# Anharmonic Stabilization of the High-Pressure Simple Cubic Phase of Calcium

Ion Errea,[1,2,3] Bruno Rousseau,[2,3] and Aitor Bergara[1,2,3]

[1]*Materia Kondentsatuaren Fisika Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea,
644 Postakutxatila, 48080 Bilbao, Basque Country, Spain*
[2]*Donostia International Physics Center (DIPC), Paseo de Manuel Lardizabal 4, 20018, Donostia, Basque Country, Spain*
[3]*Centro de Física de Materiales CFM—Materials Physics Center MPC, Centro Mixto CSIC-UPV/EHU,
Edificio Korta, Avenida de Tolosa 72, 20018 Donostia, Basque Country, Spain*

The phonon spectrum of the high-pressure simple cubic phase of calcium, in the harmonic approximation, shows imaginary branches that make it mechanically unstable. In this Letter, the phonon spectrum is recalculated by using density-functional theory *ab initio* methods fully including anharmonic effects up to fourth order at 50 GPa. Considering that the perturbation theory cannot be employed with imaginary harmonic frequencies, a variational procedure based on the Gibbs-Bogoliubov inequality is used to estimate the renormalized phonon frequencies. The results show that strong quantum anharmonic effects make the imaginary phonons become positive even at zero temperature so that the simple cubic phase becomes mechanically stable, as experiments suggest. Moreover, our calculations find a superconducting $T_c$ in agreement with experiments and predict an anomalous behavior of the specific heat.

The understanding of crystal lattice vibrations in terms of phonons provides an excellent paradigm to interpret and understand a wide range of physical phenomena [1]. In most cases, the harmonic approximation describes accurately phonon frequencies and the associated physical properties. However, there are examples where experimentally confirmed structures display imaginary phonons in *ab initio* density-functional theory calculations, indicating that in such cases anharmonicity cannot be neglected. The high-pressure simple cubic (sc) phase of calcium is an important example of the possible stabilizing role of anharmonicity. Indeed, while measurements confirm the presence and stability of this structure [2–5], theoretical calculations based on the harmonic approximation find imaginary phonon branches throughout the whole Brillouin zone (BZ) [6–9].

Under pressure, calcium exhibits a complex and interesting behavior. For instance, it becomes the element with the largest superconducting critical temperature ($T_c$), reaching 25 K at 161 GPa [10]. According to room temperature x-ray diffraction measurements [2,3,11,12], the ambient condition fcc phase transforms to bcc at 19 GPa, to sc at 32 GPa, to $P4_32_12$ at 119 GPa, to $Cmca$ at 143 GPa, and to $Pnma$ at 158 GPa. Moreover, it has recently been reported that upon cooling the sc structure transforms into a very similar monoclinic $Cmmm$ phase at 30 K and 45 GPa [5]. On the other hand, evolutionary density-functional theory simulations within the generalized gradient approximation at 0 K [13] found that the experimental phases do not always coincide with the lowest enthalpy structures. This is quite dramatic in the stability range of the sc phase considering that the $I4_1/amd$ structures (from 33 to 71 GPa) and $C2/c$ structures (from 71 to

89 GPa) have considerably lower enthalpy than sc. Recent diffusion quantum Monte Carlo calculations) [9] have brought new insight to this problem, showing that the sc phase is energetically preferred over the $I4_1/amd$ phase when the exchange-correlation energy is treated correctly. Nevertheless, the question of dynamical stability remains and a proper quantum-mechanical treatment explicitly incorporating anharmonicity is still missing.

The extreme anharmonicity in sc Ca requires a non-perturbative approach and suggests the application of the self-consistent harmonic approximation (SCHA) [14,15]. The SCHA seeks the physically well-defined Gibbs-Bogoliubov bound and, in contrast to classical molecular dynamics (MD) or statistical sampling methods [16], works at any temperature with no additional cost. However, in order to apply this theory, the knowledge of all anharmonic coefficients is needed. Calculating them from first principles is usually complicated and highly time-demanding; thus, the SCHA has been normally applied by making use of empirical potentials. Nevertheless, given the simplicity and high symmetry of the sc structure, we have calculated *ab initio* all the necessary anharmonic coefficients up to fourth order in displacement. The SCHA could then be applied to compute the temperature-dependent renormalized phonon frequencies. The calculations have been performed at 50 GPa, and, as it turns out, within this formalism the phonons of sc Ca are stable even at 0 K at this pressure. Unless stated otherwise, we use atomic units throughout, i.e., $\hbar = 1$.

