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The role of dynamical instability in the *ab-initio* phase diagram of calcium

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In the 32-119 GPa pressure range and at room temperature, a simple cubic phase was reported for calcium in many different experiments. Standard linear response theory, both within density functional perturbation theory and frozen phonon calculations, presents dynamical instabilities for the simple cubic structure in the whole pressure range. Many other possible candidate phases, as well as several possible stabilization mechanisms for the simple cubic phase, have been proposed as the result of *ab-initio* predictions but the role of temperature on the relative stability of the different phases has not been systematically investigated. We revisit the stability of the three most important candidate phases of calcium for the intermediate pressure range and for various temperatures, taking explicitly into account thermal corrections relative to electronic as well as phononic entropy and anharmonic contributions. This corrects the discrepancies among previous theoretical results and experiments, and presents a different picture of the temperature driven phase transition, which results from dynamical anharmonic stabilization of simple cubic and destabilization of the tetragonal phase.

The past decade has seen a complete transformation of the field of high pressure materials science [1]. The systematic application of diamond anvil cell techniques to elemental solids [2, 3] has revealed that no solid is simple and even a seemingly simple metal can show an extremely complex and diverse sequence of structural phase transitions under pressure and/or temperature. The standard method for analyzing these phase transitions is the comparison of experimental results with density functional theory (DFT) calculations of the electronic and phononic free energy, in order to understand the structure, dynamics and thermodynamics. The case of calcium has proven to be a deeply challenging problem for theory. X-ray dispersion analysis [4–9] showed a series of pressure-induced structural phase transitions at room temperature, with a face centered cubic (*fcc*) structure at 0 GPa, body centered cubic (*bcc*) at 19 GPa and simple cubic (*sc*) at 33 GPa. The CaIV, CaV, CaVI and CaVIII phases have been discovered more recently [7, 8, 10, 11] with non closed-packed structures, which are not yet fully determined by experimental analysis. At least one extra phase (orthorhombic CaIII') [8, 9, 12] exists for low temperature ($T < 30$ K) and for $39 < P < 42$ GPa. A orthorhombic distorted *sc* structure (*Cmmm*) was proposed as a candidate structure for this new phase [8, 9, 12], even though a satisfactory theoretical description of this phase and of its stability properties is still missing. Very recently, doubts have been raised even in experiments regarding the structure of CaIII phase, which was claimed to be a rhombohedral distortion ($R\bar{3}m$) of the simple cubic structure in Ref. [9].

Several recent theoretical studies [12–24] have accounted for the dynamical (phonon) or thermodynamical (free energy) stability of the *sc*-Ca phase with many different methods. Standard theoretical methods completely fail to reproduce the intermediate-pressure (20-60 GPa) phase diagram [16, 19, 21, 23, 24], stabilizing

other phases instead of *sc* (cfr. supplementary information - SI) which is found to be dynamically unstable in harmonic theories [18–20]. Two distinct mechanisms were so far investigated to solve this discrepancy: (i) the inclusion of anharmonic effects in the phonon frequencies of the system either using molecular dynamics (MD) [17, 23], meta-dynamics [13], or explicitly anharmonic phonon calculations [12, 20]. These techniques can stabilize the vibrational spectrum and/or favor the free energy of one phase over another. Tse *et al.* have found that *sc*-Ca becomes stable around 200 K with dynamical fluctuations to local tetragonality [12], but the same authors exclude on experimental grounds that Ca-III' can have a tetragonal structure; (ii) the use of Quantum Monte Carlo (QMC) [23] combined with DFT-GGA MD. This corrects the electronic internal energy of *sc*-Ca, which is stabilized with respect to $I4_1/amd$ by quite large exchange-correlation effects beyond DFT, independently of entropic effects. Very recently, more attention was given to the possibility of solving the problem by the use of a hybrid functional method, using for example the PBE0 or HSE functionals [25], which can stabilize phonon frequencies for the $I4_1/amd$ phase, but phonon temperature dependence was not considered in this work.

