

Comment on “High-pressure phases of group-II difluorides: Polymorphism and superionicity”

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Nelson *et al.* [*Phys. Rev. B* **95**, 054118 (2017)] recently reported first-principles calculations on the behavior of group-II difluorides (BeF₂, MgF₂, and CaF₂) under high-pressure and low- and high-temperature conditions. The calculations were based on *ab initio* random structure searching and the quasiharmonic approximation (QHA). Here, we point out that, despite the inestimable value of such calculations at high-pressure and low-temperature conditions, the high-*P* high-*T* phase diagram proposed by Nelson *et al.* for CaF₂ is not in qualitative agreement with the results of previous *ab initio* molecular-dynamics simulations, nor does it agree with the existing body of experimental data. Therefore, we conclude that the QHA-based approach employed by Nelson *et al.* cannot be applied reliably to the study of phase boundaries involving superionic phases. This conclusion is further corroborated by additional *ab initio* calculations performed in the superionic compounds SrF₂, BaF₂, Li₃OCl, and AgI.

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CaF₂ is an archetypal type-II fast-ion conductor in which above a particular transition temperature T_s , the fluorine ions start to diffuse through the crystal by successively hopping among neighboring interstitial sites. At low T and pressures $0 \leq P \lesssim 10$ GPa, CaF₂ adopts a cubic fluorite structure (α , space group $Fm\bar{3}m$) in which the Ca⁺² cations are cubic coordinated to the F⁻ anions; at low T and pressures $P \gtrsim 10$ GPa, CaF₂ presents an orthorhombic PbCl₂-like structure (γ , space group $Pnma$) in which the atomic coordination around the calcium ions is highly asymmetric. In a combined experimental and theoretical study [1], we proposed a high-*P* high-*T* phase diagram for CaF₂ in which two interesting pressure-induced superionic effects were observed [see Fig. 1(a)]: (i) an anomalous decrease of T_s in the interval $5 \lesssim P \lesssim 8$ GPa, and (ii) a temperature-induced phase transformation from the γ phase to an experimentally unresolved structure at $P \gtrsim 8$ GPa (δ) that becomes superionic before melting (ϵ phase). Our experiments were based on diamond-anvil-cell (DAC) measurements along with the laser speckle technique, and our calculations were based on *ab initio* molecular-dynamics (AIMD) simulations, which fully take into account anharmonic effects at $T \neq 0$ conditions.

In a recent study [2], Nelson *et al.* reported first-principles calculations on the high-*P* high-*T* phase diagram of CaF₂ based on zero-temperature random structure searching and the quasiharmonic approximation (QHA) [2]. The authors of that study proposed a new candidate structure for the high-*P* high-*T* δ phase with hexagonal symmetry [space group $P\bar{6}2m$; see Fig. 1(b)]; also, they estimate a series of high-*T* coexistence lines involving superionic phases based on the QHA. The

QHA strategy employed by Nelson *et al.* to determine normal-superionic phase coexistence lines is as follows. Initially, the zero-temperature threshold volume at which a particular crystal structure first develops imaginary phonon frequencies, V_{inst} , is determined; subsequently, given a fixed pressure point one finds the temperature at which according to the QHA the volume of the system equals V_{inst} , namely $V(P, T_c) = V_{\text{inst}}$. The series of T_c 's so obtained after considering different pressure points are then ascribed to a normal-superionic phase coexistence line. Nelson *et al.* claim that their results on the phase diagram of CaF₂ are in overall qualitative agreement with those previously reported by us in Ref. [1].

In this Comment, we show that (i) the high-*P* high-*T* CaF₂ phase diagram proposed by Nelson *et al.* is not in qualitative agreement with our previous *ab initio* molecular-dynamics results nor with our experiments, and (ii) the high-*P* high-*T* hexagonal $P\bar{6}2m$ phase proposed by Nelson *et al.* does not sustain superionicity and melts at temperatures well below the fusion line of the experimentally unresolved δ phase. Consequently, we argue that the QHA-based approach employed by Nelson *et al.* in Ref. [2] is not appropriate for the study of phase boundaries involving superionic phases (as we further demonstrate by performing first-principles calculations in archetypal superionic materials other than CaF₂).

