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Anharmonicity and the inverse isotope effect in the palladium-hydrogen system

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We have used the full-potential linearized-augmented-plane-wave (LAPW) method to perform electronic-structure calculations for the palladium-hydrogen system in the rocksalt structure for the static lattice and for the cases of hydrogen displacements in the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions. Utilizing the LAPW total energies, and the approximation of an isotropic anharmonic oscillator, we have determined the zone-center optic modes for PdH, PdD, and PdT and find very good agreement with experiment. Using our lattice-dynamics results and our calculations of the electron-phonon interaction in the rigid-muffin-tin approximation, we have determined the superconducting coupling parameter λ and T_c for these three hydrides. We find that the inverse isotope effect is semiquantitatively accounted for by the anharmonic lattice dynamics, without assuming an explicit dependence of the electron-phonon interaction on hydrogen isotope, in agreement with earlier calculations. However, there is a significant quantitative variation of the isotope effect with the value of the Coulomb pseudopotential parameter μ^*, which must be estimated. We also estimate the effect of pressure on T_c and on the isotope effect.

I. INTRODUCTION

The palladium-hydrogen system has exhibited many unusual properties, including strong hydrogen anharmonicity and the occurrence of superconductivity with a hydrogen isotope effect that is inverse, or opposite, to what is usually observed in superconductors.[1] That is, the sequence PdH → PdD → PdT shows an increasing superconducting transition temperature, opposite to the norm. In addition, the hydrides are good superconductors while the parent transition metal Pd does not superconduct in its stoichiometric state, presumably because of incipient magnetic behavior driven by a large Fermi-level density of states.

Early after the discovery of superconductivity in the palladium-hydrogen system[2] it was proposed that the inverse isotope effect was related to the hydrogen anharmonicity in the palladium lattice,[3] and a number of publications followed with detailed numerical calculations that appeared to support that interpretation.[4–7] These calculations utilized neutron diffraction results for the lattice dynamics[8–11] of the hydrides which showed anomalously soft hydrogen optic modes related to the anharmonicity of the H or D motion, together with electronic-structure results for the electron-phonon interaction. The latter calculations were performed using the same electronic structure for PdH, PdD, or PdT, assuming that the anharmonicity did not have a significant effect on the electronic-structure-derived quantities, with the inverse isotope effect coming from the lattice-dynamics part of the superconducting parameters. There have been suggestions that the effect of an isotope dependence of the electronic structure is important for the inverse isotope effect.[12,13]

More recently, Rowe *et al.*[14] presented experimental results on the lattice dynamics of the PdT$_x$ system which, together with refined interpretations of the earlier neutron diffraction studies of the PdH and PdD systems, led them to conclude that there was a serious discrepancy between the isotope effect results based on assuming an isotope-independent electron-phonon interaction, and experiment. That work, and the resurgence of interest in the general area of the isotope effect due to the observed anomalous behavior of the high-T_c oxides in this regard,[15] has stimulated us to perform a new, detailed study of the isotope effect in the palladium-hydrogen system, including a first-principles determination of the H, D, and T lattice dynamics as a function of volume. We conclude that the major part of the inverse isotope effect in the palladium-hydrogen system can be accounted for by the inclusion of anharmonicity only through the optic mode vibrational frequencies, although other effects, such as an isotope-dependent electronic structure, may not be insignificant.

The present study makes use of the all-electron, full-potential linearized-augmented-plane-wave (LAPW) method[16] to generate the electronic structure and total energy of the palladium-hydrogen system. The results are used to determine the anharmonic lattice dynamics and the electron-phonon scattering properties needed to calculate the superconducting transition temperature T_c.

It is important to note that our inclusion of the anharmonic lattice dynamics into the strong-coupling theory of superconductivity is approximate. Although there has been progress in developing a rigorous strong-coupling theory of superconductivity which includes anharmonic effects,[17–21] implementing such approaches in a realistic quantitative manner has been limited by the computational complexity involved. This is likely to change in the future as there is increasing evidence that anharmonicity plays some role in superconductivity in the high-T_c oxides, and there has been a renewed interest in further developing a theoretical and computational framework for including anharmonicity in the spirit of Eliashberg strong-coupling theory.[22] In addition, several authors have emphasized that the isotope effect is a rich and complex phenomenon, strongly dependent on the details of the system under investigation.[23]

Finally, we mention that Elsässer *et al.* [24] have performed total-energy studies of the palladium-hydrogen system using mixed-basis pseudopotential methods to study the cohesive properties and to generate diffusion potentials. They also present results on the lattice dynamics of this system in the harmonic approximation.

The paper is organized as follows: Sec. II gives an overview of the electronic structure, lattice dynamics, and superconductivity methods that we have used; Sec. III presents and discusses our results and compares with previous work; and in Sec. IV we summarize the conclusions we draw from this work.

II. OVERVIEW OF THE COMPUTATIONAL METHODS

A. LAPW computations

The electronic structure, total energies for frozen phonon displacements, and electron-phonon interaction within the rigid-muffin-tin approximation (RMTA) of PdH, PdD, and PdT were determined using the full-potential LAPW method[16] with the local-density approximation for exchange and correlation. In this method no shape approximations are made for either the core or valence states and no pseudopotential approximation is made. The basis set is a dual representation with plane waves in the interstitial region joined smoothly onto linear combinations of solutions of Schrödinger's equation and energy derivatives of the solutions inside spherical "muffin tins" centered around each nucleus. The core states are treated fully relativistically, and the semicore and valence states are treated semirelativistically (without spin-orbit interaction). Convergence parameters were chosen to ensure accuracy of the total-energy differences needed for the lattice-dynamics studies. Since we are only considering zone-center optic modes in this paper, the unit cells contain two atoms, a Pd and a H atom, but the displacements remove inversion symmetry from the space group, and the LAPW matrix is complex. For vibrations at other Brillouin-zone points, the methods discussed in this paper can be used, but a larger, periodically repeated supercell would be required.

