Pressure-Induced Cubic to Tetragonal Transition in CsI

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First-principles self-consistent total-energy calculations within the local-density approximation show, in agreement with experiments, that CsI undergoes a transition from the cubic (CsCl) structure to a tetragonal structure at a pressure $P_t \simeq 40$ GPa. The calculated volume at the transition is ~ 53% of the zero-pressure volume. We find that the phase transition is driven by an "intercellular" electrostatic interaction. A structural bistability is found around the transition.

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The study of physical properties under pressure is essential to the understanding of bonding in solids. The advent of the diamond anvil cell has made it possible to examine systematically pressure-induced phase transitions. Recently it has been observed[1-4] that under high pressure the cesium halides undergo a transition from the cubic ($B2$ CsCl structure) to a tetragonal structure. In this Letter we show that we can predict the phase transition in CsI from first-principles theoretical calculations. These indicate further that the phase transition is driven by an "intercellular" electrostatic Coulomb interaction. Even though only one compound, CsI, is explicitly considered here, we expect that our theoretical results should be applicable to CsBr and CsCl equally well, and other ionic compounds.

A simple model calculation of total-energy variations in ionic solids with pressure was recently presented by Vohra, Duclos, and Ruoff,[5] who found that the observed[1-4] phase transitions follow from a total-energy expression consisting of a simple Madelung term and a Born-Mayer–type repulsive term with adjustable parameters. This is probably not very surprising since related procedures have been successfully applied in calculations of elastic shear constants. First-principles calculations[6] of such quantities, however, are demanding, requiring an accurate description of the electron-electron interactions including the proper nonsphericity of the charge distributions. The simple ASA (atomic spheres approximation), which has been successfully employed for many other cases, is too crude for calculations of shear elastic constants.

The ASA theory cannot predict a phase transition as observed, but we show that a simple change to a muffin-tin formulation of the total-energy functional is sufficiently accurate to give the transition volume and pressure (the insulator-metal transition is discussed elsewhere[7]).

In the local-density approximation the total-energy functional is

$$E = T_s + U_{\mathrm{C}} + U_{\mathrm{xc}}. \tag{1}$$

Here T_s is the kinetic energy of the system of noninteracting electrons. In a muffin-tin model (MT) the exhange-correlation (U_{xc}) and Coulomb-type (U_{C}) terms are

$$U_{\mathrm{xc}} = N \sum\nolimits_i \int_{\Omega_i} \epsilon_{\mathrm{xc}}[\rho_i(\mathbf{r})]\rho_i(\mathbf{r})\,d^3r + \int_{\Omega'} \rho_0 \epsilon_{\mathrm{xc}}[\rho_0]\,d^3r, \tag{2}$$

$$U_{\mathrm{C}} = \int\int [\rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|]\,d^3r\,d^3r'. \tag{3}$$

We assume atomic Rydberg units throughout. The quantities describing the muffin-tin model are the following: Each of the N cells contains n atoms, indexed by "i." Space is divided into (nonoverlapping) muffin-tin spheres (radius s_i), centered at the atomic positions $\mathbf{h}_i$, and an interstitial regime [Ω' in Eq. (2)]. The interstitial electron density is taken to be constant, ρ_0, and inside the spheres (Ω_i) the density is made spherically symmetric. The density $\rho(\mathbf{r})$ in Eq. (3) is

$$\rho(\mathbf{r}) = \sum_{\mathbf{R},i} \{[\rho_i(|\mathbf{r}-(\mathbf{R}+\mathbf{h}_i)|) - \rho_0]\theta_i - Z_i \delta(\mathbf{r}-\mathbf{R}-\mathbf{h}_i)\} + \rho_0, \tag{4}$$

where $\theta_i \equiv \theta(s_i - |\mathbf{r}-\mathbf{R}+\mathbf{h}_i|)$ is a step function which is 1 for $\mathbf{r}$ inside the MT spheres, and 0 elsewhere; Z_i is the atomic number of atom "i," ρ_i is the spherically averaged density. The Coulomb contribution per cell to E is[8,9]

$$\begin{aligned} U_{\mathrm{C}}^{\mathrm{cell}} &= \frac{U_{\mathrm{C}}}{N} \\ &= \sum_i U_{\mathrm{C}_i}^{\mathrm{local}} + 1.8 \sum_i \frac{q_{0i}^2}{s_i} + \sum_{i,j} \frac{q_{0i} M_{ij} q_{0j}}{2S_{\mathrm{av}}} + \sum_{i,j} (Z_i - q_i) \frac{M_{ij}}{2S_{\mathrm{av}}} (Z_j - q_j) + \sum_{i,j} (Z_i - q_i) \left(\frac{M_{ij}}{S_{\mathrm{av}}} + \frac{3}{s_i} \delta_{ij} \right) q_{0j}. \end{aligned} \tag{5}$$