Figure 1 shows the high-*P* high-*T* phase diagrams proposed for CaF₂ in Refs. [1] [Fig. 1(a)] and [2] [Fig. 1(b)]. A number of important quantitative and qualitative differences are obvious. First, contrary to what has been suggested by Nelson *et al.*, the solid-liquid phase boundaries in both phase diagrams are not the same; in Fig. 1(a) the slope of the solid-liquid coexistence line is not a constant. Second, Nelson *et al.* propose a phase diagram in which the two superionic phases (denoted as “S/I” in the figure) deriving from the α and hexagonal $P\bar{6}2m$ structures coexist; this is

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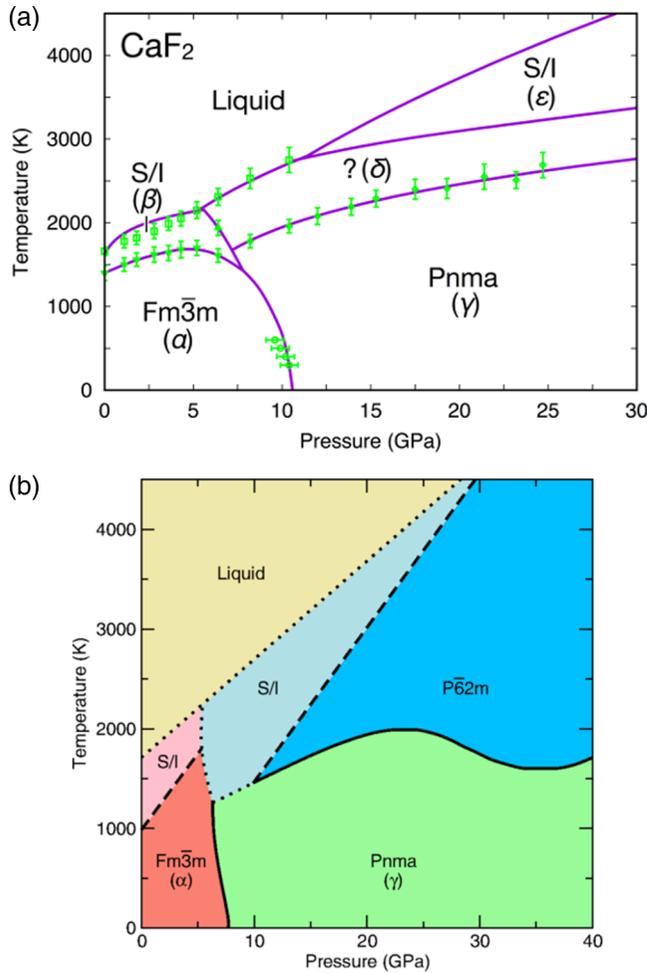


FIG. 1. High- P high- T phase diagrams proposed for CaF_2 . (a) Adapted from Ref. [1]; “S/I” stands for superionic phases, and the question mark indicates that the corresponding crystal structure has not been resolved experimentally; green dots and error bars correspond to DAC experiments [1]. (b) Adapted from Ref. [2]; the region colored in pink with the S/I label indicates that the cubic $Fm\bar{3}m$ phase develops unstable phonons; the region colored in light blue with the S/I label indicates that the hexagonal $P\bar{6}2m$ phase develops unstable phonons.

in stark contrast to the results shown in Fig. 1(a), where coexistence between superionic phases is absent. Third, the slope of the γ - $P\bar{6}2m$ coexistence line in Fig. 1(b) presents an unusual sign variation under increasing compression, which according to Clausius-Clapeyron implies a singular P -induced effect on the transition volume change (namely, $\Delta V \geq 0$ at $12 \lesssim P \lesssim 25$ GPa, $\Delta V \leq 0$ at $25 \lesssim P \lesssim 36$ GPa, and $\Delta V \geq 0$ at $P \gtrsim 36$ GPa; note that $\Delta S > 0$ independently of pressure). Such a peculiar variation of the transition volume change is not consistent with our AIMD results nor with our experimental DAC measurements reported in Ref. [1] [see the γ - δ coexistence line and green dots in Fig. 1(a)]. Fourth, the coexistence lines involving normal and superionic phases in Fig. 1(b) (dashed lines) invariably present constant, large, and positive slopes as a result of the inherent limitations of the quasiharmonic approximation; extrapolation of the S/I- $P\bar{6}2m$ coexistence