In the ground state, β phase PdH is in the rocksalt structure with full cubic symmetry (48 symmetry operations). The zone-center optic mode is triply degenerate with respect to vibrations in the x, y, and z directions. However, when the atoms move from their equilibrium positions the potential surface varies as a function of displacement direction. Since the lattice dynamics involve very large motions of the hydrogen isotopes, it was necessary to choose rather small sphere radii (kept fixed for all of our phonon calculations) for both Pd and H so as to avoid muffin-tin sphere overlap, and this in turn required the use of a large basis set for convergence. For the frozen phonon calculations, the muffin-tin sphere radii chosen were $R_{\mathrm{Pd}}=1.85$ a.u. and $R_{\mathrm{H}}=1.05$ a.u., with $R_{\mathrm{H}}K_{\mathrm{max}}=5.5$, and were kept the same for all lattice constants and H displacements, yielding a basis set of approximately 280 plane waves. For the H displacements in the $\langle 100\rangle$, $\langle 110\rangle$, or $\langle 111\rangle$ directions, the symmetry is reduced to tetragonal, orthorhombic, or rhombohedral, respectively.

For the self-consistent iterations, special **k** points were used with an $8\times8\times8$ Cartesian mesh in the full Brillouin zone for the valence window, and $4\times4\times4$ in the semicore window, which gives 20 and 1 respectively in an irreducible segment of the first Brillouin zone (IBZ) for the valence (semicore) states for the tetragonal $\langle 100\rangle$ displacements; 40 (respectively 2) for the orthorhombic $\langle 110\rangle$ displacements; 30 (respectively 2) for the rhombohedral $\langle 111\rangle$ displacements; and 10 (respectively 1) for the cubic structure.

For the density-of-states results needed to determine some of the superconducting parameters, it is appropriate to maximize the muffin-tin volumes so as to maximize the charge in the muffin-tin spheres and reduce the errors in the RMTA (see below). To achieve this we performed separate self-consistent calculations for the undisplaced lattice for the density-of-states calculations, choosing the size of the H sphere radius to give touching, or nearly touching muffin-tin spheres, and a relatively small interstitial volume. A value of $R_{\mathrm{H}}K_{\mathrm{max}}$ of 7.0 was used for the density-of-states and RMTA calculations. R_{Pd} was kept fixed at 2.3795 a.u., and R_{H} had the values of 1.485, 1.406, and 1.364 45 a.u., for the lattice constants 7.729, 7.65, and 7.50 a.u., respectively. The muffin-tin radii chosen for the $a=7.729$ a.u. calculation exactly matched the values used by Papaconstantopoulos *et al.* [6] and allow a comparison of the present LAPW and the earlier APW values of the electron-phonon coupling. Using the self-consistent potentials for these sphere radii the eigenvalues were calculated on a mesh of 145 k points and were then interpolated onto a mesh of 413 k points using Fourier interpolation,[25] and the densities of states were determined using tetrahedral integration.

B. Lattice-dynamics methods

In the harmonic approximation, the LAPW total energies for a series of atomic displacements can be used to map out the dynamical matrix and determine the harmonic phonon frequencies. For the PdH system, our results indicate that the harmonic approximation is not accurate for describing the lattice dynamics involving hydrogen motions (i.e., the optic modes), so that alternative procedures must be used. Since a fully first-principles description of the three-dimensional anharmonic oscillator in a solid is not available, we resort to a plausible set of approximations whose efficacy is borne out by very good agreement with experiment, as we will show below.

Our procedure for determining the hydride optic mode dynamics is as follows: (1) we determine the electronic total energies as a function of H (assumed the same for D or T) displacements in three high-symmetry directions, ⟨100⟩, ⟨110⟩, ⟨111⟩; (2) we fit the results to polynomials in hydrogen displacement coordinates, up to sixth order, that satisfy the lattice symmetry, yielding a vibrational potential surface; (3) a spherical average of this potential is determined; (4) the spherical potential is used as input to a one-dimensional Schrödinger equation solver, with the respective reduced masses of the hydride, deuteride, or tritide, to determine the optic vibrational frequencies of the three isotopes. The reduced mass takes the form $M_1M_2/(M_1+M_2)$, with M_1 the mass of Pd and M_2 the mass of H, D, or T. Since the mass of the hydrogen isotopes is much smaller than that of Pd, the reduced mass is very close to the hydrogen isotope mass. The frequency is determined by taking the difference between the ground and first excited states of the oscillator.

In the harmonic approximation for a cubic crystal, the potential surface would not depend on direction. For the higher-order terms needed for the anharmonicity this is not the case. We will show, by comparing with a fourth-order fit, that a fit to sixth order in the displacement components gives well-converged anharmonic frequencies.

C. Determining the superconducting parameters

In order to determine the effect of the anharmonic hydrogen motions on the superconducting transition temperature, and in particular to see whether the inverse isotope effect can be accounted for by considering anharmonic phonons with the same electronic structure for all three isotopes, we use the rigid-muffin-tin approximation[26] together with an approximate approach for determining the resulting T_c.[27]

In the RMTA, the McMillan-Hopfield parameter η is given by

$$\eta_s \equiv N(E_F)\langle I_s^2\rangle = \frac{E_F}{\pi^2 N(E_F)} \sum_l 2(l+1)\sin^2(\delta_{l,s+1}-\delta_{l,s}) \frac{N_{l,s}N_{l,s+1}}{N_{l,s}^{(1)}N_{l,s+1}^{(1)}} , \tag{1}$$

with $\langle I_s^2\rangle$ the electron-ion matrix element, $N(E_F)$ the total density of states at the Fermi level, $N_{l,s}$ the corresponding angular momentum components of the density of states (DOS), $\delta_{l,s}$ are scattering phase shifts at E_F, and $N_{l,s}^{(1)}$ are single-scatterer DOS components defined in Ref. 26. l and s are angular momentum and site indices (Pd, or H or D or T), respectively. Since the RMTA is a muffin-tin theory, the spherically averaged self-consistent LAPW potentials are used to evaluate the phase shifts and single-scatterer DOS values.