The symbols not defined so far are

$$q_i=\int_0^{s_i} 4\pi r^2\rho_i(r)\,dr, \tag{6}$$

$$q_{0i}=\Omega_i\rho_0, \quad \rho_0=\textstyle\sum_i (Z_i-q_i)/(V-\sum_i\Omega_i), \tag{7}$$

$$\Omega_i=\tfrac{4}{3}\pi s_i^3, \tag{8}$$

$$V=\text{cell volume}=\tfrac{4}{3}\pi n S_{\rm av}^3, \tag{9}$$

$$U_{\mathrm{C}_i}^{\rm local}=\int_{\Omega_i}\int d^3r\,d^3r'\,\rho_i(\mathbf{r})\frac{\rho_i(\mathbf{r}')-2Z_i\delta(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{10}$$

$$M_{ij}=\textstyle\sum_{\mathbf{R}}'\dfrac{2S_{\rm av}}{|\mathbf{h}_i-\mathbf{h}_j-\mathbf{R}|}-V^{-1}\int d^3r\,(2S_{\rm av}/|\mathbf{r}|). \tag{11}$$

In the ASA to Eq. (5), the muffin-tin spheres are replaced by overlapping atomic spheres, and ρ_0 [Eq. (7)] is replaced by a (weighted) average of the electron densities on atomic-sphere surfaces. If, for simplicity, all atomic spheres are taken to be of equal size, i.e., with radii $S_{\rm av}$, then all q_{0i} are equal. In a diatomic solid (like CsI) the last term in Eq. (5) then vanishes, and the fourth term is the usual ASA Madelung[7] term ($U_{\rm Mad}^{\rm ASA}$). The sum of the second and third terms represents the so-called "MT correction" in the ASA. In a monoatomic solid this reduces to

$$\Delta U_{\rm MT}^{\rm ASA}=(1.8-\alpha_{\rm M})q_0^2/S_{\rm av}, \tag{12}$$

where $\alpha_{\rm M}$ is the Madelung constant. The expression (12) is the MT correction[10] to the ASA which has been by Skriver[11] and others.[12,13] Inspired by the success[11] of this approximation, we tried to apply it to CsI under tetragonal deformation. For fixed volume we found only a weak dependence of q_0 on c/a. This means that the structural differences in the MT correction are given by the structural variation of $\alpha_{\rm M}$, i.e., a purely geometrical variation. The difference $\alpha_{\rm M}(\text{bcc})-\alpha_M(c/a)$ is shown in Fig. 1 as a function of c/a, together with $\Delta U_{\rm MT}^{\rm ASA}$ for CsI (dashed curve) for $V/V_0=0.503$, with V_0 being the observed equilibrium volume. For $c/a=1$ (bcc), $\alpha_{\rm M}$ is 1.791 857 and for $c/a=\sqrt{2}$ (fcc), $\alpha_{\rm M}=1.791\,747$, and $\alpha_{\rm M}(\text{bcc})-\alpha_{\rm M}(c/a)$ has a maximum for $c/a\sim 1.2$. The structural differences in the ASA total energy,

$$E_{\rm ASA}\equiv T_s(\text{ASA})+U_{\rm xc}(\text{ASA})+U_{\rm C}^{\rm local}(\text{ASA})+U_{\rm Mad}^{\rm ASA},$$

is positive for all $c/a\neq 1.0$ (cf. the dash-dotted curve in Fig. 2). Since, in ASA, the difference $\Delta U_{\rm MT}^{\rm ASA}(c/a)-\Delta U_{\rm MT}^{\rm ASA}(1)$ is positive for all c/a, it tends to sta-

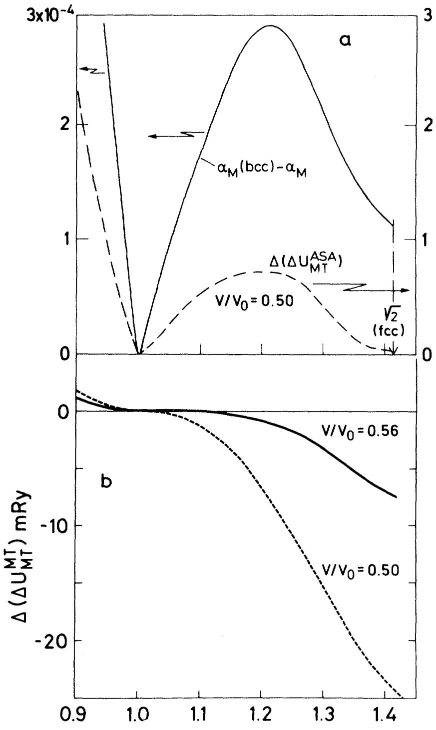

FIG. 1. (a) (Left-hand scale) Madelung-constant differences for body-centered tetragonal structure, $-[\alpha_{\rm M}(c/a)-\alpha_{\rm M}(1.0)]$, and (right-hand scale) ASA version of the muffin-tin correction [cell-cell interaction, second and third terms in Eq. (5) in the atomic-spheres approximation as described in text] for $V/V_0=0.50$, both as functions of c/a. (b) Variation, $\Delta(\Delta_{\rm MT}^{\rm MT})$, of this intercellular electrostatic energy with c/a for two volumes, $V=0.56V_0$ and $V=0.50V_0$.

