordinates Cs(1) = 0, 0, 0; Cs(2) = 0, $\frac{1}{2}$, $\frac{1}{2} + z$; I(1) = $\frac{1}{2}$, $\frac{1}{2}$, 0; and I(2) = $\frac{1}{2}$, $\frac{1}{2}$, z. Mao *et al* (1990) could not determine the magnitude of the z-components. However, in space group *Pmm*2

the Wyckoff positions a, b, c and d, used by Mao *et al* (1990) each have an unconstrained z-component. If the coordinates are correct, then there are glide planes present, and the symmetry is *Pmma* instead of *Pmm2*. For this description, the origin of the unit cell has to be shifted and then the Cs atoms occupy the Wyckoff f position with fractional coordinates $\frac{3}{4}, \frac{1}{2}, z$ and $\frac{1}{4}, \frac{1}{2}, \bar{z}$ while the I are located at the Wyckoff e position with coordinates $\frac{3}{4}, 0, z$ and $\frac{1}{4}, 0, \bar{z}$.

It should be noted that within the experimental resolution of the more recent studies there are no discontinuities in the equation of state. However, inconsistencies exist with respect to the value of the bulk modulus, B_0, and its pressure derivatives B_0', and B_0''. The values given in the literature for the bulk modulus, B_0, vary from 9.2–13.5 GPa, those for the first pressure derivative range from 5.5–8.1 and for B_0'' from -0.73 to -1.3 GPa^{-1}. It is interesting that the bulk modulus given by Mao *et al* (1990) represents one of the extreme values cited in the literature, while the proponents of a tetragonally distorted B2 structure always find significantly smaller values of 11.1–11.9 GPa. The insulator-to-metal transition is now thought to occur at $\approx$110 GPa (Knittle and Jeanloz 1984, Itie *et al* 1984, Makarenko *et al* 1984, Knittle and Jeanloz 1985, Reichlin *et al* 1986) and earlier findings of much lower transition pressures (Asaumi *et al* 1985, Vohra *et al* 1985b) seem to have been erroneous.

Theoretical studies on CsI range from ones based on ionic models with a parametrized description of the interatomic interactions to elaborate quantum mechanical calculations. Vohra *et al* (1985a) deduced from their rigid-ion model calculations that a phase transition from a cubic B2 structure to a tetragonally distorted one should occur discontinuously at a ratio of the molar volume under compression to that at 1 bar, V/V_0, of about 0.5. A number of quantum mechanical calculations have been published, such as the augmented-plane-wave calculations by Aidun and Bukowinski (1983, 1984), LMTO calculations by Satpathy *et al* (1985) and ASA-MT-LDA calculations by Christensen and Satpathy (1985). Aidun and Bukowinski (1983, 1984) investigated the insulator-to-metal transition, but did not consider any pressure-induced structural changes. The results of Satpathy *et al* (1985) indicated that at $V/V_0 = 0.56$ there was a cubic-to-tetragonal transition, and at $V/V_0 = 0.525$ a tetragonal-to-orthorhombic transition. The metal-to-insulator transition occurred in the calculations of Satpathy *et al* (1985) at $V/V_0 = 0.5$. Satpathy *et al* (1985) thought that the relative volume of metallization computed by them was in good agreement with experiment, but as they referred to the data of Vohra *et al* (1985b), this statement would have to be reconsidered in the light of the newer and more conclusive data mentioned above. To the best of our knowledge, there are no calculations for the hcp-like structure proposed by Mao *et al* (1990).

In view of the numerous discrepancies in the interpretation of experimental data and the incomplete results provided by theory it was thought worthwhile to study the pressure-induced polymorphism in CsI with a modern quantum mechanical approach.

2. Computational details

Commercial (MSI) and academic versions of the software package CASTEP (Cambridge serial total energy package), which has been described elsewhere (Teter *et al* 1989, Payne *et al* 1992) and associated programs for symmetry analysis, were used for the calculations presented here. CASTEP is a pseudopotential total energy code which employs special-points integration over the Brillouin zone, and a plane-wave basis set for the expansion of the wave-functions. The calculations were performed using norm-conserving nonlocal
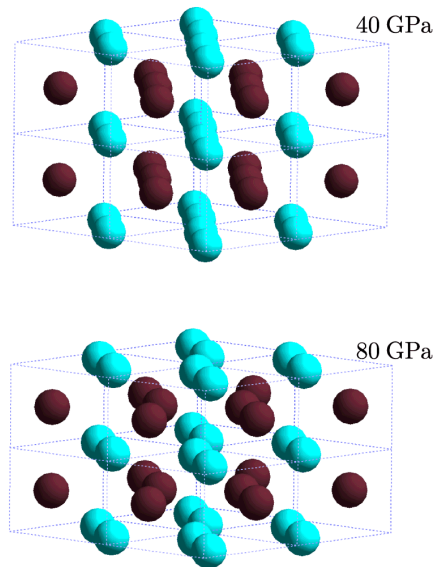
Predicted high pressure structure of CsI

Figure 1. The computed structures of CsI at 40 and 80 GPa show the small pressure-induced distortions. The unit cells at the two different pressures are not drawn to scale.

