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High-Pressure Equation of State of Cesium Fluoride to 120 GPa

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We have performed a high pressure synchrotron x-ray diffraction study of the ionic salt, cesium fluoride (CsF), up to 120 GPa. We observed the B1 \rightarrow B2 phase transition near 5 GPa as previously reported. Beyond this pressure, no phase transitions were determined to have occurred up to the highest pressure studied. Unit cell data were calculated from the known B2 (CsCl) structure for all of the pressures studied above 5 GPa, and an equation of state (EOS) was fit to the data using a 3rd order Birch-Murnaghan equation in this phase. Density Functional Theory (DFT) was also employed to compute an EOS for comparison purposes. Our experimental results agreed very well with both sets of the predicted EOS.

1. Introduction

Recent reports have suggested that Cs may become a “p-block” element at extreme conditions implying that electrons in lower energy levels may hybridize to contribute to bonding and react with highly electronegative elements such as fluorine forming CsF_x where x is an integer greater than 1 (i.e., x = 2, 3, 4, 5, ...) [1-2]. In both of these theoretical studies, CsF was examined as a starting system. In the effort to produce and observe these novel compounds at extreme conditions, we sought to first investigate the high pressure behavior of virgin CsF which has been little studied at high pressure [3-4]. We sought to first determine if there were any phase transitions at high pressure beyond the well-known B1 to B2 phase transition [5-7]. We then sought to determine the equation of state of this ionic compound in the B2 phase which, to the best of our knowledge, has not been reported.

2. Experimental Methods

A symmetric-style Diamond Anvil Cell (DAC) was utilized to generate pressures above ambient. The diamonds used each had a culet diameter of ~ 150 μm . A stainless steel gasket of 250 μm initial thickness was deformed (preindented) to ~ 15 μm thickness and a 70 μm diameter sample hole was laser drilled at the sample preparation facility of the High Pressure Collaborative Access Team (HP-CAT) at sector 16 of the Advanced Photon Source. As CsF is hygroscopic, the sample was loaded in a purified Ar-atmosphere glovebox that is located in the same facility listed above. White powdered CsF (Sigma Aldrich 99%) was manually introduced via a scalpel into the exposed gasket hole. A small amount of gold powder (Sigma-Aldrich 99.999%) was placed in with the sample for pressure measurements. No pressure transmitting medium was used. The two diamond cell halves



were brought together and closed to seal the sample, and the sample was initially pressurized to 1.9 GPa in order to ensure that it was in its low pressure NaCl (B1) phase.

X-ray diffraction (XRD) patterns were acquired at the sector 16 ID-B beamline of the Advanced Photon Source using a high speed Pilatus® silicon semiconductor based detector. The sample was placed in the path of a focused white $6\ \mu\text{m} \times 8\ \mu\text{m}$ monochromatic x-ray beam. Monochromatic x-rays of wavelength $0.406626\ \text{\AA}$ (30.5 keV) were used, and diffraction patterns were acquired for 60 seconds at each pressure. Multiple pressure points were taken up to the maximum pressure of 120 GPa. A pattern of the ambient standard was also recorded in order to determine an accurate 0 GPa reference volume. The Dioptas® program was utilized for integration of sample patterns and pressure tracking during the experiment. The integrated patterns were then fit to determine unit cell parameters with the goal of equation of state (EOS) determination. There was no evidence of radiation induced damage observed in our sample during the entire experiment, and all XRD patterns were recorded at ambient temperature.

3. Theoretical methods

Complementary *ab initio* total energy calculations were carried out to investigate the pressure induced B1-B2 transitions occurring in CsF using spin-polarized density functional theory (DFT) as implemented in the Vienna *ab initio* simulation package (VASP) [7]. The exchange-correlation energy was calculated using the generalized gradient approximation (GGA) with the parameterization of Perdew, Burke and Ernzerhof (PBE) [8]. The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method [9-10]. The plane-wave cutoff energy for the electronic wavefunctions was set to a value of 610 eV, ensuring the total energy of the system to be converged to within 1×10^{-5} eV/atom. A total of 8 atoms and 2 atoms are included in the periodic unit cell for B1 and B2 structures, respectively. Ionic relaxation was carried out using the quasi-Newton method and the Hellmann-Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.001 eV/Å. The Brillouin zone was sampled using the Monkhorst-Pack special k-point scheme [11] with $(7 \times 7 \times 7)$ and $(9 \times 9 \times 9)$ for B1 and B2 phases, respectively, in order to carry out structural optimization and total energy calculations.