The electron-phonon coupling constant λ is related to the Eliashberg spectral function $\alpha^2F(\omega)$ by the relation

$$\lambda = 2\int_0^\infty [\alpha^2F(\omega)/\omega]d\omega , \tag{2}$$

with the sum rule

$$\int_0^\infty \omega\alpha^2F(\omega)d\omega = \sum_s \frac{\eta_s}{2M_s} \tag{3}$$

being satisfied.[28,29] In relating the $\alpha^2F(\omega)$ moments to the phonon density of states, $F(\omega)$, Klein, and coworkers[27] proposed the following ansatz for compounds, a generalization of McMillan's[28] "constant α^2" approximation:

$$\lambda = \sum_s \lambda_s = \sum_s \frac{\eta_s}{M_s\Omega_s^2}$$

and

$$\bar{\Omega}^2 \equiv \frac{1}{\lambda}\sum_s \Omega_s^2\lambda_s ,$$

$$\Omega_s^2 \equiv \frac{\int \omega F_s(\omega)d\omega}{\int [F_s(\omega)/\omega]d\omega} .$$

For a compound like PdH(D,T), where Pd is much heavier than any of the hydrogen isotopes, the site-decomposed phonon densities of states $F_s(\omega)$ are, to a good approximation, the acoustic and optic modes for Pd or H (D or T), respectively.

For the transition temperatures, we make use of Kresin's strong-coupling formula given by[30]

$$T_c = 0.25\bar{\Omega}[\exp(2/\lambda_{\text{eff}})-1]^{-1/2} , \tag{4}$$

$$\lambda_{\text{eff}} = (\lambda-\mu^*)[1+2\lambda\mu^* t(\lambda)]^{-1} , \tag{5}$$

with μ^* the Coulomb pseudopotential which must be estimated, and $t(\lambda)$ a function having the approximate value of 1.25 (see Ref. 30).

We estimate the optic phonon moments from the anharmonic lattice dynamics that we have determined. Note that in this work we do not consider any isotope dependence of the η's for H, D, or T. That is, we investigate whether the inverse isotope effect can be accounted for solely by lattice-dynamics effects with the same underlying electronic structure for the hydrogen isotopes.

For the Pd (acoustic mode) moments, we use the experimental values, neglecting the small hydrogen isotope dependence.[31] This has a negligible effect on our conclusions.

The phonon moment for the optic mode, Ω_{opt}^2, must be estimated from the results for the single zone-center BZ point that we have calculated. We do this by scaling the square of our anharmonic frequency by the factor of 1.28 which is the value we determined by comparing the zone-center and phonon moment experimental results of Rowe, *et al.*[14] We note here that one of the advantages of using our theoretical results for the anharmonic phonons is that the calculations have been done for several lattice constants and, as shown in Sec. III B, there is a significant variation of the optic mode frequency with lattice constant. We can therefore match the lattice dynamics with the appropriate lattice constant corresponding to the hydrogen stoichiometry under investigation. Therefore, in this regard, the present work is an improvement over using the experimental lattice dynamics which have been limited to substoichiometric crystals with T_c's much lower than the maximum value.[8–11,14]

There are several uncertainties in our approach for estimating the transition temperatures besides our assumption of the same band structure for PdH, PdD, and PdT. First, the RMTA is an approximation, albeit one which has enjoyed a great deal of success in transition-metal systems.[32] One of the sources of error is related to the fact that there is a fairly large interstitial region where the potential is accounted for as a constant in the RMTA. In addition, the decomposition of $\alpha^2F(\omega)$ that we use, discussed above, is approximate. Finally, we must assume values for μ^*, and as we shall see, there is some sensitivity of the isotope effect results to μ^*. It is worth emphasizing, however, that the theory and analysis that we are using is internally consistent for each isotope and lattice constant, so we believe that the qualitative and semiquantitative conclusions that we will draw are valid.

III. RESULTS AND DISCUSSION

A. Ground-state properties of the undisplaced lattice

An experimental study of the dependence of the lattice constant of β-phase PdH_x and PdD_x as a function of stoichiometry (x) has been presented by Schirber and Morosin[33] with a strong indication of large zero-point motion effects as evidenced by the difference in lattice constant for the hydride and deuteride, 4.090 and 4.084 Å, respectively, for $x=1$. The tritide shows the same trend, although tritium loading has been achieved up to only $x=0.81$.[34]

Polynomial fits to our LAPW calculations give a total-energy minimum at a cubic lattice constant of 7.66 a.u. (4.05 Å), without zero-point motion corrections, which is slightly smaller than the experimental values for stoichiometric PdH and PdD. Including zero-point motion would further improve the theoretical agreement. The bulk modulus we calculate is approximately 220 GPa, about 10% greater than experiment.[35,36]

The energy bands and DOS's of the hydrides are very similar to those obtained by the muffin-tin APW method by Papaconstantopoulos *et al.*,[6] who also used a different version of the exchange-correlation potential. Reference 6 gives a full discussion of the electronic structure of palladium hydride. In Table I we compare our full-potential (LAPW) results for bandwidths and separations with these previous results. There is good agreement with the MT-APW calculations[6] and ours for the same lattice constant, especially regarding the bandwidths, indicating that the muffin-tin approximation is good for these materials. This is important to note since we have used the muffin-tin RMTA to determine the superconducting parameters of the hydrides. The s-d separation difference between the two calculations is somewhat larger than the bandwidth differences, probably due to the different exchange-correlation approximation used in the earlier calculation.

