Instability of the CsCl Structure in Ionic Solids at High Pressures

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It is shown by a simple model calculation that the ionic solids in the CsCl phase transform discontinuously to a tetragonal phase under high pressures at a fractional volume in the neighborhood of 0.5. This general result follows as a consequence of competing Madelung energy and repulsive energy terms. The c/a variation with pressure and transition volume fraction are in approximate agreement with the recent ultrahigh pressure experiments on cesium halides.

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Many ionic solids, particularly the alkali halides, crystallize in the NaCl structure ($B1$ phase) at ambient conditions. Amongst twenty alkali halides, only three, CsCl, CsBr, and CsI, crystallize in the CsCl structure ($B2$ phase). The alkali halides which start out at zero pressure in the $B1$ phase undergo the $B1 \rightarrow B2$ phase transition under high pressures[1]; the phase transition is of first order with a substantial volume change (5% to 15%). The only known exceptions to this behavior are the high-pressure phase transitions in NaI and NaBr. Here, a distorted NaCl structure has been reported instead of the CsCl structure and is attributed to the low value of the ionic radius ratio of cation to anion[2] in these compounds. It appears that the CsCl structure is the high-pressure phase of ionic solids at least for compounds where the ionic radius ratio is greater than 0.6 at the phase transition. Recent high-pressure x-ray diffraction experiments[3-7] on CsI showed a further transformation of the CsCl lattice to a tetragonal lattice around 39 ± 1 GPa ($V/V_0 = 0.544 \pm 0.003$). More recent experiments on CsBr[7,8] and CsCl[9] showed an identical transformation to the tetragonal lattice at pressures 53 ± 2 GPa ($V/V_0 = 0.546 \pm 0.003$) and 65 ± 5 GPa ($V/V_0 = 0.53 \pm 0.02$), respectively, indicating it to be a general phenomenon associated with the CsCl phase. This high-pressure transformation is unique in certain ways: No volume change was detected at the phase transition; also, optical absorption edge measurements up to 71 GPa[10] on CsI show that there is no discontinuity in the energy gap as a function of pressure across the CsCl-to-tetragonal phase transition. High-pressure x-ray diffraction studies[3-6] show that the axial ratio (c/a) in the tetragonal phase increases with increasing pressure up to the highest pressures achieved in these experiments. One study also reports[5] a further slight distortion of the tetragonal lattice to an orthorhombic phase around 56 GPa in CsI.

It is important to note that the cesium halides undergo cubic-to-tetragonal transformation at the same fractional volume of 0.53 ± 0.02 within experimental errors. However, the phase-transition pressure is different for each compound depending on the compressibility. The energy band gaps at the phase transition are still large, for CsI 2.2 to 2.4 eV[10] (color bright orange), for CsBr (pale yellow, about 3 eV) and in CsCl the band gap is even greater. The bonding in these solids may largely be ionic at these compressions. These considerations motivated us to apply a simple model to obtain a qualitative understanding of the transition. More exotic first-principles band-structure calculations of crystal-structure stability under high pressures of these ionic solids are needed to get a quantitative understanding.

In our model calculation, we ignored the thermal or entropy contribution to the energy, noncentral forces,[11] and assumed that the Helmholtz free energy of the lattice is given by the static lattice expression[12] as a sum of attractive Madelung energy and a Born-Mayer–type repulsive interaction

$$F = -Z^2 e^2 A_a / a + \textstyle\sum_j B_R / r_j^n. \tag{1}$$

Here a is the lattice parameter; for the tetragonal phase $a = b < c$.

Also A_a is the Madelung constant[13] corresponding to the a parameter, r_j is the interatomic distance, and summation over index j includes the eight first-nearest neighbors and the six next-nearest neighbors. In case of the tetragonal distortion, the six next-nearest neighbors split into four at a distance a and two at a distance c. This model ignores the change transfer between the ions under high pressures which may affect the Madelung energy and also the changes in functional form of repulsive interaction at high pressures due to perturbation of the closed-shell electrons.

Using the equilibrium condition, we show that the B_R parameter in Eq. (1) can be expressed in terms of the Madelung constant, A_a, where a_0 is the lattice parameter for the cubic phase at zero pressure. It follows that

$$F = \frac{Z^2 e^2 A_{a_0}}{a_0} \left[-\frac{a_0}{a}\frac{A_a}{A_{a_0}} + \frac{1}{nX} \sum_j \left(\frac{a_0}{r_j} \right)^n \right], \tag{2}$$

