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Isotope effect in the superconducting high-pressure simple cubic phase of calcium from first principles

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 UPV/EHU, 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*

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It has been recently shown [I. Errea, B. Rousseau, and A. Bergara, *Phys. Rev. Lett.* **106**, 165501 (2011)] that the phonons of the high-pressure simple cubic phase of calcium are stabilized by strong quantum anharmonic effects. This was obtained by a fully *ab initio* implementation of the self-consistent harmonic approximation including explicitly anharmonic coefficients up to fourth order. The renormalized anharmonic phonons make possible to estimate the superconducting transition temperature in this system, and a sharp agreement with experiments is found. In this work, this analysis is extended in order to study the effect of anharmonicity in the isotope effect. According to our calculations, despite the huge anharmonicity in the system, the isotope coefficient is predicted to be 0.45, close to the 0.5 value expected for a harmonic BCS superconductor. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4726161>]

I. INTRODUCTION

The study of the isotope effect on the superconducting transition temperature, T_c , has been crucial to determine the pairing mechanism of the Cooper pairs. Indeed, the success of the BCS theory in conventional superconductors, in which the pairing is due to electron-phonon interaction, was tightly related to its correct prediction of the isotope coefficient $\alpha = -\frac{d \ln T_c}{d \ln M}$, with M the atomic mass. Moreover, the analysis of the isotope effect is still a very active field in more complex superconductors such as cuprates and Fe-based high-temperature superconductors, since the role of lattice vibrations in their coupling mechanism is yet to be fully understood.^{2–9}

The value given by BCS theory for the isotope coefficient is $\alpha_{BCS} = 0.5$. In simple metals and alloys, α ranges typically between 0.2 and 0.5 in reasonable agreement with the theory. However, a negative isotope effect is found in palladium hydrides superconductors upon hydrogen isotope substitution. For instance, $T_c = 8$ K for PdH and $T_c = 10$ K for PdD (Ref. 10) yielding $\alpha = -0.32$. It is argued that as a consequence of the lightness of hydrogen and its isotopes, anharmonicity may be responsible for the inversion of the isotope effect.¹¹ Nevertheless, it is still not clear in general terms to which degree anharmonicity can affect α . Therefore, it becomes very interesting to study the isotope effect in strongly anharmonic crystals in order to see the effect of anharmonicity on α even within standard electron-phonon BCS superconductors. Thus, the study of the isotope effect in the highly anharmonic high-pressure simple cubic (sc) phase of Ca becomes extremely appealing.

Remarkably, calcium exhibits a complex and interesting behavior under pressure. It becomes the element with the largest T_c measured, reaching 25 K at 161 GPa.¹² As room temperature x-ray diffraction measurements show,^{13–16} the

face-centered-cubic (fcc) phase transforms to body-centered-cubic (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. It has recently been reported that below 30 K the sc structure transforms into a very similar monoclinic phase.¹⁷ Interestingly, the mechanical stability of the sc phase has been questioned by *ab initio* calculations, since imaginary phonon branches are found in different points of the Brillouin zone (BZ).^{18–21} Although there have been different theoretical proposals with stable phonons to substitute the sc phase,²² recent experiments provide a clear evidence that this phase is present.^{16,17} We have recently shown using the self-consistent harmonic theory (SCHA) (Refs. 23 and 24) that, when including anharmonicity fully *ab initio* up to fourth order in the calculations, the phonons of sc Ca become positive even at 0 K.¹ Therefore, it can be said that sc Ca is a quantum anharmonic crystal. Here, taking advantage of these results, we perform a thorough analysis of the isotope effect in sc Ca at 50 GPa and find that, despite the huge anharmonicity of the system, $\alpha = 0.45$, close to the BCS value.

The paper is organized as follows: In Sec. II, we describe briefly the *ab initio* application of the SCHA to sc Ca. The bulk of the results regarding the isotope effect is presented in Sec. III. A summary and the main conclusions are given in Sec. IV. Unless stated otherwise, we use atomic units throughout, i.e., $\hbar = 1$.

