Supporting Material for: Superionicity and Polymorphism in Calcium Fluoride at High Pressure

Claudio Cazorla
Institute of Materials Science of Barcelona (ICMAB-CSIC),
Campus UAB, 08193 Bellaterra, Spain

Daniel Errandonea
Departamento de Física Aplicada (ICMUV),
Universitat de Valencia, 46100 Burjassot, Spain

Abstract
In this supplemental document we explain the details of our ab initio density functional theory calculations and crystal structure searches performed in CaF$_2$ under pressure. Also we report the computed $P$-dependence of the formation energy of Frenkel pair defects in the cubic fluorite phase, and the vibrational phonon spectra and structural data of the predicted high-$T$ monoclinic $P2_1/c$ phase. Calculated enthalpy energies in compressed SrF$_2$ and BaF$_2$ are also presented.
FIG. 1: [Supplemental](Color online) Calculated (solid red line) and measured equation of state of CaF$_2$ at low temperatures. Experimental data are from works [1,2].

I. ZERO-TEMPERATURE DFT CALCULATIONS

Total energy calculations were carried out in CaF$_2$ under pressure in the cubic fluorite and orthorhombic cotunnite phases, employing the methods and parameters described in the main text of the present Letter. As it may be appreciated in the supplemental Fig. 1, the agreement between our calculated equation of state and experimental data from Refs. [1,2] is remarkably good.

In order to calculate the vibrational phonon frequencies of CaF$_2$, we employed the direct approach [3,4]. In this method, the force-constant matrix is directly calculated in real-space by considering the proportionality between the atomic displacements and forces when the former are sufficiently small. Large supercells must then be constructed in order to guarantee that the elements of the force-constant matrix have all fallen off to negligible values at their boundaries, a condition that follows from the use of periodic boundary conditions. In the present work, we employed simulation boxes larger than 216 atoms and dense $\mathbf{k}$-point grids in the calculation of the atomic forces with VASP. Computation of the nonlocal parts of the pseudopotential contributions was performed in reciprocal, rather than real, space. Once the
force-constant matrix is thus obtained, we can Fourier transform it to obtain the phonon spectrum at any \( q \) point. This step was done with the PHON code due to Alfe [5]. In using this code, we exploited the translational invariance of the system to impose the three acoustic branches to be exactly zero at the \( q \) point, and used central differences in the atomic forces (i.e., we considered positive and negative atomic displacements).

We must note, however, that convergence of the force-constant matrix elements with respect to the size of the supercell in ionic materials may be slow due to the appearance of charge dipoles and macroscopic electric fields in the limit of zero wave vector. Fortunately, long-range dipole-dipole interactions can be modeled at the harmonic level from knowledge of the atomic Born effective charge tensors and the dielectric tensor of the material [6,7].

Taking advantage of this result, Wang et al. proposed a mixed-space approach in which accurate force constants are calculated with the direct approach in real space and long-range dipole-dipole interactions with linear response theory in reciprocal space [8,9]. In the present work, we used Wang et al. mixed-space approach to calculate the vibrational phonon frequencies of CaF\(_2\) at different volumes.

In the supplemental Fig. 2, the Raman frequencies that we have measured (\( T = 300 \) K)
II. ONE-PHASE AND TWO-PHASE COEXISTENCE AB INITIO MOLECULAR DYNAMICS SIMULATIONS

Our *ab initio* molecular dynamics (AIMD) calculations were of two types: one-phase (i.e., solid and superionic phases) and two-phase coexistence (i.e., liquid and superionic phases coexisting in thermodynamic equilibrium) simulations. One-phase simulations were performed in the canonical \((N, V, T)\) ensemble while two-phase coexistence simulations in the microcanonical \((N, V, E)\) ensemble. In the \((N, V, T)\) simulations the temperature was kept fluctuating around a set-point value by using Nose-Hoover thermostats. Large simulation boxes containing 192 and 648 atoms were used in our one-phase and two-phase coexistence simulations, respectively. Periodic boundary conditions were applied along the three Cartesian directions in all the calculations. Newton’s equations of motion were integrated using the customary Verlet’s algorithm and a time-step length of \(10^{-3}\) ps. Γ-point sampling for integration within the first Brillouin zone was employed in all our AIMD simulations.