where

$$X = [6 + 8(2/\sqrt{3})^n].$$

The pressure is given by

$$P = -(\partial F/\partial V)_T, \tag{3}$$

and the bulk modulus by

$$B = -V(\partial P/\partial V)_T. \tag{4}$$

For the present calculations, we set the parameter $n = 13$ in the repulsive interaction. (This choice gives zero-pressure bulk modulus $B_0 = 14$ GPa for CsI, which is higher than the experimental value of 12 GPa.[4] A value of $n = 11$ which is consistent with B_0, would give a fractional transition volume equal to 0.41.) We have also used the Huggins-Mayer potential with Pauling coefficients[1,4] and note that this gives a transition volume which is much too low (less than 0.3). The Madelung constant A_a was calculated for the tetragonal lattice at each axial ratio (c/a) using Ewald's method by summing over the appropriate series in the direct and reciprocal lattice.[13,14] Figure 1 shows the lattice energy (F) as a function of c/a at constant volume for two different volume compressions. At $V/V_0 = 0.53$, the energy minimum is at $c/a = 1.00$ indicating stability for the CsCl lattice while for $V/V_0 = 0.51$, the location of the minimum shifts to $c/a > 1$ indicating a transition to the tetragonal lattice.

At each volume compression ratio V/V_0, the c/a ratio at which the lattice energy is a minimum can be determined and this is shown as a function of V/V_0 in Fig. 2. The phase transition from the CsCl lattice to the tetragonal phase occurs at $V/V_0 = 0.52$ at which point there is a discontinuous increase in c/a of 14%, and then this ratio gradually increases with decreasing volume or increasing pressure. Thus the present simple model leads to the conclusion that the transition is first order.[15] The theoretical value of $V/V_0 = 0.52$ (with the choice of $n = 13$) at the phase transition is in fair agreement with the experimental value of 0.53 ± 0.02 for cesium halides. It was pointed out earlier[7] that this tetragonal distortion observed may be due to the macroscopic instability of the CsCl lattice which is triggered by the vanishing of the shear constant $c_s = \frac{1}{2}(c_{11} - c_{12})$ at high pressures.[16] For tetragonal distortion relative to the cube axis at constant volume it can be readily shown that the second derivative of the lattice energy with respect to c/a is proportional to c_s:

$$c_s = \frac{3}{4V} \frac{\partial^2 F}{\partial^2 (c/a)}. \tag{5}$$

Also shown in Fig. 2 is the calculated shear constant $c_s(V)$; there is a slight increase in c_s with decreasing volume up to $V/V_0 = 0.7$; this is followed by dramatic decrease with further compression. However, before c_s goes to zero there is a phase transition to a tetragonal phase dictated by the energy considerations. We find that c_s for the assumed cubic phase goes to zero for $V/V_0 = 0.48$. Note that the equilibrium transformation, at $V/V_0 = 0.52$, has an activation barrier associated with it, as the volume is decreased further the minimum for the cubic phase disappears at $V/V_0 = 0.48$. Thus, if kinetic processes prevent the transformation at the equilibrium point, it will proceed readily at $V/V_0 = 0.48$.

Theoretical values of c/a at various pressures [using Eq. (2) for pressure] are compared with experimental data on CsI[10] (Fig. 3) and there is a general agreement in form. A similar jump in c/a of about 8% in CsBr[8]

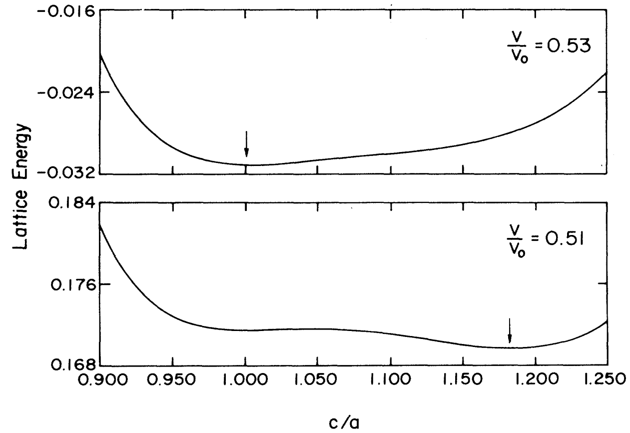

FIG. 1. The change in the lattice energy in units of $Z^2e^2A_a/a_0$ as a function of c/a at constant volume for two different compressions. The arrows indicate the lattice energy minimum.

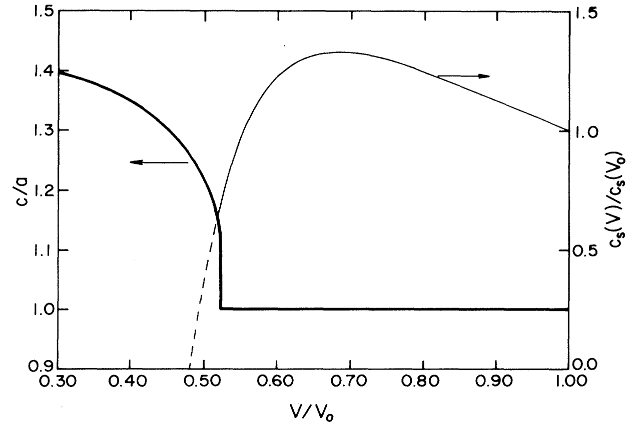

FIG. 2. The c/a corresponding to lattice energy minimum as a function of volume compression ratio (V/V_0). The curve on the right shows the variation of shear constant $c_s(V)$ for the cubic phase relative to the zero pressure value $c_s(V_0)$; the dashed portion shows the kinetically metastable region.