It is also interesting to note the bandwidth pressure dependencies shown in Table I, with our calculated values of the dimensionless derivatives $\partial \log W_{s(d)}/\partial \log V$ having the values of -0.67 and -1.66, respectively, for the s- and d-band widths. These values are indistinguishable from the values of $-2/3$ and $-5/3$ predicted by Heine,[37] based on general arguments for transition-metal systems, and discussed by Svechkarev and Panfilov.[38]

B. Optic mode vibrational frequencies

To determine the vibrational frequencies, the total-energy changes versus hydrogen displacements were fitted with polynomial functions in (x,y,z), the components of the displacement vector $\mathbf{d}$. For each of the lattice constants considered, total energies for five hydrogen displacements were used for each of three directions, $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$. The polynomial terms included satisfy the cubic symmetry of the undisplaced space lattice and have the form

$$V_4=A_4d^2+B_4d^4+C_4(x^4+y^4+z^4)\ , \tag{6}$$

$$V_6=A_6d^2+B_6d^4+C_6(x^4+y^4+z^4)+D_6d^6 +E_6d^2(x^4+y^4+z^4)+F_6x^2y^2z^2\ , \tag{7}$$

with $d^2=(x^2+y^2+z^2)$.

The fourth and sixth-order expansion coefficients are given in Table II. Finally, a spherical average of the fourth- and sixth-order potentials was taken, resulting in the following average potentials:

TABLE I. Comparison of selected bandwidths and band separations for the PdH system from the present work and the muffin-tin (MT) APW calculations of Ref. 6. LDA denotes local-density approximation. The lattice constants are in a.u., and the bandwidths are in Ry. Also shown are the pressure dependencies of the bandwidths, P_s and P_d, defined as $\partial \log W_{s(d)}/\partial \log V$, with W the bandwidth and V the volume. See Table I of Ref. 6 for a definition of the bandwith and separation parameters.

	Present work (LAPW-LDA)			Ref. 6 (MT-APW)
Lattice constant	7.420	7.500	7.729	7.729
s-band width	0.932	0.912	0.855	0.867
d-band width	0.407	0.386	0.324	0.333
s-d separation	0.577	0.565	0.509	0.546
s-band separation	1.093	1.051	0.933	0.936

$$P_s=-0.66\sim-\tfrac{2}{3}$$
$$P_d=-1.66\sim-\tfrac{5}{3}$$

TABLE II. Coefficients of the displacement potential fits for hydrogen displacements, following the notation of Eqs. (6) and (7), for three different lattice constants in a.u. (angstroms). The units of the coefficients are such that the displacement potentials are in meV if the displacements are in bohrs.

Lattice constant	A_4	B_4	C_4	A_6	B_6	C_6	D_6	E_6	F_6
7.729 (4.090 Å)	17.40	−46.40	229.30	10.04	23.22	96.50	−119.50	240.68	725.01
7.65 (4.048 Å)	48.03	−60.59	260.96	39.62	14.59	114.81	−132.67	268.73	816.89
7.50 (3.969 Å)	100.58	−68.58	326.17	104.26	6.50	144.47	−184.72	379.80	1041.76

$$\langle V_4 \rangle = R_4 d^2 + S_4 d^4 \,, \tag{8}$$

$$\langle V_6 \rangle = R_6 d^2 + S_6 d^4 + T_6 d^6 \,, \tag{9}$$

with the coefficients given in Table III.

The fitted spherical potentials, assumed the same for all three hydrogen isotopes, were then used to determine the one-dimensional oscillator eigenstates for the PdH, PdD, and PdT optic modes using the reduced center of mass for each case. The solutions were obtained numerically from a one-dimensional (1D) Schrödinger equation solver. The outputs were the optic mode frequencies and displacement vectors for the anharmonic oscillators. In Table IV we show the calculated frequencies for the fourth-order and sixth-order fits as well as the rms displacement (for the ground state) for each of the isotopes for the three different lattice constants. From Table IV we see first that the results for the fourth- and sixth-order fits are the same to approximately 1%, so that we are well converged for the latter. The remainder of the results in this paper are given in terms of the sixth-order results. Next we note a strong lattice-constant dependence of the frequencies and rms displacements as might be expected for a strongly anharmonic lattice. The lattice constant closest to the experimental lattice-dynamics measurements is 7.65 a.u. (4.048 Å) and the agreement with experiment[5,8] is excellent for the calculated Γ-point optic mode.

In comparing our results with experiment, we do not explicitly take into account the effects due to substoichiometry implicit in the experimental results. In the range of stoichiometry where the palladium-hydrogen system is superconducting, the lattice constant varies from approximately 4.05 to 4.09 Å (7.65 to 7.73 a.u.), and our optic mode results show an approximate 10% variation, decreasing with increasing volume. This is the direction expected for a solid under compression or expansion (a positive Grüneisen constant). Experimentally it is observed that the optic mode frequencies are fairly constant until very close to full stoichiometry. This indicates that the explicit effect of substoichiometry on the optic modes (variation of the force constants with stoichiometry), not accounted for here, is at most a 10% effect, opposite to the pure volume effect included in our calculations. The relative variations in optic mode frequencies due to substoichiometry are, to a good approximation, likely to be independent of hydrogen isotope, so that our conclusions about the inverse isotope effect are probably little affected.

To illustrate the inadequacy of the harmonic approximation for the optic modes we show in Fig. 1 plots of the sixth-order anharmonic potentials for the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions, the spherically averaged potential used in the one-dimensional oscillator calculation, and the harmonic (second-order) part of the spherical potential. For displacements of the order of the rms values, it is seen from Fig. 1 that there are very substantial differences between the anharmonic and harmonic potentials. In fact, using only the harmonic part of the potential in the oscillator solution for the 7.65 lattice-constant case yields values of 34.59, 24.47, and 20.08 meV for the hydride, deuteride, and tritide frequencies, respectively, much smaller than the anharmonic values shown in Table IV. The harmonic approximation is inadequate for studying the vibrational spectra of the palladium-hydrogen system. The discrepancy between the harmon-

TABLE III. Coefficients of the spherically averaged displacement potential, in meV, for hydrogen displacements, following the notation of Eqs. (8) and (9), for three different lattice constants in a.u. (angstroms). The units of the coefficients are such that the displacement potentials are in units of meV if the displacements are in bohrs.

