Effect of anharmonicity and Debye–Waller factor on the superconductivity of PdH_x and PdD_x

By R. Griessen and D. G. de Groot, Natuurkundig Laboratorium der Vrije Universiteit, Amsterdam, The Netherlands

Abstract. On the basis of existing superconducting tunnelling, neutron scattering, electrical resistivity and Raman scattering data and new thermal expansion, elastic moduli and point-contact spectroscopy data it is concluded that the anharmonicity of the proton (deuteron)-palladium potential is such that $M_H\omega_H^2/(M_D\omega_D^2) = 1.12 \pm 0.05$ ($M_{H(D)}$ is the mass and $\omega_{H(D)}$ the frequency of the vibration of hydrogen (deuterium)). This anharmonicity is approximately 2 times too weak to reproduce the observed inverse isotope effect in the superconducting transition temperature of concentrated PdH_x and PdD_x alloys. Within a pseudopotential formalism it is shown that the Debye–Waller factor arising from the large zero-point amplitude of the interstitial hydrogen (deuterium) leads to a contribution to the inverse isotope effect in T_c which is as large as that of anharmonicity alone.

I. Introduction

One of the most intriguing isotope effects observed so far in metal-hydrogen systems is the inverse isotope effect reported by Stritzker and Buckel [1] in PdH_x and PdD_x. Above 80 at % H (resp. D) these alloys are superconducting. At stoichiometry the superconducting transition temperature T_c of PdH_x reaches a value of approximately 9 K. PdD which according to a simple application of the BCS theory should have a lower T_c than PdH is however found to have a superconducting transition at 11.5 K [2].

This remarkable isotope effect has stimulated a considerable activity both on experimental and theoretical side. The various theoretical models proposed so far are all based on the difference in the amplitude of the zero-point-motion of the interstitial hydrogen or deuterium. There are essentially two lines of thoughts.

According to Ganguly [3, 4] and later Papaconstantopoulos et al. [5], Klein et al. [6] and Papaconstantopoulos et al. [7, 8] the contribution λ_{opt} of the optic modes to the electron-phonon enhancement parameter λ is significantly larger than that of the acoustic phonons at hydrogen or deuterium concentrations close to unity. As the optical phonons arise primarily from the vibrational modes of the interstitial hydrogens of deuteriums λ_{opt} may be written as

$$\lambda_{opt} = \lambda_{H(D)} = \frac{\eta_{H(D)}}{M_{H(D)}\langle\omega_{H(D)}^2\rangle} \tag{1}$$

where $M_{H(D)}$ is the mass of the interstitial and $\langle\omega_{H(D)}^2\rangle$ a weighted average of the

square of the optical phonon frequencies in *PdH* or *PdD*. $\eta_{H(D)}$ is the first moment of the "optical" Eliashberg function $[\alpha^2 F(\omega)]_{H(D)}$, i.e.

$$\eta_{H(D)} = 2M_{H(D)} \int [\alpha^2 F(\omega)]_{H(D)} \omega \, d\omega \tag{2}$$

with

$$[\alpha^2 F(\omega)]_{H(D)} = \frac{V}{\hbar(2\pi)^3} \frac{\int \frac{dS}{v_{\vec{k}}} \int \frac{dS'}{v_{\vec{k}}'} \sum_{\nu} |g(\vec{k}, \vec{k}', \nu)|^2 \delta(\omega - \omega_{H(D)}(\vec{q}, \nu))}{\int \frac{dS}{v_{\vec{k}}}} \tag{3}$$

where V is the volume of the sample under consideration, $v_{\vec{k}}$ the velocity of an electron in state $\vec{k}$ and $g(\vec{k}, \vec{k}', \nu)$ is the matrix element corresponding to the scattering of an electron in state $\vec{k}$ to a state $\vec{k}'$ by an optical phonon of frequency $\omega_{H(D)}(\vec{q}, \nu)$, wave vector $\vec{q}$ and polarization ν. The integrals in equation (3) are taken over the Fermi surface.

Assuming that (i) the electronic structure of PdH_x is the same as that of PdD_x and consequently that $\eta_H = \eta_D$ (since the McMillan–Hopfield parameter η does not depend on phonon frequencies but only on electronic quantities evaluated at E_F)

(ii) the weighted average $\langle \omega^2_{H(D)} \rangle$ is approximately given by $\langle \omega_{H(D)} \rangle^2$ and furthermore that

(iii) as a result of the difference in the amplitudes of the zero-point motions of hydrogen and deuterium, the force constants of the proton (deuteron)-palladium potential satisfy the relation

$$M_H \langle \omega_H \rangle^2 = 1.20 M_D \langle \omega_D \rangle^2 \tag{4}$$

Papaconstatopoulos *et al.* [7, 8] found that $\lambda_H = 0.369$ and $\lambda_D = 0.450$, i.e.