II. CALCULATION DETAILS

When the harmonic phonons show instabilities, anharmonicity cannot be treated in the framework of usual perturbation theory. On the other hand, variational methods such as the SCHA can provide a very efficient alternative to face the problem of anharmonicity in system with harmonic

imaginary phonons. As it is explained in Ref. 1, within the SCHA one adds and subtracts a trial harmonic term that yields well defined real phonon frequencies, $\hat{U}_0$, to the usual adiabatic Hamiltonian for the ionic motion as

$$\hat{H} = \hat{T} + \hat{U}_0 + \hat{U} - \hat{U}_0, \quad (1)$$

where $\hat{T}$ and $\hat{U}$ are the kinetic and potential energy operators for the ions, respectively. If we take $\hat{H}_0 = \hat{T} + \hat{U}_0$ as the trial Hamiltonian and $\hat{H}_1 = \hat{U} - \hat{U}_0$ as the interaction term, the exact free energy of the system satisfies the Gibbs-Bogoliubov inequality

$$F \leq F_0 + \langle \hat{H}_1 \rangle_0. \quad (2)$$

The free energy of $\hat{H}_0$ and the statistical average of $\hat{H}_1$ are given as

$$F_0 = -\frac{1}{\beta} \ln Z, \quad (3)$$

$$\langle \hat{H}_1 \rangle_0 = \text{tr}(\hat{H}_1 e^{-\beta \hat{H}_0}) / Z, \quad (4)$$

with the partition function

$$Z = \text{tr}(e^{-\beta \hat{H}_0}), \quad (5)$$

and $\beta = 1/k_B T$. Hence, the minimum of the right-hand side of Eq. (2) becomes an excellent approximation of F and sets the basis for the variational method used.

The adjustable variational parameters that can be used are the trial phonon frequencies $\{\Omega_{\nu\mathbf{q}}\}$ that diagonalize $\hat{H}_0$. If $\{\omega_{\nu\mathbf{q}}\}$ represent the phonon frequencies that diagonalize the harmonic part of $\hat{U}$, it can be shown that

$$F_0 + \langle \hat{H}_1 \rangle_0 = -\frac{1}{\beta} \sum_{\nu\mathbf{q}} \ln \left[n_B(\Omega_{\nu\mathbf{q}}) e^{\beta \Omega_{\nu\mathbf{q}} \frac{1}{2}} \right] + \sum_{\nu\mathbf{q}} \left(\frac{\omega_{\nu\mathbf{q}}^2 - \Omega_{\nu\mathbf{q}}^2}{4\Omega_{\nu\mathbf{q}}} + j_{\nu\mathbf{q}} \right) [1 + 2n_B(\Omega_{\nu\mathbf{q}})]. \quad (6)$$

Where n_B is the bosonic occupation factor and

$$j_{\nu\mathbf{q}} = \frac{1}{8N} \sum_{\nu'\mathbf{q}'} \frac{\epsilon_{\nu'\mathbf{q}'}^{\alpha_1} \epsilon_{\nu'-\mathbf{q}'}^{\alpha_2} \epsilon_{\nu'\mathbf{q}}^{\alpha_3} \epsilon_{\nu-\mathbf{q}}^{\alpha_4}}{4M^2 \Omega_{\nu\mathbf{q}} \Omega_{\nu'\mathbf{q}'}} \times \Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q}) [1 + 2n_B(\Omega_{\nu'\mathbf{q}'}). \quad (7)$$

In Eq. (7), N is the number of ions in the crystal, M the mass of Ca, $\Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q})$ the Fourier transform of the fourth derivative of the total energy with respect to the ionic displacements, $\{\alpha\}$ represent Cartesian indices, and $\epsilon_{\nu\mathbf{q}}$ is the phonon polarization vector of mode ν with momentum $\mathbf{q}$. Therefore, differentiating Eq. (6) with respect to $\Omega_{\nu\mathbf{q}}$, the equation for the trial frequencies that minimize the free energy can be obtained straightforwardly as

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

A numerical solution based on the Newton-Raphson algorithm has been used to solve this equation and obtain the

renormalized phonon frequencies $\Omega_{\nu\mathbf{q}}$. We have expanded $\hat{U}$ up to fourth order in the ionic motion so that higher order terms do not contribute to the renormalization of the frequencies at this degree of approximation. Note that during the renormalization process, the polarization vectors are not modified. This is valid for the sc phase, but in systems with different atoms in the unit cell polarization vectors may be used to minimize Eq. (6) as well.