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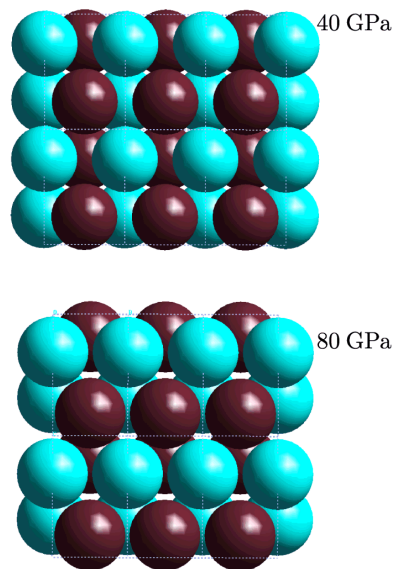
Figure 2. A comparison of the computed structures at 40 GPa and 80 GPa viewed parallel to [100] shows that the orthorhombic structure is 'hcp'-like. The unit cells at the two different pressures are not drawn to scale.

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pseudopotentials of the form suggested by Kleinman and Bylander (1982), where the pseudopotentials were taken from the CASTEP data-base. A gradient-corrected form of the exchange–correlation functional (GGA) was used in the form suggested by White and Bird (1994). A cut-off of 900 eV for the kinetic energy for the plane-wave expansion of the wave-functions was chosen to ensure numerical stability of the constant-pressure minimizer. Four to 12 k-points in the irreducible wedge of the Brillouin zone were used to sample reciprocal space. These were chosen according to a scheme described by Monkhorst and Pack (1976). The geometry optimization was performed using the BFGS minimization technique (Fischer and Almlöf 1992). The Hessian matrix in the mixed space of internal coordinates and cell variables is updated using *ab initio* calculated atomic forces and stress tensor. The Pulay stress correction was evaluated numerically by performing total energy calculations at three different values of the kinetic energy cut-off (Francis and Payne 1990).

The computations for the undistorted CsCl-type structure were performed within $Pm\bar{3}m$ symmetry. To investigate the type and number of distortive phase transitions, a variety of calculations in the range of 0–80 GPa were performed where the symmetry was constrained to be either orthorhombic or tetragonal. The calculations for the hcp-type structure were performed with the symmetry constrained to be either $Pmm2$, $Pmma$ or $P1$ with orthogonal lattice vectors.

The calculations were considered converged when the pressure and remaining stress were within 0.06 GPa of the set values. Mostly, the agreement was two orders of magnitude

better. The residual forces acting on the atoms of the hcp-like structure after achieving self-consistency were always smaller than 0.01 eV Å^{-1}, but were mostly smaller than 0.002 eV Å^{-1}.

3. Results

For calculations based on the GGA, the calculated lattice parameters of CsI in the B2 structure at 0 GPa ($a_{0,calc,GGA} = 4.636$ Å) deviate by $+1.5\%$ from experimental data ($a_{0,exp} = 4.568$ Å). From LDA calculation, a lattice constant which is too small by -3.5% with respect to the experimental value is obtained ($a_{0,calc,LDA} = 4.411$ Å). Such agreement with experimental data is expected for pseudopotential GGA and LDA calculations.
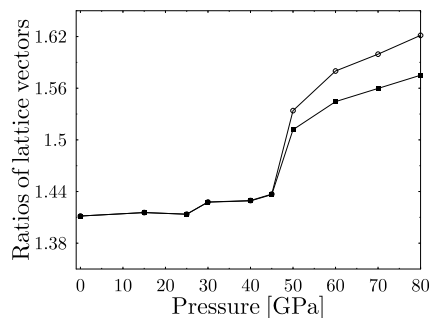