The situation is not easy to disentangle, as the methods used vary in each study, and they are not always applied to phases other than *sc*-Ca. In some cases, the (electronic) free energy of a dynamically unstable phase was used as a reference for stability comparisons. In other cases, the ergodic convergence of MD studies can be difficult to assess, and some explicitly anharmonic methods only include lower (third and fourth) order anharmonicities [20]. A systematic study of anharmonicity for different phases, pressure and temperatures does not exist to our knowledge and the origin of the calcium phase transition to *sc* is still uncertain: is the structure favored energetically with respect to other stable phases, or is it

simply the only phase which preserves phonon and elastic stability in the medium pressure range?

In this Letter, we calculate the fully anharmonic phonon spectrum, renormalized to infinite order using the self-consistent *ab-initio* lattice dynamical (SCAILD) method [26–28], for all the relevant phases (*sc*, $I4_1/amd$, and $Cmmm$) of calcium in the pressure range from 30 to 50 GPa. This allows the first systematic and consistent comparison of both dynamical and thermodynamical stability effects among these phases. We show that dynamical instabilities are the main limiting factor for the phase diagram and that anharmonicities have opposite effects on different phases. They can have weak effects on the vibrational spectra (as for $Cmmm$) but can also stabilize (as for *sc*) or even can *destabilize* a phase (as for $I4_1/amd$) at elevated temperature. The QMC [23] reduction of the internal energy of *sc* respect to $I4_1/amd$ and $Cmmm$ is therefore not the determining factor stabilizing *sc* since $I4_1/amd$ and $Cmmm$ are dynamically unstable at room temperature and their free energies can not be compared.

The main source of discrepancy between theory and experiments is the effect of temperature on phonon frequencies. Usually, in DFT, the quasi-harmonic approximation (QHA) is employed *i.e.* the phonon frequencies are calculated in the harmonic approximation for different cell volumes. The QHA takes into account only the effect of thermal expansion since the free energy will be minimal at a different volume for each T - the temperature enters through the Bose occupation of the harmonic phonons, while other sources of anharmonicities are neglected. This picture is in principle valid when phonons do not interact, for example at low T . However, when the temperature increases, phonons undergo mutual scattering, which corresponds to the anharmonic vibrations of atoms. Anharmonicity is in general weak [29] and usually hardens unstable phonon frequencies, as the restoring forces which keep atoms in the vicinity of their equilibrium positions become progressively larger with temperature. We show below that the QHA is not reliable for any of the phases under study at higher temperatures, and explicit anharmonic contributions are key to obtain correct vibrational spectra, as was also seen for the high-temperature phonons of *bcc* metals [26].

Starting with the QHA, we first determine the electronic free energy $F_{el} = U - TS_{el}$ [30] (with U the internal energy) for different values of the cell volume for the five phases *viz.* *fcc*, *bcc*, *sc*, $I4_1/amd$, and $Cmmm$. We use the ABINIT [31] implementation of DFT and the exchange-correlation functional of Perdew-Burke-Ernzerhof [32] for the generalized gradient approximation, using both norm-conserving [33] and projector augmented wave [34] potentials (for details see SI).

The electronic Gibbs free energy $G_{el} = F_{el} + pV$ is calculated for every cell volume and the results are fitted to a second order Murnaghan equation of state [35]. The

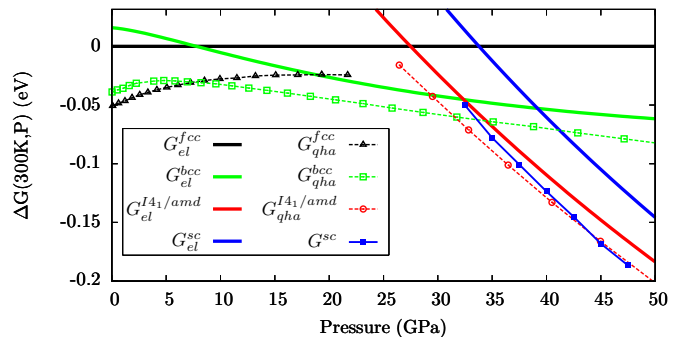


FIG. 1. (Color online) Thick lines: electronic Gibbs free energy fit at $T=300$ K of the *bcc*, *sc* and $I4_1/amd$ relative to *fcc* phase (G_{el}^{Cmmm} and G_{el}^{sc} are indistinguishable). Thin dashed lines with open symbols: harmonic total Gibbs free energy (including F_{el} and $F_{ph,qha}$) for *fcc*, *bcc* and $I4_1/amd$ in their ranges of stability. $F_{ph,qha}$ can be determined neither for *sc* nor for $Cmmm$, due to the instability of these phases in the QHA. Full line with closed squares: total Gibbs free energy for *sc* (G^{sc}) after including the anharmonically renormalized phononic contribution F_{ph} at 300 K.