Within the Born-Oppenheimer approximation, the Hamiltonian describing the dynamics of the $N$ ions in the crystal is given by $\hat{H} = \hat{T} + \hat{U}$, where $\hat{T}$ and $\hat{U}$ are, respectively, the kinetic and potential energy operators of

the ions. The potential is expanded up to fourth order as $\hat{U} = \hat{U}_0 + \hat{U}_2 + \hat{U}_3 + \hat{U}_4$ with

$$\hat{U}_n = \frac{N^{1-(n/2)}}{n!} \sum_{\{\alpha\mathbf{q}\}} \hat{u}^{\alpha_1}(\mathbf{q}_1) \dots \hat{u}^{\alpha_n}(\mathbf{q}_n) \Phi^{\alpha_1 \dots \alpha_n}(\mathbf{q}_1, \dots, \mathbf{q}_n).$$

(1)

In Eq. (1), $\{\alpha\}$ represent Cartesian coordinates, $\Phi^{\alpha_1 \dots \alpha_n}(\mathbf{q}_1, \dots, \mathbf{q}_n)$ is the Fourier transform of the $n$th derivative of the total energy with respect to the ionic displacements, and $\hat{u}^{\alpha}(\mathbf{q})$ is the Fourier transform of the ionic displacement operator. In the harmonic approximation, by neglecting the third- and fourth-order terms of the potential, the Hamiltonian is diagonalized in terms of phonons. The term $\hat{U}_3 + \hat{U}_4$ can be treated within the perturbation theory to correct the phonon frequencies and account for their finite lifetime [17]. However, in sc Ca the energy has no lower bound due to the imaginary frequencies obtained in the harmonic approximation, and, therefore, one needs to treat anharmonicity beyond the perturbation theory. In the SCHA, one adds and subtracts to the potential a trial harmonic term that yields well-defined real phonon frequencies $\hat{U}_2^0$ and redefines the Hamiltonian as $\hat{H} = \hat{H}_0 + \hat{H}_1$, with $\hat{H}_0 = \hat{T} + \hat{U}_2^0$ and $\hat{H}_1 = (\hat{U}_2 - \hat{U}_2^0) + \hat{U}_3 + \hat{U}_4$. The exact free energy $F$ satisfies the Gibbs-Bogoliubov inequality

$$F \leq F_0 + \langle \hat{H}_1 \rangle_0,$$

(2)

so that the minimum of the right-hand side of Eq. (2) becomes an excellent approximation of $F$. $F_0$ and $\langle \hat{H}_1 \rangle_0$ are given as $F_0 = -\frac{1}{\beta} \ln Z$ and $\langle \hat{H}_1 \rangle_0 = \text{tr}(\hat{H}_1 e^{-\beta \hat{H}_0})/Z$, respectively, where $\beta = 1/k_B T$ and the partition function is $Z = \text{tr}(e^{-\beta \hat{H}_0})$.

The adjustable parameters that can be used for the minimization are the trial phonon frequencies $\{\Omega_{\nu\mathbf{q}}\}$ that diagonalize $\hat{H}_0$, $\nu$ being a mode index. By differentiating Eq. (2) with respect to $\Omega_{\nu\mathbf{q}}$, the equation for the trial frequencies that minimize the free energy can be obtained straightforwardly:

$$\Omega_{\nu\mathbf{q}}^2 = \omega_{\nu\mathbf{q}}^2 + 8\Omega_{\nu\mathbf{q}} j_{\nu\mathbf{q}}.$$

(3)

A numerical solution of this equation leads to the renormalized frequencies $\Omega_{\nu\mathbf{q}}$ at any temperature. In Eq. (3),

$$j_{\nu\mathbf{q}} = \frac{1}{8N} \sum_{\nu'\mathbf{q}'\{\alpha\}} \frac{\epsilon_{\nu'\mathbf{q}'}^{\alpha_1} \epsilon_{\nu'-\mathbf{q}'}^{\alpha_2} \epsilon_{\nu\mathbf{q}}^{\alpha_3} \epsilon_{\nu-\mathbf{q}}^{\alpha_4}}{4M^2 \Omega_{\nu\mathbf{q}} \Omega_{\nu'\mathbf{q}'}}$$
$$\times \Phi^{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q})[1 + 2n_B(\Omega_{\nu'\mathbf{q}'})], \quad (4)$$