Lattice constant	R_4	S_4	R_6	S_6	T_6
7.729 (4.090 Å)	17.40	91.18	10.04	81.12	31.81
7.65 (4.048 Å)	48.03	95.83	39.62	83.48	36.36
7.50 (3.969 Å)	100.58	127.13	104.26	93.18	44.15

ic and anharmonic values decreases, as expected, in going from the hydride → deuteride → tritide. This is consistent with the smaller rms displacements and decreasing anharmonicity in this sequence going to the heavier masses of the hydrogen isotopes. Figure 1 also shows the classical turning point for the sixth-order fit for the ground-state energy of the hydride. This isoenergy surface has the shape of a rounded cube.

Finally in Table IV we show a least-squares fit to the frequency in terms of the mass dependence of the hydrogen isotope for each lattice constant of the form $\omega = BM^{-\beta}$, with B and β constants. This simple fit is excellent, with rms deviation of a few tenths of a percent. For a harmonic lattice, β would be 1/2; while for the present results there are significant variations from this value with $\beta > 1/2$ and increasing with increasing volume (increasing hydrogen-palladium nearest-neighbor separation) heading toward the value $\beta = 1.0$ for a particle in box.

C. rms displacements and Grüneisen parameters

The rms displacements are very large, from 7% to nearly 10% of the nearest-neighbor distance, scaling down inversely with isotope mass from the hydride to the tritide, as expected. Glinka *et al.* [11] extracted the average square displacement $\langle u_\kappa^2 \rangle$ for the zone-center optic mode in $\mathrm{PdD_{0.63}}$. They found a value of 0.026 ± 0.003 Å^2, independent of direction κ. This compares very favorable with our theoretical value of 0.028 Å^2 for the 7.65 a.u. (4.05 Å) lattice-constant results shown in Table IV.

The estimated Grüneisen parameters for the Γ-point optic mode are shown in Table V. These were determined from the standard expression,