electronic Gibbs free energies are shown at $T=300$ K for the five phases as thick lines in Fig. 1, with *fcc* as reference. Contributions from electronic entropy and thermal expansion give a result in agreement with previous works [16, 17]. At this level, $Cmmm$ is more stable than *sc* by about 1 meV but both have energies higher than $I4_1/amd$ by about 50 meV.

We then compute the harmonic phonon free energy and add it to the electronic Gibbs free energy to obtain the global (electron plus phonon) harmonic Gibbs free energy $G_{qha} = G_{el} + F_{ph,qha}$ as a function of pressure. We then use the same second order Murnaghan equation of state [35] to fit our results, which gives the thin dashed lines with open symbols in Fig. 1. The fit parameters are given in the SI. This approach is possible only if the phonon frequencies are stable, since the presence of imaginary modes in the vibrational spectra precludes the calculation of a free energy. In the QHA, *fcc* is stable for $P \lesssim 22$ GPa, *bcc* is stable in the whole pressure range investigated while $I4_1/amd$ is stable for $P \gtrsim 25$ GPa. The *sc* and $Cmmm$ structures are dynamically unstable in the whole 0-50 GPa pressure range, thus we can not calculate $F_{ph,qha}$: we then conclude that QHA contributions are not sufficient to correct the phase diagram, as was also found by previous authors [17, 20, 23].

Errea *et al.* [20] were the first to consider explicit anharmonic contributions in *sc*-Ca. They introduced the third and fourth order anharmonic terms of the perturbative expansion in a self-consistent harmonic approximation (SCHA). They show that the *sc* phase is stable at 50 GPa for all temperatures, even for 0 K, as a result of quantum fluctuations.

To calculate the complete phononic free energy F_{ph} we use the SCAILD method, which renormalizes phonon fre-

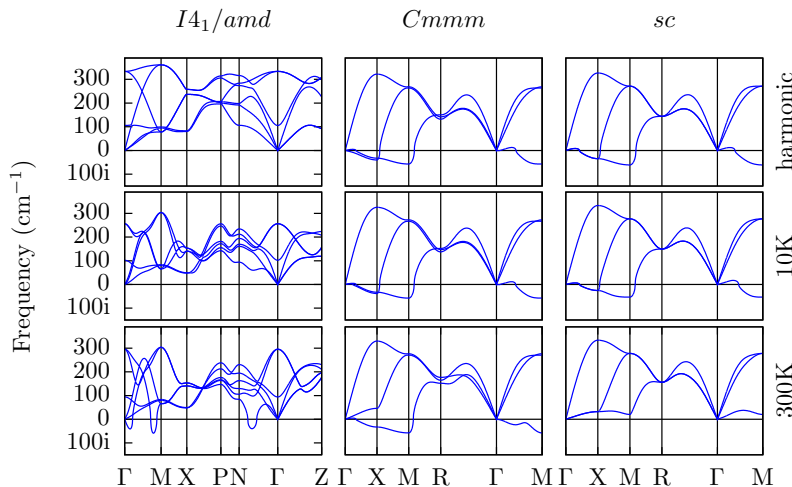


FIG. 2. (Color online) Phonon dispersion curves for $I4_1/amd$, $Cmmm$ and sc phases. Harmonic results are compared with anharmonically renormalized frequencies at finite temperature (10 K and 300 K). Anharmonic contributions destabilize $I4_1/amd$, stabilize sc and have weak effect on $Cmmm$.