$\epsilon_{\nu\mathbf{q}}$ is the phonon polarization vector, $M$ the mass of Ca, $\{\omega_{\nu\mathbf{q}}\}$ the phonon frequencies diagonalizing $\hat{U}_2$, imaginary at some $\mathbf{q}$, and $n_B$ the usual bosonic occupation factor. As can be seen, the third-order anharmonic coefficients do not contribute to $F$ at this level of approximation. It should be

noted that in the renormalization process the polarization vectors are kept fixed. This is justified for the highly symmetric sc phase, but in systems with different atoms in the unit cell polarization vectors may be used to minimize Eq. (2).

The computationally most expensive part of the method described above is the *ab initio* calculation of the fourth-order anharmonic coefficients $\{\Phi^{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q})\}$. These can be obtained by taking numerical second derivatives of dynamical matrices calculated in supercells (see, for example, Ref. [18]; the method presented there was slightly extended, given that two linearly independent real displacements must be used to generate the necessary supercells at $\mathbf{q}$ points not at the BZ edge). Such dynamical matrices were obtained by using the density-functional perturbation theory [19] as implemented in QUANTUM ESPRESSO [20] within the Perdew-Burke-Ernzerhof generalized gradient approximation [21] and making use of a 10 electron ultrasoft pseudopotential with $3s$, $3p$, and $4s$ states in the valence. A 30 Ry cutoff was used for the plane-wave basis and a $16 \times 16 \times 16$ Monkhorst-Pack $\mathbf{k}$ mesh for the BZ integrations. Phonon frequencies and anharmonic coefficients were calculated on a $4 \times 4 \times 4$ $\mathbf{q}$ grid [22], and the renormalized phonon dispersion curves were obtained by Fourier interpolation.

The strong anharmonicity in this system stabilizes all the imaginary phonon branches even at 0 K, as can be seen in Fig. 1. This is an extraordinary effect considering that, normally, anharmonic stabilization of unstable modes
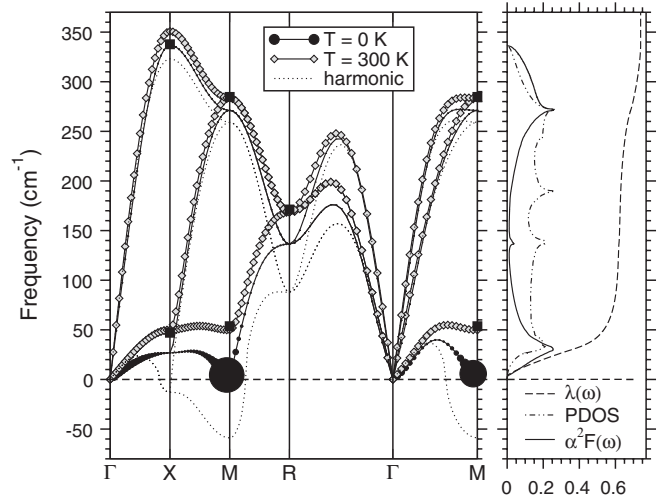


FIG. 1. (Left panel) Harmonic phonon spectra and renormalized anharmonic phonon spectra at 0 and 300 K of sc Ca at 50 GPa. For the 0 K anharmonic branches the value of the mode electron-phonon coupling $\lambda_{\nu\mathbf{q}}$ is proportional to the area of each filled circle. Filled squares depict the renormalized frequencies obtained by Teweldeberhan, Dubois, and Bonev [9] from classical MD at 300 K and 45 GPa. (Right panel) At zero temperature, the anharmonic results for the integrated electron-phonon coupling parameter $\lambda(\omega)$, the Eliashberg function $\alpha^2 F(\omega)$, and the phonon density of states (PDOS).

occurs with increasing temperature [16]. MD simulations have suggested that sc Ca may be stable at room temperature [9,23]. On the other hand, MD calculations cannot [23] predict the stabilization below the Debye temperature ($\Theta_D \sim 120$ K according to our calculations) since, as we demonstrate, sc Ca is stabilized by purely quantum anharmonic effects at 0 K. In particular, our results give 26.8 and 2.6 cm$^{-1}$ for the transverse modes, unstable in the harmonic case, at the $X$ and $M$ points, respectively. Although low-energy transverse modes show the largest renormalization, longitudinal modes also suffer a considerable anharmonic correction. As expected, phonon frequencies increase when the temperature is raised. Concretely, the temperature dependence is very strong for the transverse mode at $M$ and at $R$. At 300 K, above $\Theta_D$, our results are in close agreement with the values obtained from MD at the zone boundary by Teweldeberhan, Dubois, and Bonev [9]. Note that their calculation was performed at 45 GPa and ours at 50 GPa.