4. Results

Figure 1 displays recorded XRD patterns of pressurized CsF as a function of pressure. As is evident from the patterns in the Figure, the B1 to B2 phase transition occurs between 2 and 10 GPa which is consistent with prior reports [3-4]. Above 10 GPa, no phase transitions are evident up to the highest pressure studied (120 GPa). These diffraction patterns were fit using the x-ray unit cell modeling program Jade 7® using the B2/CsCl unit structure [5-6]. The resulting unit cell volumes are displayed as a function of pressure in Figure 2. This curve was then fit to the 3rd order Birch Murnaghan equation [12-13] to extract the bulk modulus of CsF in the B2 phase using the EOSfit® program which, to the best of our knowledge, has never been reported experimentally. Our derived value of the bulk modulus (K_0) of 29.7461 ± 1.28062 and the pressure derivative of the bulk modulus (K') of 5.17957 ± 0.12723 which somewhat agrees with the theoretically predicted values of 42.2 GPa and 5.2 respectively for CsF in the B2 phase [14]. Our present DFT results of $K = 24$ GPa and $K' = 5.2$ show improved agreement with our experimental data points.

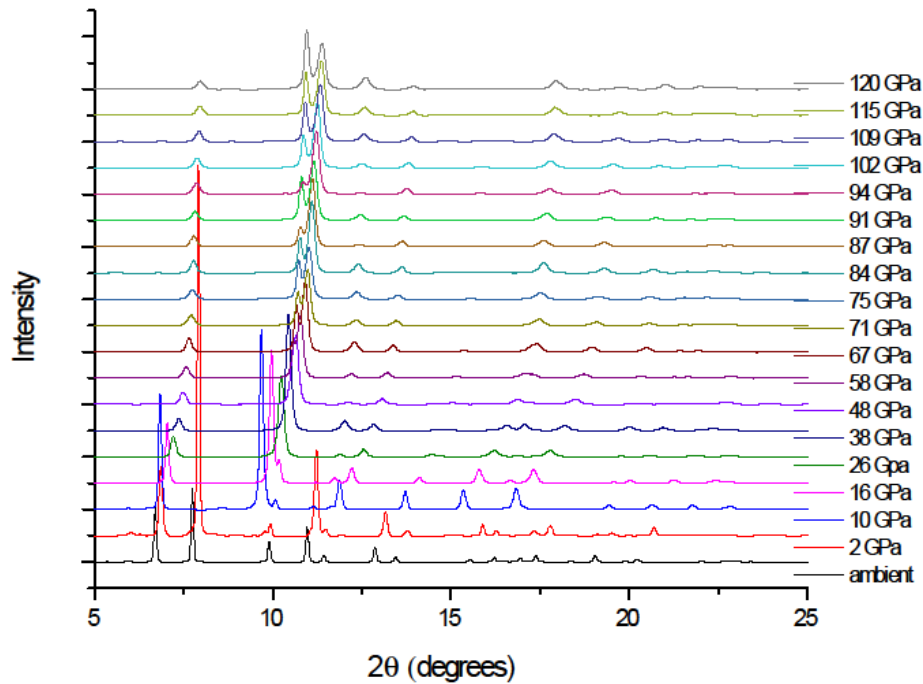


Fig. 1. Angular dispersive x-ray diffraction patterns of virgin CsF pressurized to 120 GPa.