frequencies self-consistently to all orders. In this scheme the harmonic and anharmonic free energy contributions are not separable, and one makes a classical approximation for the canonical displacement of the phonons. The entropy and free energy contributions are calculated using the SCAILD method as described in Ref. [28], in order to include also anharmonic contributions to the lattice potential. We add SCAILD results on top of QHA calculations for fixed pressures, in order to consider the effect of anharmonicities beyond thermal expansion, taking into account explicit phonon-phonon interactions. The phonon dispersion curves for the Ca III candidate phases are compared in Fig. 2 for $P=40$ GPa, and for $T=300$ K, 10 K, and the harmonic case. Our sc harmonic calculations are very close to linear-response calculations in the literature [18–20] and show unstable modes along the X and M directions (the stabilization of sc down to 0 K seems to be possible only with a fully quantum approach [20]). As the temperature increases, sc becomes dynamically stable in agreement with Ref. [12] and all the experimental reports. Full phononic free energy contributions can now correctly be taken into account and are included in the Gibbs free energy $G = G_{el} + F_{ph}$, leading to the full line with closed squares in Fig. 1, in which the sc phase has a phononic contribution of $F_{ph}^{sc} \simeq -60$ meV at 300 K and pressures between 32.5 and 47.5 GPa. More details on these calculations are given in the SI.

We stress that, within SCAILD, the difference between F_{ph} and $F_{ph,qha}$ is not an additive anharmonic part of the free energy, since F_{ph} is obtained from a renormalization process of all the frequencies with T .

To treat all phases on the same footing, we investigate the anharmonic contribution to the phonon frequencies of $I4_1/amd$ and $Cmmm$, and find that they have very different behaviors. $I4_1/amd$ is the only stable phase in

the harmonic approximation. Once temperature corrections are introduced, we find that it is still dynamically stable at low temperature, with a phononic free energy of about $F_{ph}^{I4_1/amd} \simeq 50.7$ meV at 10 K and 40 GPa (Fig. 2)

compared to $F_{ph,qha}^{I4_1/amd} \simeq 35$ meV in the harmonic case. We note that the value of F_{ph} can be positive or negative for a given T , as can the anharmonic correction $F_{ph} - F_{ph,qha}$, but the free energies all decrease as a function of T , as required by thermodynamics. The F_{ph} term is symptomatic of destabilization for $I4_1/amd$: a large anharmonic softening of phonon branches with temperature is present, which is particularly pronounced along the Γ -N and Γ -M directions. At $T=300$ K the $I4_1/amd$ phonon dispersion acquires imaginary segments along the directions to N and M. The midpoint between Γ and N is explicitly calculated and renormalized in our supercell, and shows a downward shift from 75 cm^{-1} for harmonic calculations to 64 cm^{-1} at 10 K and 30 cm^{-1} at 300 K. To our knowledge, this is the first time that anharmonic contributions have been shown to have this effect.

We examine the qualitative behavior of the free energy landscape for the N point of the $I4_1/amd$ phase at low and high temperature in a $2 \times 2 \times 2$ (16 atom) supercell for the first and second lowest energy modes (Fig. 3). The N point mode is frozen with amplitude η and all others sampled thermally and anharmonically (see SI). When the temperature is increased, the anharmonicity transforms the single-well low-temperature free energy profile into a triple well profile for the chosen phonons. The system is destabilized and any excitation of finite amplitude η produces a decrease of the total energy. The free energy considered here is averaged over 35 SCAILD iterations, and contains the intrinsic information about the entropy of the rest of the phonons.

