Anharmonicity and the isotope effect in superconducting lithium at high pressures: a first-principles approach

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Recent experiments have shown that lithium presents an extremely anomalous isotope effect in the 15-25 GPa pressure range. In this article we have calculated the anharmonic phonon dispersion of 7Li and 6Li under pressure, their superconducting transition temperatures, and the associated isotope effect. We have found a huge anharmonic renormalization of a transverse acoustic soft mode along ΓK in the fcc phase, the expected structure at the pressure range of interest. In fact, the anharmonic correction dynamically stabilizes the fcc phase above 25 GPa. However, we have not found any anomalous scaling of the superconducting temperature with the isotopic mass. Additionally, we have also analyzed whether the two lithium isotopes adopting different structures could explain the observed anomalous behavior. According to our enthalpy calculations including zero-point motion and anharmonicity it would not be possible in a stable regime.

I. INTRODUCTION

The strongly anomalous isotope effect recently measured in lithium in the 15-25 GPa pressure range brought this element back under the spotlight. The reported superconducting critical temperatures ($T_c$) contrast starkly with the BCS theory, where $T_c$ is expected to scale as $\propto 1/M^\alpha$, with $M$ being the atomic mass and $\alpha$ the isotope coefficient (0.5 within the BCS theory). Actually, for most phonon mediated superconductors, $\alpha$ does not deviate much from 0.5. However, the above mentioned experiment shows a highly erratic behavior of $\alpha$ as a function of pressure, with values ranging from 1 to 4 from 15 to 21 GPa, decreasing sharply between 21 and 25 GPa, where it even becomes negative, with values as low as -2.

It is just another fascinating example of the rich and exotic phenomena emerging in lithium under pressure. The lightest metal on the periodic table shows a nearly free-electron bcc structure at ambient conditions. Although it could be expected to evolve to an even more free-electron like system with increasing pressure, it has been shown that pressure not only induces several structural transformations, but also gives rise to a plethora of fascinating physical properties. For instance, lithium becomes a semiconductor near 80 GPa, it shows a maximum in the melting line and melts below ambient temperature (190 K) at around 50 GPa. It also presents one of the highest $T_c$ for an element and it is expected to display a periodic undamped plasmon. Additionally, according to a recent experiment lithium shows quantum and isotope effects in its low temperature and pressure phase transformations.

Experimental evidence shows that in the pressure and temperature ranges where the anomalous isotope effect was measured (15-25 GPa and below 30 K) lithium presents a fcc structure. At around 40 GPa, it transforms to the rhombohedral hR1 phase, which is just a distortion of the fcc phase along the c axis if one switches to a hexagonal representation. The transformation to the cubic cI16 phase occurs shortly after, at around 43 GPa.

Theoretical calculations within the harmonic approximation in fcc lithium show a highly softened transverse acoustic mode in the $\Gamma K$ high-symmetry line. Around $q_{\text{inst}} = 2\pi/a(2/3, 2/3, 0)$, where a is the lattice parameter, this anomalous mode presents a huge electron-phonon coupling, becoming a key factor to explain the high $T_c$ observed in lithium. This softening is associated to a well defined Fermi surface nesting and even yields imaginary phonon frequencies at pressures where fcc is known to be stable; the instability emerges at pressures higher than 30 GPa in the local density approximation (LDA), and at even lower pressures if one uses the generalized gradient approximation (GGA). As seen in other systems, such as simple cubic Ca, PbH the record superconductor $H_3S$ and NbSe$_2$, anharmonicity is expected to have a significant role stabilizing this structure and, due to phonon frequency renormalization, also determining its superconducting properties. As it has been measured at lower pressures of the phase diagram of lithium, zero-point vibrational energy could strongly impact the phase...
transitions of lithium in the 15-25 GPa pressure range, specially considering the small enthalpy differences between the most competitive candidates according to previous calculations\textsuperscript{4,28,29}. In fact, the anharmonic correction to the vibrational energy could be significant as well.