In sc Ca, as in many other cases [18,24,25], it is crucial to account for scattering between phonons with different momenta. Indeed, if we make the assumption that nondiagonal coefficients are equal to the diagonal ones in Eq. (4), $\Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q}) \sim \Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}, -\mathbf{q}, \mathbf{q}, -\mathbf{q})$, the error caused in $\Omega_{\nu\mathbf{q}}$ is quite dramatic and the temperature dependence becomes unrealistic. For example, the mode at $R$ reaches a frequency of 235.5 cm$^{-1}$ at 0 K and already 372.2 cm$^{-1}$ at 100 K, 2.6 times larger than our predicted value. At $R$ such a difference is a consequence of the huge value of the diagonal coefficients in comparison to the nondiagonal ones. As shown in Fig. 2, the importance of the diagonal anharmonic coefficients can be calculated from frozen phonon calculations. For a mode with momentum $\mathbf{q}$ at the edge of the BZ, when the atoms are displaced from their equilibrium position $\mathbf{R}$ as $\eta a \cos(\mathbf{q}\mathbf{R})\boldsymbol{\epsilon}_{\nu\mathbf{q}}$, with $a$ the lattice parameter and $\eta$ a small
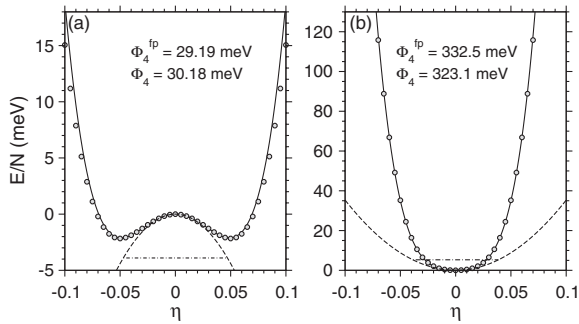


FIG. 2. Total energy per atom when the atoms are displaced along the transverse mode at $M$ (a) and $R$ (b). The dots depict the *ab initio* total energies; the solid line is the fit to the quartic potential, the dashed line the harmonic contribution, and the dash-dotted line $\frac{1}{2}\hbar\omega$. The $\Phi_{4,\nu\mathbf{q}}$ values obtained from the fit to the quartic potential, frozen phonon (fp) result, and from the differentiation of the dynamical matrices in supercells are shown.

dimensionless number, the potential is given as $E/N(\eta) = \frac{\eta^2}{2} a^2 M \omega_{\nu\mathbf{q}}^2 + \frac{\eta^4}{4!} \Phi_{4,\nu\mathbf{q}}$, with

$$\Phi_{4,\nu\mathbf{q}} = a^4 \sum_{\{\alpha\}} \epsilon_{\nu\mathbf{q}}^{\alpha_1} \epsilon_{\nu-\mathbf{q}}^{\alpha_2} \epsilon_{\nu\mathbf{q}}^{\alpha_3} \epsilon_{\nu-\mathbf{q}}^{\alpha_4} \Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}, -\mathbf{q}, \mathbf{q}, -\mathbf{q}).$$

(5)

A fit to this potential yields the frozen phonon $\Phi_{4,\nu\mathbf{q}}$ coefficient. As can be seen in Fig. 2, our values obtained by differentiating dynamical matrices in supercells are in good agreement with frozen phonon estimates.

