Inverse Isotope Effect in Palladium Hydrides Explained by the Self-Consistent Harmonic Approximation

Ion Errea\textsuperscript{1,2}, Matteo Calandra\textsuperscript{1}, and Francesco Mauri\textsuperscript{1}
\textsuperscript{1}Université Pierre et Marie Curie-Paris 6, CNRS, IMPMC-UMR7590, case 115, 4 Place Jussieu, 75252 Paris Cedex 05, France\textsuperscript{2}Ikerbasque, Basque Foundation for Science, 48011, Bilbao, Spain

Palladium hydrides display the largest isotope effect anomaly known in literature. Replacement of hydrogen in PdH with the heavier deuterium or tritium leads to higher superconducting temperatures, a behavior inconsistent with harmonic theory. Solving the self-consistent harmonic approximation by a stochastic approach, we show that the phonon spectra of palladium hydrides are strongly renormalized by anharmonic effects, far beyond the perturbative regime. We obtain the anharmonic free energy, the thermal expansion and the superconducting properties of palladium hydrides fully \textit{ab initio}. We show that superconductivity is phonon mediated and we explain the inverse isotope effect, obtaining a -0.38 value for the isotope coefficient in good agreement with experiments. Our work demonstrates that hydrogen anharmonicity is the main responsible for the isotope anomaly in palladium hydrides and provides a non-perturbative framework to investigate strongly anharmonic systems.

PACS numbers: 74.20.Pq,63.20.Ry,74.25.Kc

The explanation of the ion-mass isotope effect in phonon-mediated superconductors is one of the greatest success of BCS theory [1]. In a BCS superconductor composed of only one type of ions of mass \(M\), the superconducting critical temperature (\(T_c\)) is expected to behave as \(T_c \propto M^{-\alpha}\), where \(\alpha = 0.5\) is the isotope coefficient. In conventional superconductors with more atomic species, the total isotope coefficient should also be close to 0.5. However, in many superconductors like MgB\(_2\) (\(\alpha = 0.32\)) [2], fullerides (\(\alpha = 0.21\) for Rb\(_3\)C\(_{60}\)) [3] or high-\(T_c\) cuprates [4–6] the isotope coefficient is substantially reduced and, in the most extreme case of palladium hydrides (PH), it is even negative [7–9].

In a phonon-mediated superconductor, an isotope effect coefficient \(\alpha = 0.5\) relies on the following assumptions: (i) the phonon frequencies are harmonic, consequently, (ii) the electron-phonon interaction is mass independent, and (iii) the electron-electron interaction is not affected by the isotope substitution. Thus, a reduced isotope effect can either be the fingerprint of a non-conventional mechanism (e.g. spin-fluctuations or correlated superconductivity) or the breakdown of one of these assumptions (e.g. anharmonicity). In both cases, the superconducting state is considered anomalous and current state-of-the-art calculations do not quantitatively account for the behavior of \(T_c\) as a function of the isotope mass. This is due to the difficulties of dealing either with non-conventional mechanisms or with anharmonic effects.

Here we consider the most pathological case present in literature, namely the inverse isotope effect in PH. PdH has \(T_c = 8\) – 9K [7, 8]. Hydrogen substitution with the \textit{heavier} deuterium leads to a \textit{higher} \(T_c\), as \(T_c(\text{PdD}) \approx 10\) – 11K [7, 8], leading to \(\alpha = -\ln T_c(\text{PdD}) - \ln T_c(\text{PdH})/\ln 2 \approx -0.3\). Remarkably, PdT has a higher \(T_c\) than PdD, but there is no experimental value at full stoichiometry [9]. A considerable theoretical and experimental effort [7–21] has been devoted to explain this phenomenon over the last decades and explanations based on electronic properties [16], zero-point motion [21], volume effects [20] and anharmonicity [19] have been invoked. Inelastic neutron scattering experiments [14] show strongly temperature dependent phonon lifetimes, a clear fingerprint of anharmonicity. Furthermore, \textit{ab initio} total energy calculations [18, 19] suggest that the potential felt by the hydrogen atoms is very anharmonic. Nevertheless, no state-of-the-art calculations of the electron-phonon interaction and anharmonicity are present in literature so that the interplay of these effects is still unclear.