The origin of the observed unconventional isotope effect in high pressure lithium remains unclear. Here we consider the following two hypothesis to explain this behavior. (i) Phonon frequencies scale with the atomic mass differently as expected within the harmonic approximation. Therefore, while in the harmonic approach the electron phonon coupling constant $\lambda$ is independent of the isotopic mass, anharmonicity could make it differ from one isotope to the other, as it happens in palladium hydride\textsuperscript{24}. (ii) $^6$Li and $^7$Li isotopes adopt different crystal structures due to the significant role of the vibrational energy in the phase diagram. Experimental evidence and previous theoretical calculations claim Li adopts the fcc phase from as low as 7 GPa to as high as 40 GPa in the temperature regime where superconductivity has been measured\textsuperscript{13,5,6,9}. However, there is a considerable lack of experimental data in the mentioned region of the phase diagram and all previous calculations have been done in the static approach.

In this work we present an exhaustive analysis of the superconducting properties of fcc and c116 structures of lithium in the 15-45 GPa pressure range, with vibrational degrees of freedom treated at the anharmonic level. We also analyze the possible existence of the hR1 phase in the pressure range of interest.

II. COMPUTATIONAL DETAILS

Our density functional theory (DFT) calculations were done within the Perdew-Burke-Ernzerhof (PBE) parametrization of the GGA\textsuperscript{30}. Harmonic phonon frequencies and the electron-phonon deformation potential were calculated within density functional perturbation theory (DFPT)\textsuperscript{31} as implemented in QUANTUM ESPRESSO\textsuperscript{32}. The electron-proton interaction was considered making use of an ultrasoft pseudopotential\textsuperscript{33} which includes $1s$ and $2s$ electrons. Anharmonic calculations, including the vibrational contribution to the enthalpy, were performed using the stochastic self-consistent harmonic approximation (SSCHA)\textsuperscript{34}. Anharmonic force constant matrices of fcc lithium were obtained by calculating forces in $3 \times 3 \times 3$ supercells. Therefore, anharmonic dynamical matrices were obtained in the respective commensurate $q$-point grids and interpolated to a finer $9 \times 9 \times 9$ mesh afterwards. These were combined with DFPT electron-phonon calculations obtained in the fine $9 \times 9 \times 9$ mesh to calculate the anharmonic Eliashberg function $\alpha^2 F(\omega)$. The same procedure was used for the c116 structure, being $2 \times 2 \times 2$ and $6 \times 6 \times 6$ the coarse and fine grids respectively. The vibrational contribution to the enthalpy of hR1, which is a distortion of the fcc phase, was calculated using a $2 \times 2 \times 2$ grid for obtaining anharmonic force constant matrices and interpolating the differences with respect to the undistorted fcc structure. More details and the convergence parameters are given in the Supplementary Material.

III. RESULTS AND DISCUSSION

Fig. 1 shows the DFPT harmonic phonon dispersion of fcc $^7$Li at 26 GPa and the anharmonic corrections calculated within the SSCHA. Anharmonic force constant matrices were obtained by calculating forces in $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells. Consequently, anharmonic dynamical matrices were obtained in the respective commensu-
and quite larger than the ones by Maheswari et al. shows the superconducting critical temperature $T_c$ increases monotonically with pressure the same way $\alpha$ does, ranging from 11.2 K (10.7 K) at 15 GPa to 34.8 K (32.5 K) at 36 GPa for $^6$Li ($^7$Li). As in the case of $\alpha$, we do not see any anomalous scaling of the superconducting temperature with the isotopic mass; as it can be seen in Fig. 5, $\alpha$ is close to the conventional harmonic BCS value of 0.5 within the entire pressure range except at 15 GPa where, even though it shows a lower value, it does not, in any case, explain the experimentally observed anomalous isotope effect. Using McMillan’s formula with $\mu^*=0.22$ $T_c$ compares better with literature and experiments, even though values are still larger than in previous works due to the choice of the $\mathbf{q}$-point grid as in the case of $\lambda$ in any case, $\alpha$ does not almost change, and the conclusion remains unaltered. The overestimation of $T_c$ could also indicate that vertex corrections in the electron-phonon coupling and anisotropic effects in the Migdal-Eliashberg equations might be important. However, anisotropic ef-
fcts should not be isotope dependent and, due to the harmonic scaling of phonon frequencies, we do not expect vertex corrections to yield any anomalous isotope effect either. Therefore, we discard hypothesis (i).