$$\gamma_G = -\frac{d\ln\omega}{d\ln V}, \tag{10}$$

with the volume dependence determined from a simple,

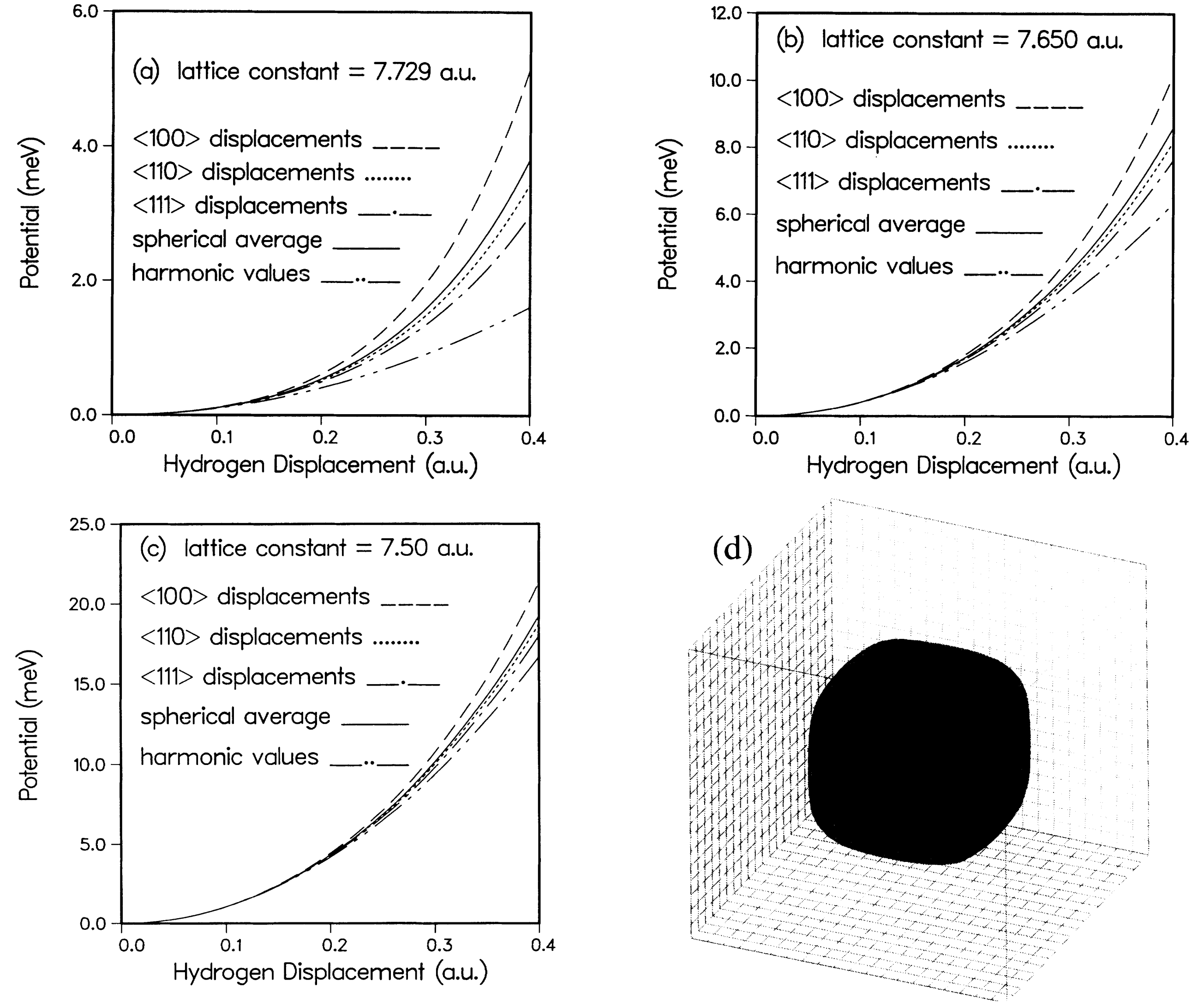

FIG. 1. (a) – (c) Sixth-order (see text) hydrogen displacement potential energies (change in total energy as a function of hydrogen displacement from the equilibrium rocksalt structure positions corresponding to a zone-center optic mode) for three different lattice constants. (d) Classical turning points for the ground-state vibrational energy in PdH, at $a = 7.729$ a.u. The isopotential surface looks like a rounded cube. The outer box is 2 bohrs on each edge.

but very accurate linear with lattice-constant fit of the optic mode frequency shown in Fig. 2, so that γ_G is given by

$$\gamma_G = -\frac{1}{3}\frac{BV^{1/3}}{\omega} , \tag{11}$$

with

$$\omega = A + Ba . \tag{12}$$

These Grüneisen parameters scale inversely with the isotopic hydride masses and have rather large values which are related to the anharmonicity. For comparison, Geerken *et al.*[36] estimate average Grüneisen parameters for PdH(D) that are close to our calculated values.

D. Superconducting parameters

Following the procedures outlined in Sec. II C, we have calculated η, λ, and T_c as a function of μ^* for the three different lattice constants. Tables VI and VII and Fig. 3 show some of our results and the experimental values[39] for the maximum T_c's observed. No adjustments were made to the theoretical electron-phonon parameters to force quantitative agreement with any measurements. The experimental values of T_c are listed below the

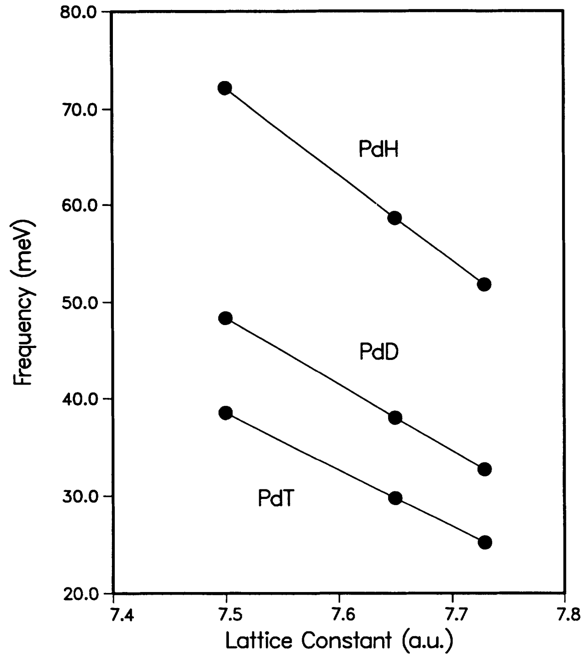

FIG. 2. Γ-point optic mode frequency vs cubic lattice constant for PdH, PdD, and PdT.

TABLE IV. Optic mode frequencies ω (meV) and rms displacements $\langle u^2 \rangle^{1/2}$ (a.u.) for PdH, PdD, and PdT. The numbers in parentheses for the 7.65-a.u. lattice-constant results are the experimental results for lattice constants very close to this value. Below the rms displacement values, which are for the oscillator ground state, is the percent of the nearest-neighbor hydrogen-palladium separation. The last line in each panel shows a fit to the frequency in terms of a power of the isotopic reduced mass.

	Lattice constant	ω (fourth-order fit)	ω (sixth-order fit)	$\langle u^2 \rangle^{1/2}$
PdH	7.729 a.u. (4.090 Å)	51.14	51.82	0.379 (9.8%)
PdD		33.07	32.75	0.339 (8.8%)
PdT		25.76	25.19	0.317 (8.2%)
			$\omega = 51.07M^{-0.6366}$	
PdH	7.650 a.u. (4.048 Å)	58.46	58.61 (56.0)[a]	0.357 (9.3%)
PdD		38.69	38.04 (37.6)[a]	0.315 (0.305)[b] (8.2%)
PdT		30.57	29.76 (30.1)[a]	0.293 (7.7%)
			$\omega = 58.38M^{-0.6019}$	
PdH	7.500 a.u. (3.969 Å)	72.05	72.16	0.322 (8.6%)
PdD		48.53	48.35	0.280 (7.5%)
PdT		38.75	38.56	0.258 (6.9%)
			$\omega = 71.95M^{-0.5759}$	

[a] Experiment from Refs. 8–10, 14.

[b] Experiment from Ref. 11.

TABLE V. Grüneisen parameters as a function of lattice constant for the palladium-hydrogen systems. These were determined from linear fits to the frequency vs lattice constant as discussed in the text.

Lattice constant (a.u.)	Grüneisen parameter PdH	PdD	PdT
7.729	4.43	5.37	5.97
7.650	3.87	4.57	5.01
7.500	3.08	3.53	3.79

TABLE VI. Calculated electron-phonon interaction parameters η for the acoustic and optic modes, and calculated λ for three different lattice constants. η is in eV/Å^2 and a is in a.u.