In this work we study the occurrence of phonon-mediated superconductivity in PH. We show that anharmonicity is so large that perturbative approaches [22, 23] are not feasible. To solve this issue, we implement the self-consistent harmonic approximation (SCHA) [24] within a first-principles approach. Differently from other methods developed to deal with anharmonic effects [25–27], our method allows to access directly the free energy of the system and is variational in the free energy with respect to the trial harmonic potential. Moreover, compared to other implementations of the SCHA [28, 29], we replace the cumbersome calculation of anharmonic coefficients by the evaluation of atomic forces on supercells with suitably chosen stochastic ionic configurations. We apply the method to PH and show that the inverse isotope effect is quantitatively explained by the inclusion of anharmonicity.

The ionic Hamiltonian is \(\hat{H} = \hat{T} + \hat{V}\), where \(\hat{T}\) and \(\hat{V}\) are the kinetic and potential energy operators. Then, the free energy of the ionic system can be calculated as \(F_\text{H} = -\frac{1}{\beta} \ln Z_\text{H}\), where the partition function is \(Z_\text{H} = \text{tr}[e^{-\beta \hat{H}}]\).
In particular, terms of the phonon frequencies and polarizations \([30]\).

The free energy can be established for an arbitrary trial configuration. The equality holds for \(\hat{E}\) where \(\rho\) is the probability to be in a general \(R\) representing the phonon frequencies and polarizations. This is accomplished by calculating \(F_H[\hat{H}]\) and its gradient \(\nabla F_H[\hat{H}]\) with respect to \(C\), and performing a conjugate-gradient minimization. Both \(F_H[\hat{H}]\) and \(\nabla F_H[\hat{H}]\) are calculated stochastically making use of importance sampling and reweighting techniques. We create a set of \(\{R_i\}_{i=1,...,N_c}\) ionic configurations in a supercell according to the \(\rho_H(\hat{R}_i)\) distribution of the starting trial \(\hat{H}_0\) Hamiltonian \([32]\). At a given step \(j\) of the conjugate-gradient minimization, the trial free energy is stochastically approximated as

\[
F_H[\hat{H}_j] \approx F_H + \frac{1}{N_c} \sum_{i=1}^{N_c} \left[ V(\hat{R}_i) - V(\hat{R}_j) \right] \rho_H(\hat{R}_i) \rho_H(\hat{R}_j),
\]

where \(V(\hat{R}_i)\) is the total energy of the supercell of the \(I\)-th configuration. Interestingly, the gradient can also be approximated from the knowledge of the forces on the atoms in the supercell at the configurations \(\{R_i\}_{i=1,...,N_c}\), which require a negligible additional effort in a total energy calculation \([33]\). Namely

\[
\nabla F_H[\hat{H}_j] \approx - \frac{1}{N_c} \sum_{\alpha\beta\mu} \sqrt{\frac{M_{\alpha}}{M_s}} \left( \epsilon_{\mu\hat{H}_j} \nabla \ln a_{\alpha \beta \mu} + \nabla \epsilon_{\mu\hat{H}_j} \right) \epsilon_{\mu\hat{H}_j} \times \frac{1}{N_c} \sum_{i=1}^{N_c} \left[ f_s^{\alpha\beta}(\hat{R}_i) - f_s^{\alpha\beta}(\hat{R}_j) \right] \rho_H(\hat{R}_i) \rho_H(\hat{R}_j),
\]

where \(f_s^{\alpha\beta}(\hat{R}_i)\) is the force on the \(s\)-th atom of the supercell along \(\alpha\) of the \(I\)-th configuration and \(f_s^{\alpha\beta}(\hat{R}_j)\) is the same force derived from \(\hat{V}_j\). Eqs. (3) and (4) show that with the reweighting procedure the need of new force and total energy calculations at each conjugate-gradient iteration step \(j\) is avoided. Nevertheless, if \(\frac{1}{N_c} \sum_{i=1}^{N_c} \rho_H(\hat{R}_i) / \rho_H(\hat{R}_j)\) deviates substantially from one, \(F_H[\hat{H}_j]\) and \(\nabla F_H[\hat{H}_j]\) cannot be accurately evaluated anymore. When this occurs, we use the probability distribution of the current step, \(\rho_H(\hat{R}_i)\), to create a new set of configurations for which we recompute atomic forces and total energies to be used in the present and subsequent conjugate-gradient iterations. The process continues till the gradient vanishes. In the rock-salt structure of \(PH\) the equilibrium \(\hat{R}_{eq}\) coordinates are fixed by symmetry, but, if it were not the case, \(F_H[\hat{H}]\) could be minimized as well with respect to them \([32]\).