Figure 3. The pressure dependence of the ratios of the lattice parameters: a/b (squares) and c/b (circles). The lines are guides to the eye. A ratio of $\sqrt{2}b = a = c$ corresponds to a B2-type structure, while for an ideal hcp packing a/b would be 1.633 and $c/b = \sqrt{3}$.
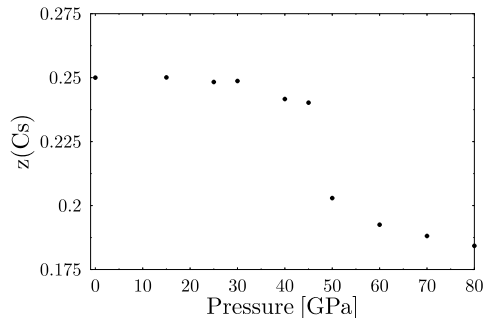
Figure 4. The pressure dependence of the z-component of the fractional coordinates shows a disconinuity at $\approx$45 GPa, indicating that the transition is of first order.
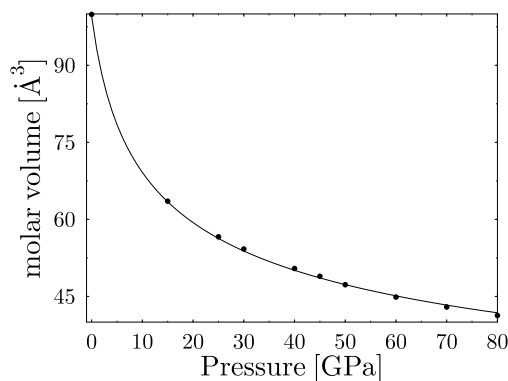

Figure 5. The filled circles represent the molar volumes of CsI in the orthorhombic 'hcp-like' structure. The line is the equation of state derived for a hypothetical undistorted B2-type structure. Hence, the current calculations imply that the hcp-like phase is slightly denser than the B2-type structure at high pressures. In agreement with experiment, there is no discernible discontinuity in the pressure dependence of the molar volume.

The relaxations at high pressures all showed that a structure with symmetry *Pmma* was the most stable (figures 1 and 2). The present calculations show that with increasing
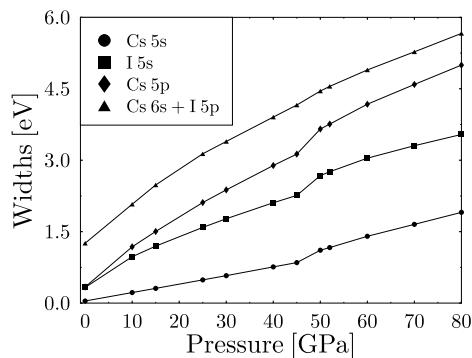
Figure 6. The pressure dependence of the width of Cs 5s (filled circles), I 5s (squares), Cs 5p bands (diamonds), and of the upper valence band (triangles). The lines are guides to the eye.
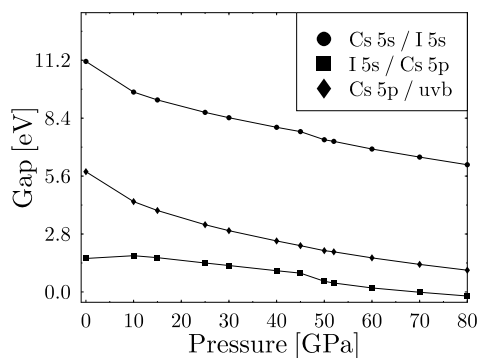
Figure 7. The pressure dependence of the separation between Cs 5s and I 5s (filled circles), I 5s and Cs 5p (squares), and Cs 5p and the upper valence band, uvb (diamonds). The lines are guides to the eye.

pressure the structure is at first continuously distorted. This slight distortion commences at 30–35 GPa, which coincides with the pressure at which peak broadening has been observed experimentally. At $\approx$47 GPa our calculations predict a weakly first-order isosymmetric structural phase transition. This is deduced from the discontinuity of the pressure dependences of the ratios of the lattice parameters (figure 3) and of the z-component of the fractional coordinates (figure 4). This pressure coincides with the lowest pressure at which Mao *et al* (1990) could unambiguously observe a splitting of reflections.

The transition is very weakly first order, and hence the excess volume is negligibly small. This is in agreement with most experimental data sets which show no discontinuity in the $P(V)$ curves (Asaumi 1984, Knittle and Jeanloz 1984, Zisman *et al* 1985, Vohra *et al* 1985b, Knittle and Jeanloz 1985, Asaumi *et al* 1985, Mao *et al* 1990). As can be seen from figure 5, the molar volume of the orthorhombic phase is slightly smaller than that of a hypothetical B2-type phase at the same pressure. When a Birch equation is fitted to the calculated data in the range 0–80 GPa, the bulk modulus B_0 is $\approx$13.5 GPa, $B_0' = 3.6$ and the molar volume at 0 GPa is $\approx$99.4 Å^3. Hence the current calculations are in good agreement with the result of Mao *et al* (1990) for the bulk modulus ($B_{0,exp} = 13.5$ GPa) and in reasonable agreement for the molar volume ($V_{0,exp} = 95.32$ Å^3).