In order to apply *ab initio* the method described above, the knowledge of the anharmonic coefficients $\{\Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q})\}$ needs to be obtained from first principles. Although computationally expensive, these can be obtained taking numerical second derivatives of dynamical matrices calculated in supercells.²⁵ The supercell needed for the calculation is caused by the distortion of a phonon mode with momentum $\mathbf{q} = \sum_i \alpha_i \mathbf{a}_i^*$ in the first Brillouin zone (1BZ), where $\mathbf{a}_i$ are the primitive lattice vectors of the sc cell and $\mathbf{a}_i^*$ those of the reciprocal lattice. There are two possibilities to build the supercell since the atoms can be shifted from their lattice $\mathbf{T}_n$ positions as $\mathbf{r}_n = \mathbf{T}_n + \mathbf{b}_n$ with the following two options for $\mathbf{b}_n$:

$$\mathbf{b}_n^A = \eta a \cos(\mathbf{q} \cdot \mathbf{T}_n) \epsilon_{\nu(\mathbf{q})}, \quad (9)$$

$$\mathbf{b}_n^B = \eta a \sin(\mathbf{q} \cdot \mathbf{T}_n) \epsilon_{\nu(\mathbf{q})}. \quad (10)$$

In Eqs. (9) and (10), a is the lattice parameter and η a dimensionless parameter that controls how much the atoms are moved from their equilibrium position. The supercell contains $N_1 \times N_2 \times N_3$ atoms at $\delta = \sum_i n_i \mathbf{a}_i$ positions with $0 \leq n_i < N_i$, n_i being an integer, and $N_i = |1/\alpha_i|$. Similarly, the 1BZ of the sc cell shrinks so that a $\mathbf{q}$ vector of 1BZ of the supercell has $N_1 \times N_2 \times N_3$ equivalent points within the 1BZ of the sc cell as $\bar{\mathbf{q}} + \bar{\mathbf{G}}$, $\bar{\mathbf{G}}$ being a reciprocal lattice vector of the supercell. From now on, symbols with a bar will belong to the supercell. Interestingly, it can be shown that the anharmonic coefficients and the second derivatives of the dynamical matrices calculated in such a supercell are related as follows:

$$\begin{aligned} \sum_{\alpha_3 \alpha_4} \Phi^{\alpha_1 \alpha_2 \alpha_3 \alpha_4}(\mathbf{q}', -\mathbf{q}', \mathbf{q}, -\mathbf{q}) \epsilon_{\nu(\mathbf{q})}^{\alpha_3} \epsilon_{\nu(\mathbf{q})}^{\alpha_4} \\ = \frac{1}{a^2} \frac{1}{N_1 N_2 N_3} \sum_{\delta_1 \delta_2} e^{-i\mathbf{q}' \cdot (\delta_1 - \delta_2)} \\ \times \frac{d^2}{d\eta^2} \left[\bar{D}_{\delta_1 \delta_2}^{\alpha_1 \alpha_2}(\bar{\mathbf{q}}, \eta; A) + \bar{D}_{\delta_1 \delta_2}^{\alpha_1 \alpha_2}(\bar{\mathbf{q}}, \eta; B) \right]. \end{aligned} \quad (11)$$

In Eq. (11), $\bar{\mathbf{q}}$ is a vector of the 1BZ of the supercell and $\mathbf{q}'$ is any vector of the 1BZ of the sc original cell related as $\bar{\mathbf{q}} + \bar{\mathbf{G}}$. Moreover, $\bar{D}_{\delta_1 \delta_2}^{\alpha_1 \alpha_2}(\bar{\mathbf{q}}, \eta; X)$ are the elements of the dynamical matrix calculated in the supercell at $\bar{\mathbf{q}}$, where $\delta_1 \delta_2$ label the atoms of the supercell. Finally, if $X = A$ the supercell is created according to Eq. (9) and if $X = B$ according to Eq. (10). The second derivative of Eq. (11) is obtained taking finite differences.