After discarding that the anomalous isotope effect comes from strong anharmonicity in the fcc phase, we analyzed the possibility of the two isotopes showing different structures at the same pressure in a thermodynamically stable way. Fig. 6 shows the enthalpies of the competing phases cII6 and hR1 relative to their respective fcc ones for the two isotopes. Our static calculations, i.e. not including zero-point energy (ZPE), compare well with literature (there are no previous works including ZPE) and just show the fcc to cII6 transition. No important changes are shown for both isotopes when anharmonic ZPE is included and, although in the pressure range where this phase transition happens the enthalpy difference with the hR1 is less than 1 meV per atom, that is, roughly the same as the error one assumes when converging total energy calculations within DFT, it remains metastable. Therefore, small changes in the calculation parameters or the choice of exchange and correlation potential might cause modifications in the transition pressures and phase sequence. Accordingly, when ZPE is included the fcc to cII6 transition pressure shifts from 37 GPa to 33 GPa for both isotopes, as the enthalpy difference is reduced by around 3 meV due to lattice vibrations. Additionally, in the 21-25 GPa pressure range, where the inverse isotope effect was observed, the enthalpy difference between cII6 and fcc structures is really small (around 4-6 meV/atom). In conclusion, our results do not support hypothesis (ii) as 6Li and 7Li isotopes are not expected to adopt different stable crystal structures.

Due to the extremely small enthalpy differences metastable coexistence of phases cannot be discarded as it happens at ambient pressure for its martensitic transition. In order to see if 6Li and 7Li adopting different structures could lead to the observed anomalous isotope effect, we have also made lattice dynamics and electron-phonon coupling calculations in the cII6 structure. We do not further consider hR1 as a candidate because, according to our calculations, the local minimum in the total energy surface associated to hR1 disappears for pressures lower than 28 GPa (see Supplementary Material). In Fig. 3 we show the total electron-phonon coupling \( \lambda \) for cII6 Li at 15, 19, 27 and 44 GPa. \( \lambda \) does not vary with pressure as much as it does in the fcc phase, it

Figure 5. The isotope coefficient \( \alpha \) against pressure. Lines with symbols show the coefficients obtained for the cases in which the two isotopes adopt the same crystal structure (either cII6 or fcc). Curves without symbols show the coefficients for the cases in which the isotopes adopt different structures.
and yield values higher.

4. Physical Review calculations do not predict both isotopes can stabilize at lower pressures. Although our enthalpy calculation is quantitatively. All this agrees with the higher anharmonicity we find at 15 and 19 GPa as it yields 0.57, respectively, while it deviates considerably from 0.5, which is close to the harmonic value at 27 and 44 GPa, with \( \alpha \approx 0.42 \) and 0.57, respectively, while it deviates considerably from 0.5 at 15 and 19 GPa as it yields \( \alpha \approx 0.77 \) and 0.34, respectively. All this agrees with the higher anharmonicity we found at lower pressures. Although our enthalpy calculations do not predict both isotopes can stabilize in different structures, we have also analyzed this metastability driven hypothetical scenario: \(^6\)Li stabilizing in the fcc phase and \(^7\)Li in the cI16, and vice versa. As shown in Fig. 5, in the pressure range where the inverse isotope effect was experimentally observed (21-25 GPa), experimental values would only be qualitatively reproduced if \(^6\)Li adopted the cI16 structure while \(^7\)Li were in the fcc phase. This qualitative picture does not vary much if one uses the McMillan formula with \( \mu^* = 0.22 \), but it could notably change if we used different \( \mu^* \) values for the different phases.