We apply this method to stoichiometric PdH, PdD and PdT at several temperatures and volumes. Total energies, atomic forces, harmonic phonons and electron-phonon coefficients are computed with density-functional theory (DFT) and linear response \([33, 34]\). We use the Perdew-Zunger local-density approximation \([35]\) and ultrasoft pseudopotentials \([36]\).

We first demonstrate the capability of our developed method to obtain the free energy as a function of temperature. We calculate \(F_H[\hat{H}]\) and \(\nabla F_H[\hat{H}]\) from a model potential combining the \(ab\ initio\) harmonic potential with a fourth-order on-site anharmonic potential fitted to the DFT total energies \([37]\). The potential satisfies the symmetries of the rock-salt structure \([18]\) and

\[
\text{FIG. 1. (Color online) Equilibrium lattice parameters as a function of temperature for PdH, PdD and PdT compared to experimental results \([12, 20]\). In the inset the calculated thermal expansion coefficients are shown together with the measured values in Ref. \([31]\).}
\]
allows us to estimate the free energy at several volumes and temperatures very efficiently. Minimizing the free energy we obtain the lattice parameter of each isotope as a function of temperature. As it can be observed in Fig. 1, the absolute values of the lattice parameters and the thermal expansion coefficients are in good agreement with measurements [12, 20, 31]. The differences among isotopes in the thermal expansion coefficients are due to the different thermal population of the optical modes that are softer for heavier isotopes, leading to an increased population of the mode as a function of the isotope mass at fixed temperature.

Having determined the equilibrium volumes of PH, we overcome the approximation of a model potential by calculating the forces on the \( \{ R_i \}_{i=1,\ldots,N} \) configurations completely from first principles when determining phonon dispersions [37]. The results are shown in Fig. 2 and compared with available experimental data on deuterium and tritium deficient samples. The breakdown of the harmonic approximation is evident in all systems, particularly in PdH and PdD displaying imaginary phonon frequencies. The anharmonic correction given by the SSCHA is larger than the harmonic phonon frequency itself, invalidating any possible perturbative approach. Interestingly, both the low-energy acoustic and high-energy optical modes are affected by anharmonicity even if the largest correction involves the H-character optical modes. At zone center the PdH optical modes are degenerate at 488 cm\(^{-1}\), in good agreement with the main peak found in inelastic neutron and Raman experiments [10–13] (around 450-472 cm\(^{-1}\) at different temperatures and hydrogen concentrations).

From the calculated phonon spectra we obtain the Eliashberg function as

\[
\alpha^2 F(\omega) = \frac{1}{N(0)N_k N_q} \sum_{q_{\text{config}}} \sum_{\alpha \beta} \frac{\epsilon_{\alpha}(\mathbf{q})^* \epsilon_{\beta}(\mathbf{q})}{2\omega_{\mu}(\mathbf{q}) \sqrt{M_k M_l}} \\
 \times \delta_{\alpha \beta}^{\text{E}} d_{\mathbf{k}_n, \mathbf{k}+\mathbf{q}m}^{\text{E}, \mathbf{q}m} d_{\mathbf{k}_n, \mathbf{k}+\mathbf{q}m}^{\text{E}, \mathbf{q}m} \delta(\epsilon_{\mathbf{k}_n}) \delta(\epsilon_{\mathbf{k}_n+\mathbf{q}m}) \delta(\omega - \omega_{\mu}(\mathbf{q})),
\]

where \( d_{\mathbf{k}_n, \mathbf{k}+\mathbf{q}m}^{\alpha} = (\mathbf{k}_n | \delta V / \delta u^{\alpha}(\mathbf{q}) | \mathbf{k}+\mathbf{q}m) \) is the deformation potential, \( |\mathbf{k}_n\rangle \) is a Kohn-Sham state with energy \( \epsilon_{\mathbf{k}_n} \) measured from the Fermi level \( (\epsilon_F) \), \( N_k \) and \( N_q \) are the number of electron and phonon momentum points used for the Brillouin-zone (BZ) sampling, and \( N(0) \) is the density of states per spin at \( \epsilon_F \). Polarization vectors are given in Fourier space. The Eliashberg function can be calculated in the harmonic or anharmonic case if the harmonic or SSCHA phonon frequencies and polarizations are used in Eq. (5). The electron-phonon coupling constant \( \lambda \), as well as the logarithmic frequency average \( \omega_{\log} \), can be calculated from \( \alpha^2 F(\omega) \). We estimate \( T_c \) from the solution of the single-band Migdal-Eliashberg equations, using \( \mu^* = 0.085 \) as calculated by Klein et al. [17]. In the harmonic approximation the equilibrium volume of PdT is used for all isotopes as, in this case, there are no imaginary phonons. The Eliashberg functions are shown in Fig. 3 and the results for \( T_c \) are pre-
\[ \alpha F(\omega), \lambda(\omega) \]