			PdH			PdD			PdT		
a	η_{ac}	η_{opt}	λ_{ac}	λ_{opt}	λ	λ_{ac}	λ_{opt}	λ	λ_{ac}	λ_{opt}	λ
7.729	0.898	0.342	0.147	0.417	0.564	0.147	0.528	0.675	0.147	0.601	0.748
7.650	0.975	0.348	0.160	0.332	0.492	0.160	0.398	0.558	0.160	0.438	0.598
7.500	1.140	0.368	0.187	0.231	0.418	0.187	0.260	0.447	0.187	0.276	0.464

TABLE VII. Calculated superconducting transition temperatures T_c (K) for the hydride, deuteride, and tritide for two different values of the Coulomb pseudopotential μ^* and three different lattice constants a (a.u.). A third value of $\mu^*=0.115$, chosen to match the theoretical and experimental T_c values for PdH, is shown for the $a=7.729$ a.u. lattice constant.

a	μ^*	T_c (PdH)	T_c (PdD)	T_c (PdT)
7.729	0.13	6.59	7.89	8.25
	0.115	8.00	9.12	9.34
	0.10	9.61	10.47	10.52
		8.0[a]	10.0[a]	~11.0[a]
7.650	0.13	3.93	4.60	4.77
	0.10	6.39	6.76	6.72
7.500	0.13	1.78	1.86	1.83
	0.10	3.48	3.34	3.17

[a] Experiment from Ref. 39.

TABLE VIII. Calculated harmonic and anharmonic isotope effect exponents α, compared with α determined from the experimental T_c values. Results are for a lattice constant of 7.729 a.u. and $\mu^*=0.115$.

	α_{harm}	α_{anharm}	α_{expt}
PdD	0.44	-0.19	-0.32
PdT	0.43	-0.14	-0.29

TABLE IX. Calculated values of $\partial T_c/\partial P$ in K/GPa.

	PdH	PdD	PdT
$\mu^*=0.13$	-0.326	-0.405	-0.429
$\mu^*=0.10$	-0.402	-0.465	-0.477

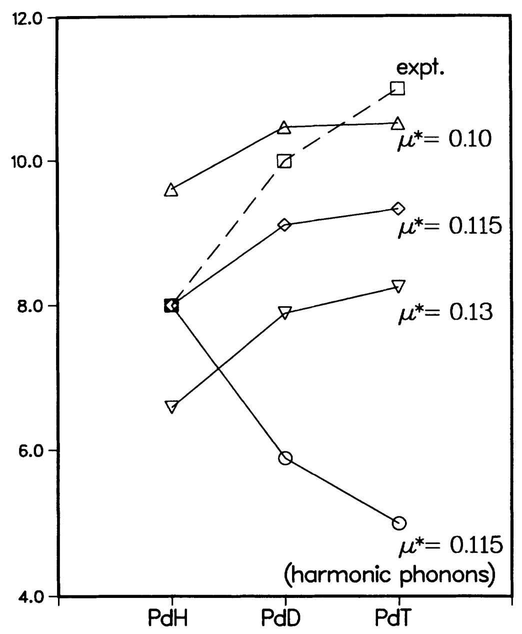

FIG. 3. Calculated superconducting transition temperature T_c, for PdH, PdD, and PdT for several different values of μ^* compared with experiment. Also shown are theoretical values for harmonic phonons (see text). Lines connecting the points are guides for the eye.

$a = 7.729$ a.u. results as this lattice constant is the closest to that of the fully stoichiometric, highest-T_c compounds. We note that experimentally there is a systematic decrease of the observed T_c's with hydrogen vacancies,[39] and this correlates with a decreasing lattice constant.[33,34] This trend is reproduced in the theoretical calculations.

Comparing our calculated η values with the APW results of Papaconstantopoulos *et al.*[6] for the $a = 7.729$ a.u. calculations we find good agreement, $\sim 10\%$, with their $\eta_{ac} = 0.865$ and $\eta_{\rm opt} = 0.392$. Differences can be ascribed to the present full-potential methods and to our more accurate k-point sampling for the DOS. Additional differences in the λ values are a result of the approximate treatment of the phonon moments in the earlier work (there were limited experimental results).

The only free parameter in the theory is μ^*. Table VII presents T_c results for μ^* values of 0.13 and 0.1, within the range of "accepted" values, and a third value of $\mu^* = 0.115$ chosen to match the theoretical value of T_c for PdH with $a = 7.729$ a.u. with the experimental value.[39] Note that the strong-coupling theory yields a significant variation of the isotope effect with μ^* as discussed recently.[19,21,23]

From the $a = 7.729$ a.u. results it is apparent that the major portion of the inverse isotope effect is accounted for by the anharmonicity of the hydrogen isotope vibrations. This is perhaps most clear from the results shown in Table VIII and Fig. 3 where we compare results for harmonic and anharmonic phonons as they affect T_c and the isotope exponent α. We have defined the harmonic phonons to be those obtained by scaling the hydride optic mode frequency value by $M_{\rm D\,(T)}^{-1/2}$ for the deuteride and tritide.

For decreasing lattice constant (increasing pressure) the inverse isotope effect tends to decrease. Using our calculated T_c as a function of volume, together with our calculated equation of state, we find values of $\partial T_c/\partial P$ shown in Table IX. The second derivative $\partial^2 T_c/\partial P^2$ is approximately 0.015 K/GPa^2. The strong dependence on volume of the optic mode dynamics and the resultant variation of T_c accounts for some of the differences between the present results and previous theoretical estimates of the isotope effect.[6,13,14]

It has been argued that the feedback of the anharmonicity of the hydrogen isotope motion into the electronic structure may be important for explaining the inverse isotope effect in the palladium-hydrogen system.[12-14] Most recently, Rowe *et al.*[14] argued that there are major discrepancies between the isotope effect results determined following a procedure like ours (but using the experimental phonon frequencies), and the experimental T_c results. The major differences in the present analysis are (1) that we used our calculated optic mode frequencies for the stoichiometric lattice constant, and there is a substantial lattice-constant variation of this frequency; (2) we have found a substantial variation of the isotope effect exponent with μ^*; and (3) we used our updated values of η.

Although the present results do not rule out the possibility that electronic-structure variations with hydrogen isotope may have some quantitative importance for the inverse isotope effect, the indications are that these kinds of effects will be secondary to the effect of the anharmonic lattice dynamics.