An analysis of the electron density distribution shows that the structural phase transition at $\approx$47 GPa is accompanied by a hybridization of the Cs 5p orbitals with the I 5s orbitals and the concomitant overlap of Cs 5p orbitals of different Cs atoms. This is deduced from the maximum value of the Cs 5p density in the I planes which increases from 0.01 to 0.13 electrons Å^{-3} when the pressure is increased from 0 to 80 GPa. This analysis is consistent with that derived from atomic calculations, where the Cs 5p orbitals have a maximum at a radius of 1.7 Å. When the pressure is increased, the distance between neighbouring Cs atoms decreases below 3.4 Å at $\approx$50 GPa, i.e. at the transition pressure. In atomic calculations the I 5p orbitals have a maximum at a radius of 2.05 Å, and are delocalized at 0 GPa already. The atomic 5s orbitals of Cs and I each have a radius of 1.65 Å, and hence it is the Cs 5p orbitals which will start overlapping first. The structural activity of the Cs 5p orbitals is an important observation which could only be made due to the fact that the Cs outer core electrons have been treated as valence states in this calculation. The electronic nature of the pressure-induced transition is further confirmed by the analysis of the pressure dependence of the electronic density of states as illustrated

by figures 6 and 7. The total valence density of states in this calculation includes Cs 5s, I 5s, Cs 5p bands and the upper valence band that is formed by highly hybridized I 5p and Cs 6s electrons. The pressure dependence of the width of these four bands (figure 6) and of their separations (figure 7) exhibit obvious discontinuities at around 47 GPa. It should be noted that the band width and band gaps were estimated from the eigenvalues at the special Monkhorst–Pack points used in the self-consistent calculation. Consequently the values presented in figures 6 and 7 represent the lower boundary for the band widths and the upper boundary for the band separations. We estimate the error in determining the band width in this way to be at most 0.1 eV for the low-lying states and up to 0.2–0.3 eV for the highly dispersive upper valence band, with the band separation error being roughly twice these values. This analysis indicates that at the transition pressure the gap between the Cs 5p and I 5s bands disappears and we observe the energy resonance between formally core states of Cs and valence states of I. This change in the energy spectrum agrees well with the observed spatial redistribution of the related electron charge densities and emphasizes the importance of a correct description of p states of the cation. Finally, one might note that the extrapolation of the results in figure 7 to higher pressures would result in the overlap between the upper valence band and the now hybridized Cs 5p/I 5s band at pressures of 110–120 GPa. However, there is a possibility that the calculations give the pressure of the metallization transition at lower values, an issue that we have not addressed here. Assuming that the insulating phase remains the ground state of CsI one might expect an electronic transition at 110–120 GPa which would be due to yet another change in the chemical activity of formally inert core states.

4. Discussion

The calculations presented here strongly support the interpretation of the energy-dispersive x-ray data presented by Mao *et al* (1990), which are based on a distortion of the B2 structure and a displacement of the atoms from the special positions that they occupy in the cubic B2 structure. The correct symmetry of the high-pressure polymorph has been determined to be *Pmma*, and the fractional coordinates have been given as a function of pressure. In agreement with the interpretation of the experimental data by Mao *et al* (1990), the current calculations exclude suggestions of tetragonally or orthorhombically distorted B2-type structures. The model proposed here for the response of the structure to increasing pressure is a small continuous distortion up to 47 GPa, and then an isosymmetric first-order phase transition. Then the structure closely resembles a hcp packing, which is the expected high-pressure structure. Hence, it is very unlikely that there will be a further structural phase transition.

In a *Pmma* setting, the structure corresponds to an undistorted cubic B2 type if $\sqrt{2}b = a = c$ and the z-components of the fractional coordinates are $\frac{1}{4}$ or $\frac{3}{4}$. In a perfect hcp packing of the atoms the ratio would be $c/b = \sqrt{3}$ and $a/b = 1.633$. From an extrapolation of the data given in figure 3 it may be concluded that the hcp packing would be achieved at pressures above $\approx$120 GPa, which is consistent with the data given by Mao *et al* (1989). The current calculations, however, were restricted to an insulating structural state and hence this could not be tested.

In a comparison of the data presented here to that of future experiments it should be noted that the small differences between the enthalpies of the different structures imply that in stressed samples the relative stabilities may be different.

Acknowledgments

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