IV. CONCLUSIONS

According to our calculations, even though anharmonicity is crucial to stabilize the fcc phase in lithium under pressure, its \( \lambda \) remains almost the same for both isotopes and yields a conventional scaling of \( T_\text{c} \) with isotopic mass and, therefore, it does not explain the experimentally observed anomalous isotope effect. On the other hand, including anharmonic ZPE in the enthalpy curve does not modify lithium phase diagram in the pressure range of interest, so that it is unexpected to have both isotopes in different structures. The anomalous isotope effect could only be qualitatively explained if \(^7\)Li adopted the fcc structure while \(^6\)Li adopted the cI16 one in a metastable way. All these, added to the large error bars and quite chaotic behavior of \( T_\text{c} \) with pressure in Ref. 1—with considerably different temperature values for the same pressure—puts in question the experimental observation of an anomalous isotope effect in lithium at high pressure. This way, our work encourages further research to determine the phase sequence and superconducting properties of the two stable isotopes of lithium.

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Supplementary Material

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1 Phonon spectra and electron-phonon coupling

1.1 fcc structure

Harmonic dynamical matrices of fcc Li have been obtained in a $9 \times 9 \times 9$ \( q \)-grid for every analyzed pressure and isotope. A proper convergence of phonon frequencies required a $30 \times 30 \times 30$ \( k \)-point grid and a Methfessel-Paxton smearing width of 0.01 Ry for electronic integrations in the first BZ. An energy cutoff of 65 Ry was necessary for expanding the wave-functions in the plane-wave basis. The electron-proton interaction was considered making use of an ultrasoft pseudopotential[1], in which 1s\(^2\) core electrons were also included (the same pseudopotential has been used for the whole work). In Fig. 1 we show the harmonic phonon spectra obtained at 15, 21, 26 and 36 GPa for \(^7\)Li after Fourier interpolating the dynamical matrices from the $9 \times 9 \times 9$ grid to the desired path.

Anharmonic dynamical matrices where obtained in a $3 \times 3 \times 3$ \( q \)-grid commensurate to the supercell size for our SSCHA calculations, in which we calculate forces acting on atoms. The difference between the harmonic and anharmonic dynamical matrices was interpolated to the finer $9 \times 9 \times 9$ grid, so that anharmonic dynamical matrices were obtained in $9 \times 9 \times 9$ grid after adding the harmonic dynamical matrix to the interpolation.

Electron-phonon matrix elements where calculated within DFPT, where converging the double Dirac delta in the equation for the phonon linewidth required a denser $80 \times 80 \times 80$ \( k \)-point mesh. Superconducting $T_c$ was calculated solving isotropic Migdal-Eliashberg equations considering that for large electron-phonon coupling constants McMil-
lan’s equation underestimates $T_c$. In Fig. 3a we can see how converging $T_c$ and $\lambda$ with the $q$-point grid becomes tedious due to the large contribution of $q_{\text{inst}}$ to the total electron-phonon coupling. Our chosen $9 \times 9 \times 9$ grid overestimate $T_c$ by 2.5 K comparing to the $12 \times 12 \times 12$ case while $\lambda$ is 0.2 larger. However, increasing the grid size would make the calculation really demanding and, our goal being to check whether anharmonicity could explain the anomalous isotope effect, this overestimation would only make anharmonic effects to be more visible. However, even in this case anharmonic effects are not big enough to explain the anomalous isotope effect. Moreover, we clearly see grids not containing $q_{\text{inst}}$ (dimensions not multiple of 3) yield smaller $T_c$ and $\lambda$ values that the ones they do, and using such grids would obviously neglect how anharmonicity affects the electron-phonon coupling and superconductivity.