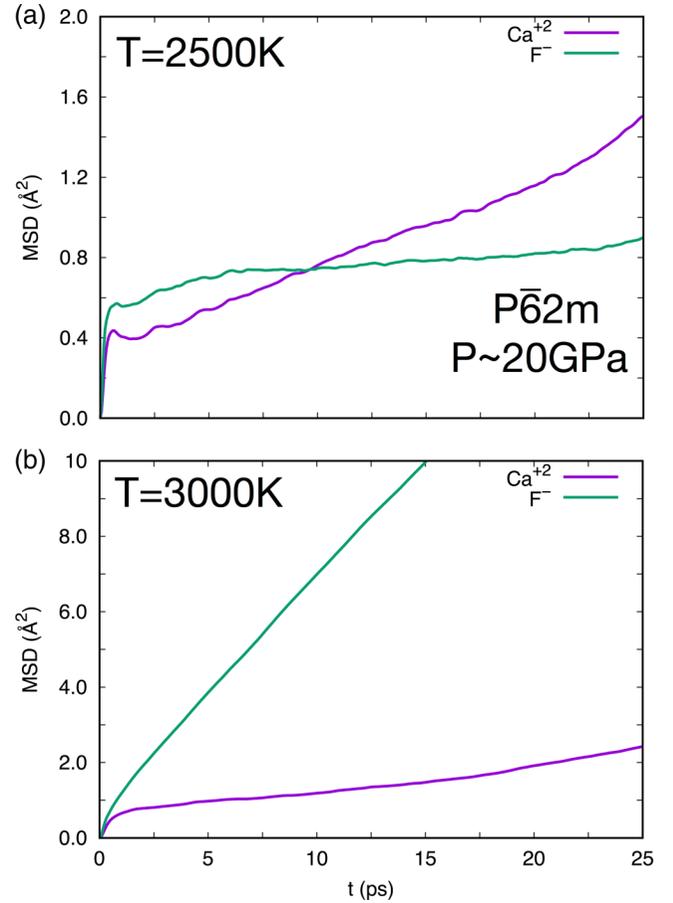


FIG. 2. Ionic mean-squared displacements calculated for CaF_2 in the hexagonal $P\bar{6}2m$ phase at $P = 20(1)$ GPa and $2500 \leq T \leq 3000$ K. The slope of the curves at long simulation times are proportional to the diffusion coefficients of the ions. (a) The sublattice of Ca^{+2} ions becomes vibrationally unstable. (b) All the ions diffuse, hence the system is a liquid.

line suggests the loss of superionicity at pressures above ~ 30 GPa. This behavior is not consistent with the results presented in Fig. 1(a), in which the equivalent phase boundaries have a less pronounced slope, and the δ - ϵ and solid-liquid coexistence lines do not intersect at around 30 GPa.

Based on *ab initio* random structure searching, Nelson *et al.* have proposed a hexagonal $P\bar{6}2m$ phase as the likely candidate for the δ phase appearing in Fig. 1(a) [2]. As has been demonstrated by Nelson *et al.*, and as we have explicitly corroborated, that structure is energetically very competitive with respect to the γ phase at high- P and zero-temperature conditions. By employing the same AIMD techniques as in Ref. [1], we have analyzed the superionic behavior and structural stability of the hexagonal $P\bar{6}2m$ phase at $T \neq 0$ conditions. In Fig. 2, we enclose the ionic mean-squared displacements [1] calculated at $P = 20(1)$ GPa and $2500 \leq T \leq 3000$ K. We find that at $T = 2500$ K the hexagonal $P\bar{6}2m$ phase becomes vibrationally unstable as the sublattice formed by Ca^{+2} atoms *melts* and the mobile cations start to diffuse through the crystal [Fig. 2(b)]; the same conclusion is reached via the computation of position correlation functions [1] (not shown here). The thermodynamic state