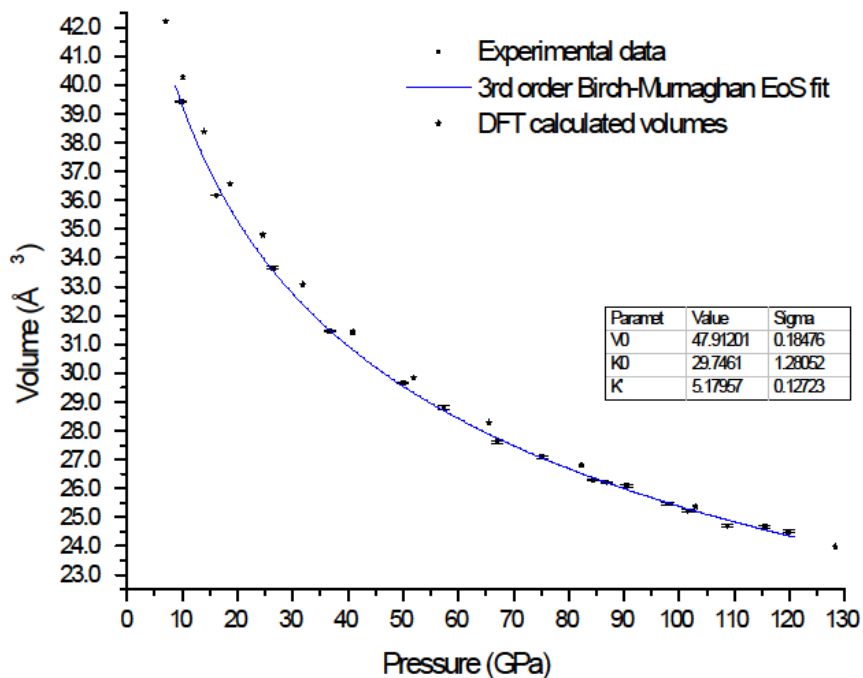


Fig. 2. Equation of state of CsF in the B2 phase as determined experimentally (error bars included) via our XRD study and calculated via the Murnaghan EOS fit and DFT. Fit parameters from the Murnaghan fit are also included in the table insert.

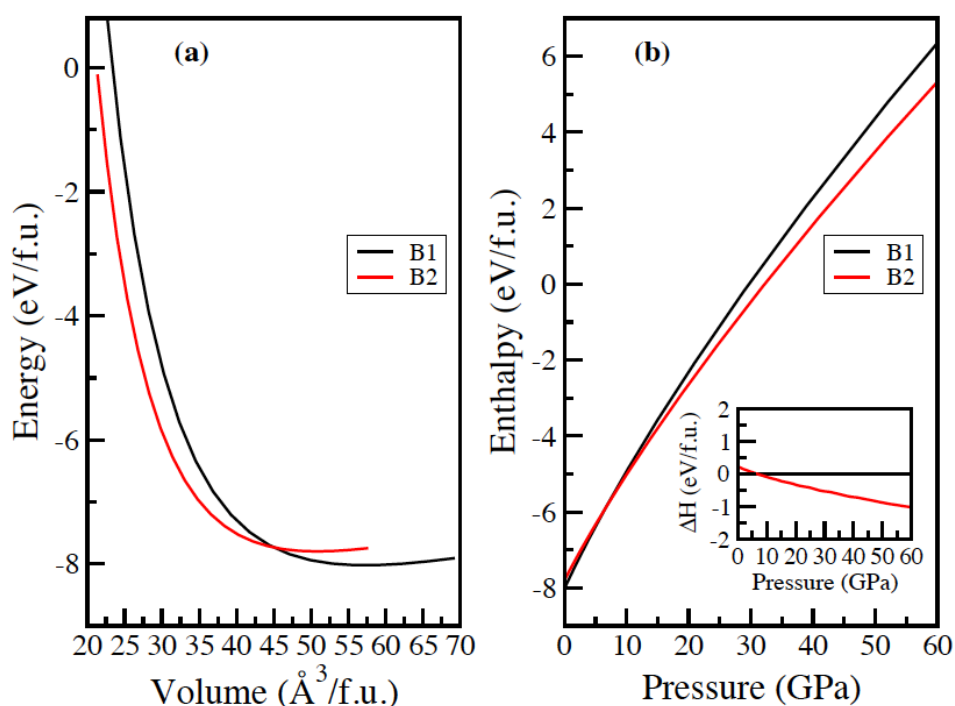


Fig. 3. Energetics of CsF calculated at the DFT/PBE level: (a) Total energy versus volume and (b) enthalpy versus pressure. The inset exhibits the enthalpy difference versus pressure for the B2 phase (red), referenced to the lattice energy, volumes, and pressure in units of eV, \AA^3 , and GPa, respectively.

To better understand the B1 \rightarrow B2 phase transition, we present a calculation of the total lattice energy vs. unit cell volume in Figure 3(a). This graph shows that CsF is stable in the B1 phase at low pressures and that the pressure induced B1 \rightarrow B2 transition to the B2 phase is expected. The calculated transition pressure is at about 6.6 GPa as shown in the inset of Figure 3(b) which displays the enthalpy vs. pressure. The crossing point is in good agreement with the experimentally determined value of the phase transition near 5 GPa.

Conclusion

We have performed a powder x-ray diffraction study of the important salt, CsF, up to 120 GPa. This is the highest pressure reported for XRD characterization of this system, to the best of our knowledge. We have found that the ionic compound undergoes only one phase transition (B1 \rightarrow B2) near 5 GPa and have determined for the first time the high pressure EOS for this compound in the B2 phase. Experimental findings have been confirmed by density functional theory calculations, with a significantly improved agreement between experimental and computational values of the CsF bulk modulus. This study will help further efforts to examine bonding changes in CsF in a high-pressure environment that has an excess of molecular fluorine.

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