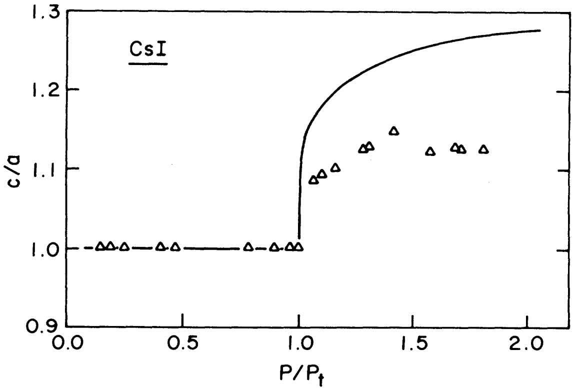

FIG. 3. The pressure variation of the axial ratio c/a. The solid curve is theoretical and Δ are the experimental data on CsI (Ref. 8). The pressure shown is scaled to the transition pressure, P_t.

and CsCl[9] is observed at the phase transition, but experimentally it cannot be concluded that there is a discontinuity in c/a because of inherent deconvolution problems close to the phase transition (made more difficult by peak broadening due to nonhydrostatic and nonhomogeneous pressure). It is interesting to note that c/a tends to a value of $\sqrt{2}$ at extreme compressions (Fig. 2). At that point the Bravais lattice will again become cubic and now the various ions are located at sites on a face-centered-cubic lattice. However, before this situation arises, perhaps most of the ionic solids will become metallic by band overlap.[17] We have also investigated the possibility of further distortion of the tetragonal lattice into an orthorhombic lattice but the minimum in the lattice energy always occurs at $b/a = 1$ at all pressures, and no orthorhombic distortion is found stable.

It should be added that the tetragonal distortion of the CsCl lattice in ionic solids at a fractional volume of about one-half appears to be a general phenomenon which arises because of competition between the Coulombic and repulsive energy interactions as the lattice is distorted. Figure 4 shows the various contributions to the total energy as a function of lattice distortion at $V/V_0 = 0.45$ in the tetragonal phase after the transition. The Madelung energy increases with increasing c/a and opposes the distortion (curve a). The distortion is favored by the resulting sharper decrease in the repulsive energy due to first-nearest neighbors (curve c). Note, however, that it is the increase in the repulsive energy of the second-nearest neighbors (curve d) which produces a minimum in the total energy (curve e) at $c/a > 1$. It is important to note that second-nearest-neighbor repulsions play a crucial role in this transition and at large distortions the total energy is largely determined by them as a result of mutual cancellation of the other terms.

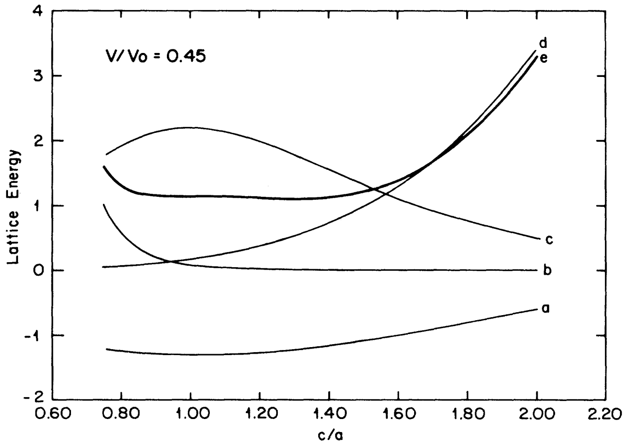

FIG. 4. The contributions to the total energy (curve e) in the tetragonal phase as a function of c/a at $V/V_0 = 0.45$. Madelung energy (curve a), repulsive-energy first-nearest neighbors (curve c), repulsive-energy second-nearest neighbors (curve d), and repulsive-energy third-nearest neighbors (curve b).

In the high-pressure x-ray diffraction study of RbI and KI no tetragonal distortion was observed up to 70 GPa.[18] This is rather expected because the parameter n in the repulsive interaction for rubidium and potassium halides is low ($n \lesssim 10$, Ref. 14) and tetragonal distortion will be stable only at lower volume fractions and higher pressures. We also expect several other alkali halides and ionic solids to show this tetragonal distortion in the megabar pressure range which has now become available with the diamond anvil cell.

In summary, the simple model calculation including next-nearest-neighbor repulsions predicts: (1) A first-order isovoluminal transition from the cubic CsCl-type structure to a tetragonal structure in the neighborhood of $V/V_0 \simeq 0.5$. (2) A discontinuous increase in the c/a ratio at the transition after which this ratio increases gradually with pressure. (3) That within the framework of this qualitative model the tetragonal phase is always stable relative to the orthorhombic phase.

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