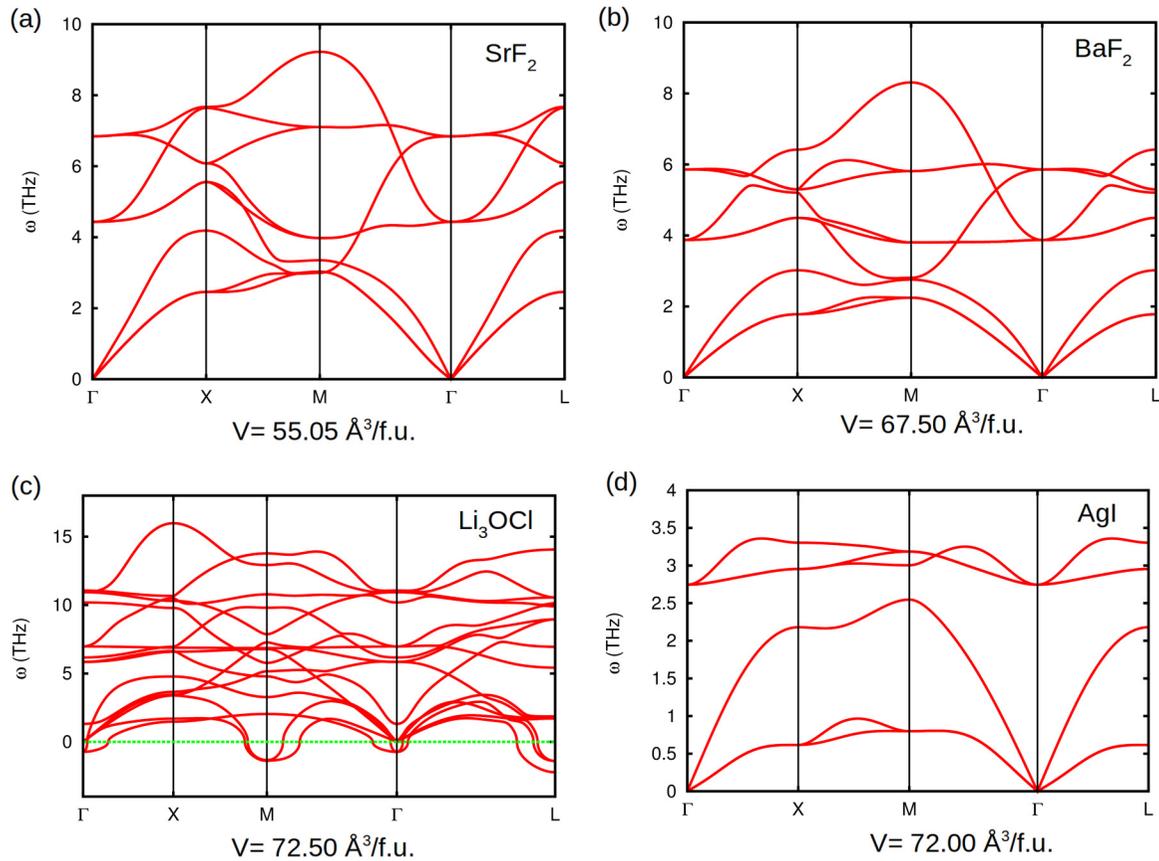


FIG. 3. Vibrational phonon spectrum calculated in several archetypal superionic materials. (a) SrF_2 considering the volume at which it becomes superionic at $P = 0$ in our AIMD simulations. (b) BaF_2 considering the volume at which it becomes superionic at $P = 0$ in our AIMD simulations. (c) Stoichiometric Li_3OCl considering a volume at which imaginary phonon frequencies appear. (d) AgI considering the volume at which it becomes superionic at $P = 0$ in our AIMD simulations.