The harmonic approximation strongly overestimates \( T_c \) to the BCS 0.5 value. The harmonic approximation overestimates the fluctuations of the zero-point motion. This makes \( T_c \) mass-dependent and larger the heavier the isotope. Remarkably, the differences in \( \alpha \) explain the inverse isotope effect in \( T_c \) and the value we obtain for the isotope coefficient \( \alpha \) is in good agreement with experiments (see Table I). The obtained \( T_c \) 's are close to experimental results even if no anharmonic corrections were incorporated into the deformation potential. As noted by \( \alpha^2 F(\omega) \) and the integrated electron-phonon coupling \( \lambda(\omega) \) in Fig. 3, H-character optical modes have the largest contribution to \( \lambda \), between 75% and 79% of the total depending on the isotope. The contribution of the low-energy Pd-character acoustic modes is practically the same for the three hydrides. Therefore, we can conclude that superconductivity and the inverse isotope effect in PH is driven by hydrogen anharmonicity.

In summary, we present a stochastic implementation of the SCHA that allows us to treat anharmonic effects in the non-perturbative regime. The method gives access directly to the free energy of the system and is variational in the free energy with respect to a trial harmonic Hamiltonian. The method is applied to PH calculating the free energy, the thermal expansion, the anharmonic phonon spectra and the superconducting properties. We demonstrate that superconductivity in PH is phonon-mediated and the anomalous inverse isotope effect is due to the large anharmonicity of hydrogen vibrations. Our findings open new perspectives in the interpretation of reduced isotope effects in superconductors. More generally, our methodological developments will allow to investigate strongly anharmonic systems in the non-perturbative regime, ranging from ferroelectrics [38], charge-density wave systems [39], high-pressure materials [40] and many more.

The authors are grateful to A. Bergara for fruitful discussions. I.E. would like to acknowledge financial support from the Department of Education, Language policy and Culture of the Basque Government (Grant No. BFI-2011-65). Computer facilities were provided by CINES, CCRT and IDRIS.

\[ [1] \text{J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).} \]
\[ [2] \text{D. G. Hinks, C. H., and J. D. Jorgensen, Nature 411,} \]
\[ [3] \text{C. H. and J. D. Jorgensen, Nature 411,} \]
457 (2001).

[3] M. S. Fuhrer, K. Cherrey, A. Zettl, M. L. Cohen, and V. H. Crespi, Phys. Rev. Lett. 83, 404 (1999).

[4] D. G. Hinks, H. Claus, and J. D. Jorgensen, Nature 457, 457 (2001).

[5] B. Batlogg, R. J. Cava, A. Jayaraman, R. B. van Dover, G. A. Kourouklis, S. Sunshine, D. W. Murphy, L. W. Rupp, H. S. Chen, A. White, K. T. Short, A. M. Mujic, and E. A. Rietman, Phys. Rev. Lett. 58, 2333 (1987).

[6] R. H. Liu, T. Wu, G. Wu, H. Chen, X. F. Wang, Y. L. Xie, J. J. Ying, Y. J. Yan, Q. J. Li, B. C. Shi, W. S. Chu, Z. Y. Wu, and X. H. Chen, Nature 459, 64 (2009).

[7] B. Stritzker and W. Buckel, Zeitschrift für Physik 257, 1 (1972).

[8] J. E. Schirber and C. J. M. Northrup, Phys. Rev. B 10, 3818 (1974).

[9] J. E. Schirber, J. M. Mintz, and W. Wall, Solid State Communications 52, 837 (1984).

[10] A. Kolesnikov, I. Natkaniec, V. Antonov, I. Belash, V. Fedotov, J. Krawczyk, J. Mayer, and E. Ponyatovsky, Physica B: Condensed Matter 174, 257 (1991).