$$\frac{\lambda_D}{\lambda_H} = 1.20 \tag{5}$$

The corresponding values for the superconducting transition temperatures of the stoichiometric alloys are $T_c(PdH) = 7.9$ K and $T_c(PdD) = 9.6$ K. The calculated *relative* isotope effect $\Delta T_c/T_c \equiv 2 [T_c(PdD) - T_c(PdH)]/[T_c(PdD) + T_c(PdH)] = 0.19$ is slightly smaller than the experimental value of 0.24. In order to reproduce the experimental $\Delta T_c/T_c$ one would require an anharmonicity $M_H \langle \omega_H \rangle^2 = 1.25 M_D \langle \omega_D \rangle^2$. As shall be shown in Section II such a large difference in force constants is not confirmed by existing experimental data.

A different explanation of the inverse isotope effect has been proposed by Miller et al. [9] and Satterthwaite [10]. According to these authors the difference between the amplitude of the zero-point motion of a proton and that of a deuteron at the interstitial sites of palladium is responsible for a difference in the electronic structures of these alloys. This idea has recently received experimental support from the de Haas–van Alphen measurements of Venema [11] and Bakker et al. [12] on dilute α-phase PdH_x and PdD_x alloys. Their findings that Fermi surface sheets with a strong s-character (at the octahedral interstitial site occupied by hydrogen or deuterium in the *fcc* palladium lattice) are affected in the same way by H and D, but that *large isotope effects* are present in the hydrogen

(deuterium) concentration dependence of the size of d-like Fermi surface sheets indicate clearly that electronic states are influenced by the zero-point motion of the interstitial atoms. This implies that the assumption $\eta_H = \eta_D$ made in Refs. 5–7 is questionable. In Section III an evaluation of the difference between η_H and η_D will be made on the basis of a pseudopotential model for *PdH* and *PdD*.

II. Experimental results for the anharmonicity of the proton (deuteron)-palladium potential

For a harmonic proton-palladium potential the ratio ω_H/ω_D of the average frequencies of the optical modes in PdH_x and PdD_x should be $\sqrt{2}$. Since deviation from $\sqrt{2}$ will lead to isotope effects in the electron–phonon enhancement parameters λ and consequently in T_c, many experiments have been carried out to measure ω_H/ω_D or $M_H\langle\omega_H\rangle^2/(M_D\langle\omega_D\rangle^2)$. In this section we give a short review of existing data obtained from neutron scattering, superconducting tunnelling and Raman scattering and present new data derived from thermal expansion, elastic moduli and point-contact spectroscopy measurements on α'-phase PdH_x and PdD_x ($x \gtrsim 0.66$).

(a) *Existing data*

Rahman et al. [13] measured the incoherent scattering of neutrons on a polycrystalline $PdH_{0.63}$ sample. From a comparision of these data with the *incoherent* scattering line shape derived from a "non-stoichiometric lattice dynamics" model fitted to the *coherent* neutron scattering data for $PdD_{0.63}$ [14] they concluded that the force constant $M_H\langle\omega_H\rangle^2$ of the proton-palladium potential

Table 1

Anharmonicity of the proton (deuteron)-palladium potential in PdH_x (PdD_x) as determined by means of various experimental methods.

x_H	x_D	$M_H\omega_H^2/M_D\omega_D^2$	Experimental method	Ref.
0.63	0.63	1.20	neutron scattering	13
>0.63	>0.63	1.09	neutron scattering	20
0.63	0.63	1.10*)	neutron scattering	13, 16
0.79	0.75	1.09	Raman scattering	17
0.93	0.96	1.14 ± 0.06	superconducting tunneling	18
0.97	0.94	0.92; 1.11	superconducting tunneling	19
0.99	0.95	1.13 ± 0.23	electrical resistivity	21
0.65	0.66	1.14 ± 0.03	thermal expansion	22
0.66	0.65	1.09 ± 0.06	elastic moduli	23
0.63	0.67	1.07 ± 0.05	point-contact spectroscopy	27

*) This value is derived from the maxima of the incoherent-scattering lines as presented in Fig. 1 of Ref. 13 and Fig. 3 of Ref. 16.

was 20% higher than that of the deuteron-palladium potential. As pointed out by Rowe and Rush [15] the same lattice dynamics potential led to quantitative discrepancies for the coherent neutron scattering line shapes [16].

Since a direct determination of ω_H/ω_D by means of neutron scattering is seriously complicated by the large differences in the coherent and incoherent cross-sections of hydrogen and deuterium other spectroscopic methods such as superconducting tunneling and Raman scattering have also been used. A summary of the force constant ratios obtained by means of these techniques is given in Table 1.