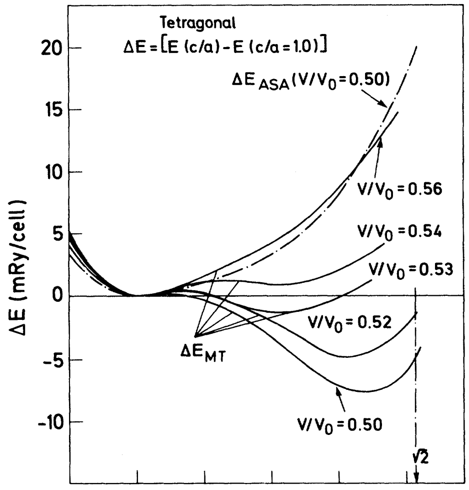

FIG. 2. The dash-dotted curve is the ASA total energy vs c/a for $V/V_0=0.50$. The solid curves show total-energy variations calculated in the *muffin-tin model* for five volumes, $V/V_0=0.50$, 0.52, 0.53, 0.54, and 0.56.

bilize further the cubic structure. This term cannot drive a transition to the tetragonal structure.

The ASA total-energy functional includes for a monoatomic solid only intrasphere electrostatic interactions, and for a compound, in addition, only monopole sphere-sphere interactions via the Madelung term $U_{\text{Mad}}^{\text{ASA}}$. We refer to the difference $\Delta U_{\text{MT}}^{\text{MT}}$ between the Coulomb energy calculated in the muffin-tin model [Eq. (5)] and the ASA Coulomb energy, $U_C^{\text{local}}(\text{ASA}) + U_{\text{Mad}}^{\text{ASA}}$, as an "intercellular" electrostatic interaction energy. Figure 1(b) shows the structural variation, $\Delta(\Delta U_{\text{MT}}^{\text{MT}})$, of this term versus c/a for two fixed volumes. This correction is strongly volume dependent, and for sufficiently small volumes it favors the tetragonal structure. The differences between the ASA and the MT values of the exchange-correlation energy are extremely small. This follows from Fig. 2 where the total-energy variations obtained[14] from the MT functional (ΔE_{MT}) for five volumes are shown. The difference between ΔE_{MT} and ΔE_{ASA} is to high precision $\Delta U_{\text{MT}}^{\text{MT}}$). This term is considered as driving the phase transition. This assignment can be further supported by application of the "frozen-potential" approach.[13,15] The method prescribes how to calculate the structural energy difference as essentially a change in one-electron energy plus an electrostatic contribution. Using the MT model we find that this latter term is nearly the same as $\Delta(\Delta U_{\text{MT}}^{\text{MT}})$ in the case of CsI. The reason[13,15] for this is that there is almost no self-consistent charge redistribution when c/a is altered. We could separate the total-energy change into a Madelung term [cf. fourth term in Eq. (5)] and a remainder, which then would represent a first-principles calculation of the repulsive term of Ref. 5 (apart from modification due to a different ionicity in our case[7])). However, in doing this, it can be seen that the originally simple looking Born-Mayer term in fact contains several contributions of very different nature. We prefer to group the electrostatic terms together giving one term which is somewhat more complex than just the point-ion interaction. A discussion, also relevant to this work, of closed-shell interactions is given elsewhere.[11]

The theoretical value of V/V_0 at the transition is 0.531 and the calculated pressure at which the transition occurs is 402 kbar, i.e., in good agreement with experiments[2] (0.56 and 400 ± 10 kbar, respectively). As follows from Fig. 3 we find theoretical c/a ratios that are larger than those observed (this is also the case in Ref. 5). It remains to be investigated whether a further refinement of the description of the nonsphericity of the charge density will reduce this discrepancy between theory and experiment.

The total-energy curves (Fig. 2) show that although the tetragonal phase for $V/V_0 < 0.54$ has the lower energy, the cubic phase represents a (meta)stable state. A small energy barrier separates the two phases, i.e., the tetragonal elastic shear constant c' is positive for $c/a = 1$. Three of the total-energy curves shown in Fig. 2 correspond to volumes for which the tetragonal phase is stable, $V/V_0 = 0.53$, 0.52, and 0.50. The barrier heights in these cases are 0.5, 0.4, and 0.2 mRy, respectively. Extrapolation predicts that the barrier vanishes (i.e., c' in the metastable phase would go to zero) at the volume ratio $V/V_0 \simeq 0.48$. This is the same volume at which the metastable cubic phase disappears according to the fitted model of Ref. 5.

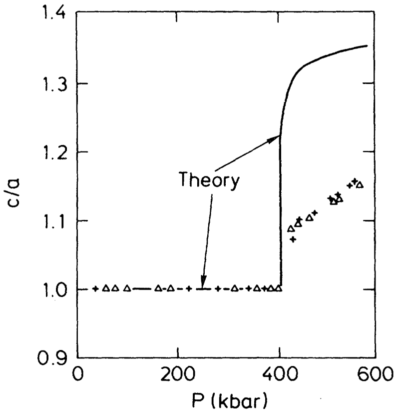

FIG. 3. Theoretical (curve) and experimental (crosses, Ref. 2; triangles, see Ref. 8 of Ref. 5) values of c/a for CsI as functions of pressure.

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