$P = 20$ GPa and $T = 2500$ K coincides roughly with a point of the $S/I-P\bar{6}2m$ coexistence line shown in Fig. 1(b), however the observed behavior cannot be identified with superionicity as for that the F^- anions should be diffusing instead [3]. At $T = 3000$ K, we find that the $P\bar{6}2m$ phase totally melts in our one-phase AIMD simulations [as all the ions are diffusing, see Fig. 2(c)], which indicates that the corresponding melting temperature at $P = 20(1)$ GPa is very likely to lie below that point [4–6]. Since the melting temperature that we accurately calculated for the ϵ phase at $P = 20(1)$ GPa by means of two-phase coexistence AIMD simulations is noticeably above 3000 K [see Fig. 1(a)], we may conclude that the hexagonal $P\bar{6}2m$ structure is not a good candidate for either the δ or ϵ phases proposed for CaF_2 in Ref. [1]. Likewise, we conclude that the QHA-based approach employed by Nelson *et al.* is not appropriate for describing superionic CaF_2 at high temperatures due to the neglect of anharmonic effects that are inherent to fast-ion conductors (e.g., the creation of T -induced lattice defects).

To further assess the performance of the QHA-based method introduced by Nelson *et al.* in identifying normal-superionic transition points in general, we have performed additional phonon calculations and AIMD simulations in the fast-ion conductors SrF_2 , BaF_2 , Li_3OCl , and AgI . For SrF_2 and BaF_2 , the zero-pressure normal-superionic transition temperatures that we have estimated with AIMD simulations

are $T_s(0) = 1150(100)$ and $1135(100)$ K, respectively, which are in very good agreement with the available experimental data [7,8]. In Figs. 3(a) and 3(b), we show the phonon spectra calculated at the volumes corresponding to those superionic transition points; as can be appreciated therein, no imaginary phonon frequencies develop. For Li_3OCl , we have first calculated the threshold volume at which imaginary phonon frequencies begin to appear [see Fig. 3(c)]. Then, by constraining that volume, we have performed a series of AIMD simulations in which the temperature is steadily raised until reaching a completely melt state ($T \leq 1500$ K). We have observed that at such conditions the system never becomes superionic; the reason for this result is that, as is well known, superionicity only appears in nonstoichiometric Li_3OCl systems [9–11]. Finally, we have analyzed AgI where the normal-superionic phase transition is of first-order type as it has an associated large latent heat, a change of volume, and the crystal symmetry of both the cation and anion sublattices changes during the transformation [3,11,12]. Again, the phonon spectrum calculated at the volume at which the system becomes superionic at zero pressure [$T_s(0) = 400(20)$ K [3]] does not exhibit any imaginary phonon frequency [see Fig. 3(d)]. We note that in this latter case the QHA could have been expected to be valid, as the superionic transition temperature is well below the corresponding melting temperature, $T_m(0) = 840(20)$ K; however, due to the first-order character of the transformation,

superionicity cannot be identified through the analysis of unstable phonon modes.

In conclusion, we have shown that the QHA-based approach introduced by Nelson *et al.* in Ref. [2] is not appropriate to describe phase coexistence lines involving superionic phases in the high- P high- T phase diagram of CaF_2 , and in general in any superionic material. The main reasons behind such a QHA failure are the neglect of T -induced anharmonic effects, such as the creation of lattice defects, which are crucial for the stabilization of the superionic state, and the fact that the normal-superionic phase transition normally is not soft-phonon-mode driven (as exemplified by Li_3OCl and AgI). Our criticisms of the QHA approach used by Nelson *et al.* to determine superionic transition points appear to be backed also by the experimental evidence, as superionicity occurs only in very specific compounds [3] whereas the vast majority of materials present positive thermal expansions and zero-temperature

threshold volumes at which imaginary phonon frequencies develop. In addition, we have shown that the hexagonal $P\bar{6}2m$ phase proposed by Nelson *et al.* is neither superionic nor vibrationally stable at high- P high- T conditions.

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