Our method yields the whole renormalized phonon spectrum at 0 K, and, thus, we can estimate the superconducting transition temperature in sc Ca. The usual electron-phonon vertex is not modified by anharmonicity since the matrix elements of the gradient of the crystal potential are independent of the phonon frequencies [26]. Therefore, the electron-phonon coupling constant $\lambda$ can be calculated straightforwardly by using the electron-phonon matrix elements and the renormalized frequencies $\Omega_{\nu\mathbf{q}}$ at 0 K. The convergence of the electron-phonon matrix elements required a denser $80 \times 80 \times 80$ **k** grid. Integrating the Eliashberg function $\alpha^2 F(\omega)$, we obtain $\lambda = 0.74$ and $\omega_{\log} = 53$ K, leading to $T_c \simeq 2.1$ K, an estimate obtained from the Allen-Dynes modified McMillan equation [27] (we have used $\mu^* = 0.1$ for the Coulomb pseudopotential). As can be seen in Fig. 1, the greatest contributions to $\lambda$ come from the soft transverse modes which are unstable in the harmonic approximation. Indeed, the integrated electron-phonon coupling parameter $\lambda(\omega)$ reaches the value of 0.54 at 50 cm$^{-1}$ (that is, 73% of the total value of $\lambda$), so that, if it were not for these soft modes, sc Ca would superconduct only below 0.1 $\mu$K. The value calculated for $T_c$ at 50 GPa is in close agreement with the experimental 1.2 K value obtained by Okada *et al.* [28] and with the 1.7 K value obtained by extrapolating linearly the $T_c$ values measured for sc Ca at higher pressure in more recent experiments [10]. Finally, despite the strong anharmonicity, the isotope coefficient $\alpha = -\frac{d \ln T_c}{d \ln M}$ is predicted to be 0.45, close to the 0.5 value of a BCS superconductor.

The temperature-dependent renormalized frequencies $\{\Omega_{\nu\mathbf{q}}\}$ allow us to estimate the anharmonic free energy directly from Eq. (2) and the constant volume specific heat as $C_V = -T(\frac{\partial^2 F}{\partial T^2})_V$. As shown in Fig. 3, the high-temperature limit of the specific heat per atom is reduced by 17% from the classical $3k_B$ value given by the equipartition theorem. Such a reduction from the Dulong-Petit law is a sign of strong anharmonicity [29,30] and has been observed in different systems [31,32]. Moreover, the low-temperature behavior of $C_V$ is strongly modified from the $T^3$ relation of harmonic crystals. The anomalies of the specific heat are mainly driven by the temperature dependence of the phonon frequencies in $F_0$. Indeed, as depicted in Fig. 3, when the specific heat is calculated from $F_0$, assuming that the 0 K renormalized phonons are not
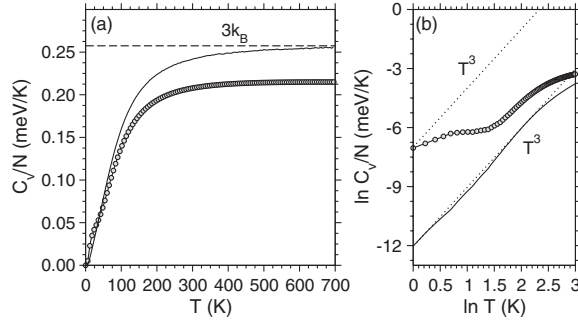
FIG. 3. (a) Constant volume specific heat per atom for the sc Ca anharmonic crystal (line with gray circles). For comparison, the specific heat calculated with the usual harmonic formula including the renormalized $\Omega_{\nu\mathbf{q}}$ frequencies at 0 K is shown (solid line). The $3k_B$ line is depicted too (dashed line). (b) Low-temperature specific heat in the logarithmic scale.

modified under temperature, the Dulong-Petit law and the low-temperature $T^3$ behavior are recovered as expected.

In summary, within the SCHA, using a variational procedure based on the Gibbs-Bogoliubov inequality, we have shown that the high-pressure sc phase of Ca is stabilized even at 0 K by strong quantum anharmonic effects. This procedure has been used in calculating fully *ab initio* the anharmonic coefficients up to fourth order in the whole BZ and may be applied as well in many cases where the phonons are imaginary or anharmonicity needs to be treated beyond the standard perturbation theory. Although below 30 K the sc phase may transform to a rather similar monoclinic *Cmmm* phase [5], which is mechanically unstable in the harmonic approximation as well and shows very similar harmonic phonons [9], we have calculated the superconducting $T_c$ of sc Ca, finding a good agreement with experiment. Moreover, the huge anharmonicity in this system makes the specific heat very anomalous with a large reduction from the high-temperature $3k_B$ limit. An experimental confirmation of this last feature would indirectly show the strong anharmonic behavior predicted.

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