The dynamical matrices needed in Eq. (11) were obtained using density functional perturbation theory

FIG. 1. (Left panel) The anharmonic renormalized phonon spectra of different isotopes of Ca at 50 GPa in the sc structure (solid thick line) are compared to the harmonic unstable phonon dispersion (thin dotted line). (Right panel) Integrated electron-phonon coupling parameter $\lambda(\omega)$ (thin line), the phonon density of states (PDOS) (thick line), in arbitrary units, and the Eliashberg function $\alpha^2F(\omega)$ (dashed line) for the different isotopes studied.

(DFPT)²⁶ as implemented in Quantum ESPRESSO (Ref. 27) within the generalized gradient approximation (GGA) in the Perdew, Burke and Ernzerhof (PBE) parametrization.²⁸ The electron-ion interaction was modulated with 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 1BZ integrations. The size of the mesh was adapted to each supercell. Phonon frequencies and anharmonic coefficients were calculated on a $4 \times 4 \times 4$ $\mathbf{q}$ grid. At $\mathbf{q} = 2\pi/a[0.25, 0.25, 0.25]$ and symmetry related points of the mesh, the anharmonic coefficients were calculated with a coarser $\mathbf{k}$ mesh in order to reduce the very large computational cost of the method for these points. Phonon dispersion curves were obtained by Fourier interpolation. Finally, converging the double delta in the electron-phonon coupling required a finer $80 \times 80 \times 80$ mesh.

III. RESULTS AND DISCUSSION

As it was demonstrated in Ref. 1 following the method described in Sec. II, quantum anharmonic effects stabilize the phonons of the sc high-pressure phase of Ca even at 0 K. Despite the huge anharmonicity, having the whole renormalized phonon spectrum makes possible to calculate the superconducting transition temperature in this system. Indeed, the usual electron-phonon vertex is not modified by anharmonic-

ity since the matrix elements of the gradient of the crystal potential are independent of the phonon frequencies.²⁹ Therefore, the electron-phonon coupling constant λ can be calculated straightforwardly using the electron-phonon matrix elements and substituting the old unstable $\omega_{\nu\mathbf{q}}$ frequencies by the $\Omega_{\nu\mathbf{q}}$ renormalized frequencies obtained from Eq. (8). The renormalized frequencies used for the electron-phonon coupling are obtained at 0 K. Remarkably, the T_c obtained within this procedure is in good agreement with experiments.^{1,12,30} In order to estimate the isotope coefficient in T_c , we solve Eq. (8) but with the $\omega_{\nu\mathbf{q}}$ and M corresponding to a different isotope. Thus, the $\Omega_{\nu\mathbf{q}}$ frequencies are obtained for different masses and T_c can be calculated from them. We perform this procedure for ^{40}Ca , the most common isotope in nature of calcium, ^{42}Ca , ^{43}Ca , ^{44}Ca , ^{46}Ca , and ^{48}Ca isotopes.