[11] R. Sherman, H. K. Birnbaum, J. A. Holy, and M. V. Klein, Physics Letters A 62, 353 (1977).

[12] D. K. Ross, V. E. Antonov, E. L. Bokhenkov, A. I. Kolesnikov, E. G. Ponyatovsky, and J. Tomkinson, Phys. Rev. B 58, 2591 (1998).

[13] M. Chowdhury and D. Ross, Solid State Communications 13, 229 (1973).

[14] J. M. Rowe, J. J. Rush, H. G. Smith, M. Mostoller, and H. E. Flotow, Phys. Rev. Lett. 33, 1207 (1974).

[15] J. M. Rowe, J. J. Rush, J. E. Schirber, and J. M. Mintz, Phys. Rev. Lett. 57, 2955 (1986).

[16] B. Monserrat, N. D. Drummond, and R. J. Needs, Phys. Rev. B 33, 1072 (1981).

[17] O. Hellman, I. A. Abrikosov, and S. I. Simak, Phys. Rev. B 57, 144302 (2013).

[18] I. Errea, B. Rousseau, and A. Bergara, Journal of Applied Physics 111, 112604 (2012).

[19] S. Rossano, F. Mauri, C. J. Pickard, and I. Farnan, The Journal of Physical Chemistry B 109, 7245 (2005).

[20] J. E. Schirber and C. J. M. Northrup, Phys. Rev. B 10, 3818 (1974).

[21] J. E. Schirber, J. M. Mintz, and W. Wall, Solid State Communications 52, 837 (1984).

[22] P. Jena, J. Jones, and R. M. Nieminen, Phys. Rev. B 29, 4140 (1984).

[23] L. Paulatto, F. Mauri, and M. Lazzeri, “Anharmonic properties from a generalized third order ab initio approach: theory and applications to graphite and graphene.” (2013), preprint arXiv:1304.2626.

[24] D. J. Hooton, Philosophical Magazine Series 7 46, 422 (1955).

[25] P. Souvatzis, O. Eriksson, M. I. Katsnelson, and S. P. Rudin, Phys. Rev. Lett. 100, 095901 (2008).

[26] V. H. Crespi, Phys. Rev. Lett. 457 (2001).

[27] B. M. Klein and R. E. Cohen, Phys. Rev. B 62, 353 (1977).

[28] I. Errea, A. Y. Jia, and A. Bergara, Phys. Rev. Lett. 106, 165501 (2011).

[29] I. Errea, B. Rousseau, and A. Bergara, Journal of Applied Physics 111, 112604 (2012).

[30] S. Rossano, F. Mauri, C. J. Pickard, and I. Farnan, The Journal of Physical Chemistry B 109, 7245 (2005).

[31] R. Abbenseth and H. Wipf, Journal of Physics: Condensed Matter 21, 395502 (2009).

[32] J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[33] Calculations are performed applying the QUANTUM-ESPRESSO [34] code. A 50 Ry cutoff is used for the plane-wave basis and a $24 \times 24 \times 24$ mesh for the BZ integrations in the unit cell. The sum over $k$ in Eq. (5) required a $72 \times 72 \times 72$ grid.

[34] Total energies and forces needed in Eqs. (3) and (4) are computed in a $2 \times 2 \times 2$ supercell containing 16 atoms. The difference between the SSCHA force constant matrix and the harmonic force constant matrix in the $2 \times 2 \times 2$ supercell is interpolated to a $4 \times 4 \times 4$ supercell. The harmonic $4 \times 4 \times 4$ force constant matrix is added to the result. We verified that the anharmonic phonon dispersion obtained for the model potential in this way coincides with that obtained directly in a $4 \times 4 \times 4$ supercell. We use $N_c = 20000$ and $N_c = 300$ for the calculations with the model and $ab$ initio potential, respectively. For the $ab$ initio calculation a single set of $\{R_i\}_{i=1,...,N_c}$ is sufficient if the result of the model potential is used as $\hat{H}_0$.

[35] W. Zhong, D. Vanderbilt, and K. M. Rabe, Phys. Rev. B 52, 6301 (1995).

[36] G. Gr"uner, Density Waves in Solids (Addison-Wesley, Reading, MA, 1994).

[37] D. Y. Kim, R. H. Scheicher, H.-k. Mao, T. W. Kang, and R. Ahuja, Proc. Natl. Acad. Sci. USA 107, 2793 (2010).