Going beyond the present set of approximations would be very difficult due to the lack of a complete theory of superconductivity in anharmonic crystal. Starts in this direction have been made, motivated by the "anomalous" isotope effects seen in the high-T_c superconducting oxides.[20,21] The vibrational frequency and electron-phonon interaction results presented here are likely to be important ingredients in more sophisticated calculations.

IV. CONCLUSIONS

Hydrogen anharmonicity is intrinsic to superconductivity in the palladium-hydrogen system and for other properties as well. We have shown in this work that a first-principles description of the anharmonic optic modes of PdH, PdD, and PdT may be derived from total-energy electronic-structure calculations with very good agreement with experiment for the zone-center values. Using these results, and assuming no variation in the electron-phonon interaction parameters with hydrogen isotope, we were able to account for the major part of the inverse isotope effect, although some quantitative discrepancy remains, and we must estimate the value of μ^* empirically.

Our present LAPW-derived superconductivity results are also in good agreement with earlier muffin-tin APW studies which used experimental values of the lattice dynamics.[6] This is consistent with the fact demonstrated here that the APW electronic structure is in good agreement with the present more accurate full-potential LAPW results.

Although the approach that we have used appears reasonable, and shows good agreement with experimental trends, it would be desirable to utilize a more rigorous formulation of anharmonic superconductivity theory in order to corroborate our conclusions that changes in the electronic structure with hydrogen isotope are not important for T_c. Until this is done, effects such as the latter cannot be definitely excluded from contributing to the isotope effect.

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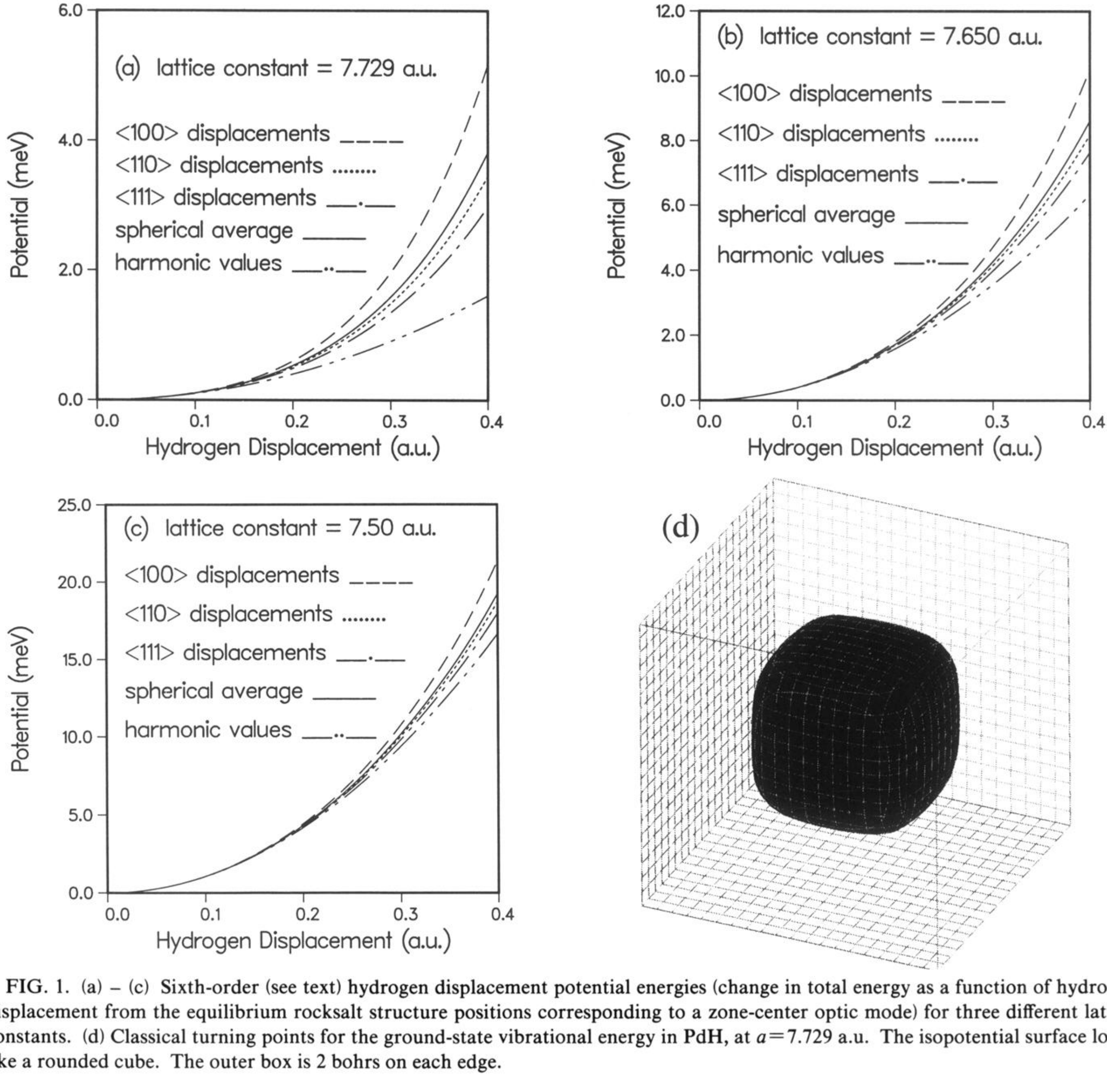

FIG. 1. (a) – (c) Sixth-order (see text) hydrogen displacement potential energies (change in total energy as a function of hydrogen displacement from the equilibrium rocksalt structure positions corresponding to a zone-center optic mode) for three different lattice constants. (d) Classical turning points for the ground-state vibrational energy in PdH, at $a = 7.729$ a.u. The isopotential surface looks like a rounded cube. The outer box is 2 bohrs on each edge.