The renormalized phonon frequencies for all these isotopes are plotted in Fig. 1. No matter what the isotope is, quantum anharmonic effects stabilize the phonons as it was already predicted for the standard ^{40}Ca isotope.¹ As can be seen, the anharmonic frequencies show the expected behavior since the heavier the isotope the lower the phonon frequencies. Although in a harmonic crystal the phonon frequencies scale according to $1/\sqrt{M}$, this is not necessarily true in the anharmonic case. Nevertheless, as shown in Table I at some high-symmetry points, the renormalized frequencies are very close to those estimated by the harmonic scaling law for all isotopes. The greatest disagreement is observed for the transverse mode at the M point, where for ^{48}Ca a 14% deviation from the $1/\sqrt{M}$ rule is estimated. This can be understood considering that anharmonic effects are crucial to stabilize the transverse mode at this point. In general, the correction is slightly larger the lighter the isotope. This fact is pointing to the intuitive idea that light atoms due to their larger mean square displacement feel the potential farther from equilibrium than heavy atoms, so that anharmonic effects are more important in their description. Finally, it is worth noting that the anharmonic renormalized frequencies are generally lower than those predicted by the mass ratio. As we shall see, this fact will be important to understand the behavior of the electron-phonon coupling parameter λ upon isotope substitution.

Within harmonic BCS theory, λ is independent of the isotope mass. The mode electron-phonon coupling, $\lambda_{\nu\mathbf{q}}$, is proportional to the electron-phonon linewidth, $\gamma_{\nu\mathbf{q}}$, and inversely proportional to the square of the phonon frequency, $\lambda_{\nu\mathbf{q}} \propto \gamma_{\nu\mathbf{q}}/\omega_{\nu\mathbf{q}}^2$. The linewidth scales as $1/M$ and, thus, $\lambda_{\nu\mathbf{q}}$ is independent of the mass. Taking the Allen-Dynes modified McMillan equation,³¹

TABLE I. $\Omega_{\nu\mathbf{q}}$ renormalized frequencies for the transverse mode at X (TX) and at M (TM), for the longitudinal mode at X (LX) and at M (LM) and the mode at R (R). Together with the renormalized frequencies $\Omega'_{\nu\mathbf{q}} = \Omega_{\nu\mathbf{q}}(^{40}\text{Ca})\sqrt{M_{40\text{Ca}}/M}$ values are given as well. Frequencies are in cm^{-1} units.

	Ω_{LX}	Ω'_{LX}	Ω_{TX}	Ω'_{TX}	Ω_{LM}	Ω'_{LM}	Ω_{TM}	Ω'_{TM}	Ω_{R}	Ω'_{R}
^{40}Ca	336.84	336.84	26.78	26.78	271.12	271.12	2.60	2.60	136.42	136.42
^{42}Ca	329.08	329.20	26.07	26.17	264.82	264.97	2.45	2.54	132.92	133.33
^{43}Ca	324.21	325.35	25.65	25.87	261.64	261.87	2.37	2.51	131.04	131.77
^{44}Ca	320.46	321.64	25.31	25.57	258.58	258.89	2.30	2.48	129.48	130.26
^{46}Ca	314.24	314.57	24.73	25.01	252.76	253.20	2.17	2.43	126.27	127.40
^{48}Ca	307.52	307.94	24.12	24.48	247.31	247.86	2.05	2.38	123.28	124.72

TABLE II. M , $\omega_{\log}$, λ , and T_c , calculated with $\mu^* = 0.1$, for different isotopes of calcium.

	M (u)	$\omega_{\log}$ (K)	λ	T_c (K)
^{40}Ca	40.078	53.35	0.740	2.11
^{42}Ca	41.959	51.89	0.737	2.04
^{43}Ca	42.959	51.09	0.739	2.02
^{44}Ca	43.955	50.34	0.741	2.01
^{46}Ca	45.953	48.88	0.746	1.97
^{48}Ca	47.952	47.54	0.750	1.94

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1 - 0.62\lambda)}\right), \quad (12)$$

we observe that within harmonic BCS theory only the logarithmic frequency average, $\omega_{\log}$, depends on the mass and, thus, T_c will decrease with higher M . Normally, $\omega_{\log}$ scales as $1/\sqrt{M}$ and $\alpha_{\text{BCS}} = 0.5$ is obtained. On the other hand, as it was explained above, the anharmonic $\Omega_{\nu\mathbf{q}}$ do not necessarily scale as $1/\sqrt{M}$ and, hence, λ can depend on the mass of an isotope. Clearly, this can affect T_c and the isotope coefficient.