Comprehensive one-phase \((N, V, T)\) molecular dynamics simulations were carried out in order to compute the \(\alpha - \beta\) and \(\delta - \epsilon\) phase boundaries in \(\text{CaF}_2\) as a function of pressure. Calculations comprised large simulation boxes and long simulation times of up to \(~30\) ps. We systematically carried out simulations at temperature intervals of 250 K, from 1000 up to 3500 K, at each considered volume.

Following previous works \([11, 16]\), we performed comprehensive \((N, V, E)\) two-phase coexistence MD simulations in order to determine the melting curve of \(\text{CaF}_2\) at low and high pressures. Starting with a supercell containing the perfect crystal structure (i.e. either cubic fluorite or orthorhombic \(Pnma\)), we thermalize it at a temperature slightly below the expected melting temperature for about 4 ps. The system remains in a superionic state. The simulation is then halted and the positions of the atoms in one half of the supercell are held
fixed while the other half is heated up to a very high temperature (typically five times the expected melting temperature) for about 4 ps, so that it melts completely. With the fixed atoms still fixed, the molten part is rethermalized to the expected melting temperature (for about 2 ps). Finally, the fixed atoms are released, thermal velocities are assigned, and the whole system is allowed to evolve freely at constant \( (N, V, E) \) for a long time (normally more than 20 ps), so that the solid and liquid come into equilibrium. The system is monitored by calculating the average number of particles in slices of the cell taken parallel to the boundary between the solid and liquid. With this protocol, there is a certain amount of trial and error to find the overall volume which yields the coexisting solid and liquid system. An example of a successful coexistence run is shown in the supplemental Fig. 3.

III. FORMATION ENERGY OF FRENKEL PAIR DEFECTS UNDER PRESSURE

We calculated the formation energy of Frenkel pair defects (FPD) in cubic CaF\(_2\) at different pressures. We used a simulation box containing 96 atoms and a \(2 \times 2 \times 2\) Monkhorst-Pack \(k\)-point grid for integrations within the first Brillouin zone. We found that the series of calculated energies (see the supplemental Fig. 4) could be very well fitted to the power law function

\[
E_{FPD}(P) = E_0 + a \cdot P^b,
\]

where the optimal values of the parameters are \(E_0 = 2.07\) eV, \(a = 0.054\) eV and \(b = 0.851\). It is noted that the formation energy of FPD increases monotonically and appreciably with compression.

IV. CRYSTAL STRUCTURE SEARCHES

Our crystal structure searches performed in compressed CaF\(_2\) relied on two different strategies, namely (i) comprehensive atomic relaxations of configurations generated in constrained low-\(T\) AIMD runs, and (ii) enthalpy calculation of phases that have been recently observed and predicted in isomorphic AB\(_2\) compounds under pressure.

In our restricted low-\(T\) AIMD runs, we used a small simulation cell containing 24 atoms in the orthorhombic \(Pnma\) phase and set the temperature to ambient conditions. Consistently
to the observed $\gamma \rightarrow \delta$ transition, we constrained the Ca$^{2+}$ cations not to move during the dynamical simulations. The total duration of these AIMD runs was $\sim 20$ ps. Once these simulations were finished, we randomly selected 100 configurations out of 10,000 and performed atomic and crystal cell relaxations in them. During the geometry optimizations all cations and anions were allowed to move. Subsequently, we identified the crystal symmetry of the final equilibrium structures with the ISOTROPY package [17]. Following this strategy, we obtained the five candidate high-$T$ crystal phases that we mention in the main text of the present Letter (i.e., orthorhombic $P2_12_12_1$ and $Pmn2_1$, and monoclinic $Pc$, $P2_1$ and $P2_1/c$).

We also computed the energy of the post-cotunnite $P112_1/a$ and $P2_1/n$ phases in CaF$_2$ under pressure. These phases have been recently observed and predicted in bulk AuIn$_2$ and AuGa$_2$ respectively [18,19], which are isomorphic materials to CaF$_2$. By following this strategy, however, we did not find any promising high-$T$ candidate crystal phase since their corresponding enthalpies were too large in comparison to those of the crystal structures obtained with strategy (i).