In the $Cmmm$ case, anharmonicity leads to smaller

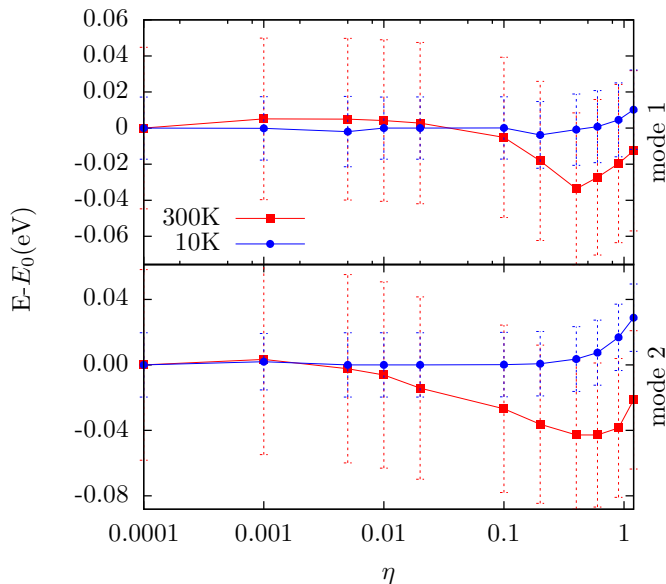


FIG. 3. (Color online) Anharmonically averaged potential energy surfaces for the two lowest energy modes of the $I4_1/amd$ phase at the N point at high and low temperature, as a function of the frozen normal mode coordinate η (unitless) - see SI. Note the log scale on the horizontal axis, and the local minimum at 300 K for extremely small displacements. The error bars show the standard deviation of the energy for the set of random displacements.

changes. Its stability range is known to be very narrow in the phase diagram [12]. In our case, $Cmmm$ is stable neither at $P=40$ GPa (up to room temperature) nor for the conditions proposed in Ref. [12] or in Ref. [8] (cfr. SI) though, again, the SCAILD method can not exclude a quantum stabilization at these very low temperatures.

Teweldeberhan *et al.* found $Cmmm$ stable for 45 GPa and 300 K with MD [23], but this observation must be tempered. They calculate the phonon frequency at high symmetry points finding the peaks in frequency of the velocity autocorrelation function. By construction, the autocorrelation function is calculated for real frequencies: it can confirm the presence of a real frequency, but not the absence of imaginary modes. The latter correspond to transient phenomena, which will not show up in the Fourier transform of an ergodic propagation. The frequency which may appear is that of the oscillation between equivalent distorted structures, if they are visited periodically. The system may also lack a reference structure with appropriate symmetry: imposing a specific cell shape can impede certain phase transitions, in particular if the cell is too small or is incommensurate with other structures (e.g. sc versus $Cmmm$). The local environment analysis carried out in Ref. [17] is more robust for identifying phases, but also depends on ergodic, size, and symmetry conditions.

In conclusion, anharmonic phonon renormalized corrections can have very different effects on the same chem-

ical element, depending on its crystalline phase. They provide crucial insights into the phase diagram of calcium and clarify both the reason for the stability of the sc phase and the mechanism behind the temperature-driven phase transitions $Ca\ III' \rightarrow Ca\ III$. Adding anharmonic corrections to the QHA, the correspondence with experiment is restored at room temperature and we show that sc is the correct structure for the CaIII phase, with a critical pressure for the $bcc \rightarrow sc$ phase transition at 300 K is of about 33.7 GPa, consistent with the experimental value (33 GPa). On the other hand, the $I4_1/amd$ destabilization is both dynamical and (as a consequence) thermodynamical. According to our calculations, the CaIII' phase can be identified with tetragonal $I4_1/amd$ at low temperature, though additional quantum effects may affect both phonons and free energies at extremely low T . Note that, given our anharmonic analysis, the dashed red line with open symbols for $I4_1/amd$ in Fig.1 does not correspond to a physical phase, and its intersections with other lines do not represent phase transitions.

Recent experiments show that the calcium phase diagram has a complicate shape: [5, 7] predict sc stable up to 119 GPa, though high pressure work suggests that sc is never fully stabilized with respect to rhombohedral distortions [9]. Alternative phases of calcium (e.g. a small sc distortion [9]) may exist between the sc and the tetragonal $P4_3$ phase [7]. Ishikawa *et al.* [36] have shown good agreement with experiment in the higher pressure region using only the enthalpy, suggesting phononic and anharmonic contributions are not dominant for $P > 70$ GPa.

Our analysis shows that sc is dynamically stable between 32.5 GPa and 47.5 GPa (in agreement with [4] - see SI). The similarity between the experimental XRD patterns of $I4_1/amd$ in [12] and the one simulated in [25], together with our results on its dynamical stability support the idea that Ca III' has indeed a $I4_1/amd$ structure. This shows that the inclusion of anharmonic effects is essential to understand the complex problem of the CaIII' phase. A fully quantum treatment of the vibrations [20] will probably be necessary clarify the low temperature part of the calcium phase diagram.

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