Despite the strong anharmonicity in sc Ca, the value of λ is barely modified upon isotope substitution. As shown in Table II, apart from ^{40}Ca , the heavier the isotope the larger the value of λ , but the difference among all of them is tiny. The slightly larger value of λ for the standard isotope is related to the behavior of the longitudinal modes along Γ -X and XM, beyond high-symmetry points not listed in Table I. As it was pointed out above, the low-frequency transverse modes show a smaller frequency than the one expected by the $1/\sqrt{M}$ relation. Due to its low frequency, this is the mode with largest contribution to the electron-phonon coupling as noted in Fig. 1. Interestingly, when the peak in the Eliashberg function associated with this mode is integrated, $\lambda(\omega)$ reaches larger values for heavier isotopes. This is a direct consequence of the fact that the $1/\sqrt{M}$ rule overestimates the anharmonic

frequencies for the low-energy modes. Moreover, this also explains the different values obtained for λ .

The value of T_c is estimated making use of Eq. (12) and the value $\mu^* = 0.1$ for the Coulomb pseudopotential, the standard value assumed for Ca.^{1,22,32,33} Although there are some slight differences in λ as discussed above, these are not enough to strongly modify the values of T_c and its behavior is determined by the prefactor $\omega_{\log}$ in Eq. (12). Thus, as the mass is increased, $\omega_{\log}$ and T_c decrease accordingly. The values obtained in the calculation are summarized in Table II and plotted in Fig. 2. The values obtained for T_c fit very well to a linear relation and the isotope coefficient, $\alpha = -\frac{d \ln T_c}{d \ln M}$, can be estimated easily from the slope of the line. We obtain $\alpha = 0.45$, a value close to 0.5, the result expected for a harmonic BCS superconductor. Considering that, as noted in Table I, the anharmonic phonon dispersion scales close to the $1/\sqrt{M}$ relation, a value close to 0.5 is not surprising for the isotope coefficient.

IV. CONCLUSIONS

In this work, we have presented a theoretical *ab initio* study of the anharmonic phonons and the superconducting isotope effect in sc Ca at 50 GPa. It has been shown that the harmonic unstable phonons are stabilized by strong quantum anharmonic effects for all the isotopes of calcium. According to our results, the anharmonic correction is larger for lighter isotopes as they feel the more anharmonic parts of the potential farther from equilibrium. The anharmonic phonons are obtained making use of the SCHA applied fully *ab initio* including anharmonic coefficients up to fourth order. In order to estimate the anharmonic coefficients from first principles, we take numerical second derivatives of dynamical matrices calculated in supercells. Due to the variational character of the method, it may be very useful to understand different systems with unstable harmonic phonons and those in which anharmonicity needs to be treated beyond perturbation theory. Indeed, in cases where experimentally observed crystal structures show unstable phonons in DFT harmonic calculations, this method may be very efficient to overcome the apparent contradiction.

Despite the strong renormalization of the phonons due to anharmonicity, the anharmonic phonons scale close to $1/\sqrt{M}$ as in the harmonic model. Therefore, λ is very similar for all the isotopes, although it is slightly enhanced for heavier isotopes. This small effect is attributed to the fact that the $1/\sqrt{M}$ scaling overestimates the frequencies of the low-energy modes. Thus, T_c is reduced as $\omega_{\log}$ is reduced when the isotope mass is increased and an isotope coefficient of 0.45 is obtained, close to the BCS harmonic value. The prediction for the isotope effect made here may guide future experiments. Finally, our work shows that strongly anharmonic crystals do not necessarily show a very anomalous isotope effect. Nevertheless, our work does not discard the possibility of anomalies in α in anharmonic crystals. Indeed, the small changes we have observed in λ may be much larger for anharmonic crystals with lighter atoms and might induce strong anomalies in the isotope effect. This can be the case of the inverse isotope effect in palladium hydrides.

FIG. 2. Anharmonic values for T_c for different Ca isotopes at 50 GPa (a) and in logarithmic scale (b). The filled squares are the result of the calculation and the dashed red line depicts a linear fit to the data.

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