V. STRUCTURAL DATA, PHONONS AND ENTHALPY OF THE PREDICTED HIGH-$T$ MONOCLINIC $P2_1/c$ PHASE

A sketch of the new high-$T$ monoclinic $P2_1/c$ phase predicted in CaF$_2$ at high-$P$ is shown in the supplemental Fig. 5. This structure has a similar cation coordination polyhedra to that of the orthorhombic $Pnma$ phase. On it each calcium is coordinated to 9 fluorine atoms that form an elongated tricapped trigonal prism. Structural data of this monoclinic phase obtained at different pressure conditions are enclosed in Table I.

We computed the phonon spectrum of this high-$T$ monoclinic phase at different pressures employing the methodology explained in this supplemental document (see Sec. I), and found that it was vibrationally and mechanically stable (see the supplemental Fig. 6).

The results of our enthalpy calculations in SrF$_2$ and BaF$_2$ compounds are enclosed in the supplemental Fig. 7. In particular, we computed the enthalpy energy of the cubic fluorite, orthorhombic $Pnma$, hexagonal $P6_3/mmc$, and monoclinic $P2_1/c$ phases in the corresponding pressure regimes of interest. As we found in CaF$_2$, the monoclinic $P2_1/c$ phase turns out to be energetically very competitive with respect to the orthorhombic $Pnma$
\[
P2_1/c \quad a = 3.347 \, \text{Å} \quad b = 6.032 \, \text{Å} \quad c = 7.477 \, \text{Å} \\
(P = 13.4 \, \text{GPa}) \quad \alpha = 90^\circ \quad \beta = 116.6^\circ \quad \gamma = 90^\circ
\]

| Atom | Wyc. | \(x\) | \(y\) | \(z\) |
|------|------|------|------|------|
| Ca   | 4e   | 0.37156 | 0.75481 | 0.12145 |
| F    | 4e   | 0.31867 | 0.14034 | 0.06867 |
| F    | 4e   | 0.08291 | 0.53005 | 0.83343 |

| Atom | Wyc. | \(x\) | \(y\) | \(z\) |
|------|------|------|------|------|
| Ca   | 4e   | 0.36963 | 0.75135 | 0.11987 |
| F    | 4e   | 0.31873 | 0.14546 | 0.06872 |
| F    | 4e   | 0.07811 | 0.52958 | 0.82824 |

**TABLE I:** [Supplemental] Structural data of the predicted high-\(T\) monoclinic \(P2_1/c\) phase calculated at different pressures. Wyckoff positions were generated with the ISOTROPY package.\textsuperscript{17}

phase, and actually under some conditions the enthalpy difference between the two phases is zero within our numerical accuracy (i.e., 3 meV/f.u.).
FIG. 3: [Supplemental](Color online) Determination of melting temperatures based on two-phase coexistence ab initio molecular dynamics simulations. Top: Atomic positions projected over the \(x-y\) plane of the simulation box. Calcium and fluorine ions are represented with large (dark blue) and small (bright blue) spheres, respectively. Bottom: Number of particles histogram represented as a function of position along the direction parallel to the initial superionic-liquid boundary.
FIG. 4: [Supplemental] Calculated formation energy of Frenkel pair defects in α-CaF$_2$ under pressure. The solid line represents a numerical fit to the series of computed points (see text).
FIG. 5: [Supplemental](Color online) Sketch of the predicted high-$T$ monoclinic $P2_1/c$ phase. Large (Blue) and small (grey) spheres represent calcium and fluorine atoms, respectively.
FIG. 6: [Supplemental] Calculated phonon spectrum of the predicted high-$T$ monoclinic $P2_1/c$ phase at different pressures.
FIG. 7: [Supplemental] Calculated enthalpy of several crystal structures referred to that of the cubic $\alpha$ phase and expressed as a function of pressure in SrF$_2$ and BaF$_2$. Inset: Detail of the enthalpy difference between the $P2_1/c$ and $Pnma$ phases.
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