### 1.2 CI16 structure

Harmonic dynamical matrices have been obtained in a $6 \times 6 \times 6$ $q$-grid for every analyzed pressure and isotope. A proper convergence of phonon frequencies required a $16 \times 16 \times 16$ $k$-point grid and Methfessel-Paxton smearing width of 0.01 Ry for electronic integrations.
in the first BZ. An energy cutoff of 65 Ry was necessary for expanding the wave-functions in the plane-wave basis. In Fig. 2 we show the phonon spectra obtained at 18, 27 and 44 GPa for both 6Li and 7Li after Fourier interpolating the dynamical matrices from the 6 × 6 × 6 grid to the desired path.

Anharmonic dynamical matrices where obtained in a 2 × 2 × 2 q-grid, commensurate to the supercell in which the SSCHA was performed. We interpolated the results to the finer 6 × 6 × 6 grid with the same method as in the fcc case. In this case anharmonicity has practically no influence on phonon frequencies at 27 and 44 GPa, while at 15 and 19 GPa low frequency modes are more noticeably affected. We can see this in Fig. 2 for 6Li (we do not show the result for 7Li as they are practically identical).

Converging the double Dirac delta in the equation for the phonon linewidth required a 32 × 32 × 32 k-point mesh. Superconducting Tc was calculated solving isotropic Migdal-Eliashberg equations. Converging Tc within 1 K required to calculate the electron-phonon matrix elements in a 6 × 6 × 6 q-point grid (see Fig. 3b).

The cI16 structure (Space Group I-43d) has all the Li atoms placed in the Wyckoff 16c positions (conventional coordinates (x, x, x) and all symmetry equivalent), which has a free parameter x. As the SSCHA minimization of the free energy is also performed with respect to x, final average atomic positions are different from the harmonic or static ones. In principle, one should perform the electron-phonon coupling calculations in the new anharmonic atomic positions for each isotope and pressure. However, we checked that the impact on λ and Tc for 6Li at 19 GPa, where the change in x is the greatest (Δx =0.004) is within the convergence criteria. Therefore, we use the electron-phonon coupling calculation calculated at the static equilibrium positions at each pressure for both isotopes.

Figure 3: Convergence of Tc and λ with the q-grid for Fcc and cI16 7Li, using McMillan equation and µ∗ = 0.17.
2 Enthalpy curves

For obtaining the enthalpy $H = E_T + PV$ of the different structures, we calculated each contribution to the total energy $E_T = E_{el} + E_v$ at several unit-cell volumes and fitted them separately, due to the fact that the computational cost of a data point differs significantly from one contribution to another, as electronic energy $E_{el}$ is faster to compute than the vibrational $E_v$ one.

We calculated $E_{el}$ for fcc and cI16 Li for volumes per atom ranging from 50 to 100 $a_0^3$ with a step size of approximately 1.5 $a_0^3$. We fitted the data using a Birch-Murnaghan equation of state. Due to the different properties of the phonon spectra, the vibrational contribution required a different treatment for each crystal structure. We find convenient to write the total vibrational contribution as $E_v = E_{freq} + < V - \mathcal{V}>[2]$, where $E_{freq}$ comes from the sum of the SSCHA frequencies over all the modes of the crystal and $< V - \mathcal{V}>$ comes from the difference of the actual anharmonic energy surface and the SSCHA harmonic one. $E_{freq}$ can be further splitted into the harmonic contribution and the anharmonic correction, $E_{freq} = E_{har} + E_{anh}$, where $E_{har}$ is the energy coming from the harmonic frequencies.

For cI16 calculating harmonic dynamical matrices in a $2 \times 2 \times 2$ q-grid was enough to converge $E_{har}$ within 0.5 meV/atom. We calculated $E_{har}$ at seven different volumes, from 50 to 100 $a_0^3$, and fitted a fourth order polynomial to the data points. We calculated $E_{anh}$ and $< V - \mathcal{V}>$ at four different volumes per atom (60, 70, 80 and 84 $a_0^3$) by performing SSCHA calculations in $2 \times 2 \times 2$ supercells, and fitted the data with a second order polynomial.

Fcc Li presents a more complex situation due to the anomaly in the Γ-K path. We computed $E_{har}$ using a $8 \times 8 \times 8$ grid, which does not show any imaginary frequency down to at least 65 $a_0^3$/atom (which corresponds to around 35 GPa), and converges $E_{har}$ within 0.2 meV/atom (see Fig. 4). We calculated $E_{har}$ at seven different volumes, from 50 to 100 $a_0^3$, and fitted a fourth order polynomial to the data points. To estimate
the anharmonic contribution, we performed SSCHA calculations to obtain anharmonic dynamical matrices and $<V-V>$ in a $3 \times 3 \times 3$ grid for four different volumes (66, 72, 77 and 84 $a_0^3$). To overcome the situation of using different grids for each contribution of the vibrational energy, we needed to treat $E_{an}^h$ carefully. We interpolated our anharmonic dynamical matrices from the $3 \times 3 \times 3$ grid to a finer $9 \times 9 \times 9$ one to obtain $E_{freq}$, and substracted the harmonic contribution in a $8 \times 8 \times 8$ grid as $E_{an}^h = E_{freq} - E_{har}$, as imaginary frequencies prevent us obtaining $E_{har}$ in a $9 \times 9 \times 9$ grid. Finally, we fitted these four data points with a second order polynomial.

For hR1 we have proceeded in a different way due to the fact that it shows plenty of imaginary frequencies in the harmonic phonon spectra (see Fig. 5). These imaginary frequencies are strongly renormalized by anharmonicity and become real after applying the SSCHA in a $2 \times 2 \times 2$ $q$-grid. However, the interpolation method was not useful in this case as some of the interpolated anharmonic matrices in a $6 \times 6 \times 6$ remained yielding imaginary frequencies. We overcame this situation making use of the similarity of hR1 with the fcc phase. If one chooses a rhombohedral unit cell, hR1 differs from fcc only by the rhombohedral angle $\alpha$. Thus, taking $\alpha$ and the unit cell volume $V$ as variables, we can focus our attention to their associated potential energy surface. We define the total energy as $E_T(\alpha, V) = E_{T,fcc}(V) + \Delta E(\alpha, V)$, where $E_{T,fcc}(V)$ is the total energy of the fcc phase ($\alpha = 60^\circ$) and $\Delta E(\alpha, V)$ is the difference in energy due to the change in rhombohedral angle. We only need to calculate $\Delta E(\alpha, V)$ in this case as we had previously calculated $E_{T,fcc}(V)$. $\Delta E(\alpha, V)$ is the sum of electronic and vibrational contributions. The electronic contribution $\Delta E_{el}(\alpha, V)$ is easily obtained by DFT total
Figure 6: $\Delta E(\alpha, V)$ against $\cos(\alpha)$ for different unit-cell volumes (in atomic units). In the dashed curves vibrational energy is not included.

energy calculations. For obtaining the vibrational contribution $\Delta E_v(\alpha)$ we assumed that it is independent of the unit cell volume. This way, we performed SSCHA calculations in $2 \times 2 \times 2$ supercells at four different $\cos(\alpha)$ values ($0.25, 0.35, 0.412$ and 0.5) for a single volume ($60 a_0^3$) and fitted it with a 3rd order polynomial. In Fig. 6 we show $\Delta E(V, \alpha)$ against $\alpha$ for different choices of the unit cell volume $V$, which is kept constant in each curve. Two relative minima can be distinguished below $70 a_0^3$: one at $\cos \alpha = 0.5$, which corresponds to the fcc structure, and another one corresponding to the hR1 phase, which even has a lower energy than the previous one for volumes smaller than $63 a_0^3$. Plus, the angle at which this minimum occurs increases with decreasing volume. Above $70 a_0^3$ hR1 could not exist as it lacks of a local energy minimum.

In Fig. 7 we show the pressure vs. volume curves for each isotope and structure, obtained by taking the first derivative of $E_T$ with respect to the volume.

References

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Figure 7: Pressure of fcc, c116 and hR1 Li for both isotopes. The symbols show data points in which harmonic ($E_{\text{har}}$) and anharmonic ($E_{\text{anh}}$) vibrational data has been explicitly calculated.