For the Raman scattering data [17] the value indicated in the table corresponds to the transverse optical phonon peaks observed at $\hbar\omega_H = 58.5$ MeV and $\hbar\omega_D = 39.7$ MeV. For $\langle\omega_{H(D)}\rangle$ averaged over the whole optical phonon spectra $M_H\langle\omega_H\rangle^2/(M_D\langle\omega_D\rangle^2) < 1$ since the high energy shoulder of the spectrum in $PdH_{0.79}$ is quite smaller than in $PdD_{0.75}$.

The two values indicated for the superconducting tunneling data of Ref. 19 arise from the fact that the optical phonon signal in $PdH_{0.97}$ exhibit a double-peak structure in contrast to the data for $PdD_{0.90}$ and $PdD_{0.94}$ where only one peak is present.

(b) Thermal expansion

The contribution of optical phonons to the thermal expansion of PdH_x of PdD_x is, in the spirit of the quasi-harmonic approximation, given by

$$\left(\frac{V(T) - V_0}{V_0}\right)_{H(D)} = \frac{1}{B_0 V_0} \sum_{q, \nu} n_{H(D)}(\vec{q}, \nu)\hbar\omega_{H(D)}(\vec{q}, \nu)\gamma_{H(D)}(\vec{q}, \nu) \tag{6}$$

where $V(T)$ and V_0 are the volumes of the sample at temperature T and $T = 0$ K without the contribution of acoustic phonons but in the presence of the zero-point motion of hydrogen or deuterium. B_0 is the bulk modulus and $n(\vec{q}, \nu)$ is the Bose–Einstein distribution function. The volume Grüneisen parameter $\gamma(\vec{q}, \nu)$ is defined as

$$\gamma(\vec{q}, \nu) \equiv -\frac{\partial \ln \hbar\omega(\vec{q}, \nu)}{\partial \ln V} \tag{7}$$

Assuming that in PdD_x the optical phonon frequencies are the same as in PdH_x but scaled by a factor α such that for all $\vec{q}$ and ν

$$\omega_H(\vec{q}, \nu) = \alpha \cdot \omega_D(\vec{q}, \nu) \tag{8}$$

and further that

$$\lambda_H(\vec{q}, \nu) = \sigma \cdot \lambda_D(\vec{q}, \nu) \tag{9}$$

we find that

$$\left(\frac{V(\alpha T) - V_0}{V_0}\right)_H = \alpha \cdot \sigma\left(\frac{V(T) - V_0}{V_0}\right)_D \tag{10}$$

This scaling law is very useful to analyze experimental data. In Fig. 1 we show the optical contribution to the linear thermal expansion of $PdH_{0.65}$ and $PdD_{0.66}$ as
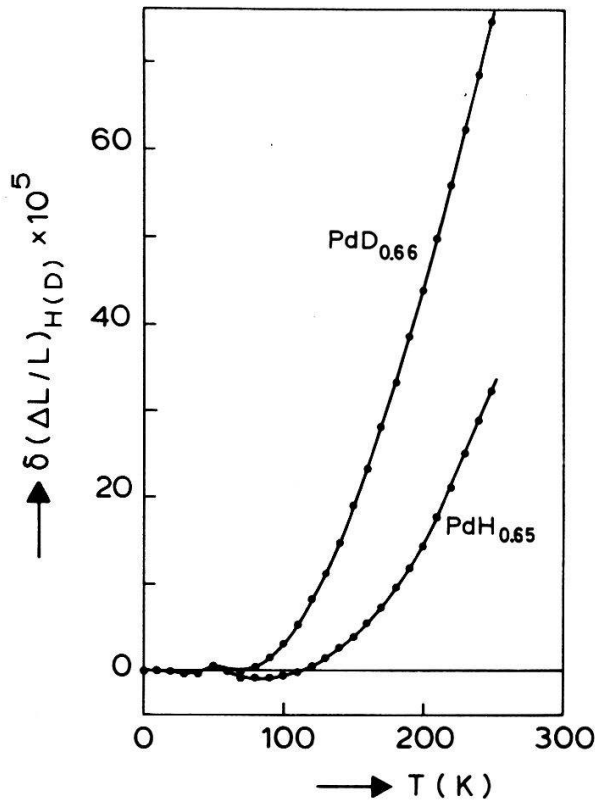
Figure 1
Contribution of optical phonons to the linear thermal expansion of $PdH_{0.65}$ and $PdD_{0.66}$. The peculiar behaviour of the curves below $\sim$100 K is due to the so-called "50 K" transition [31].

measured by Hemmes et al. [22] by means of a dual capacitance dilatometer. In the hydride the optical phonons are excited at higher temperatures than in the deuteride and therefore, at a given temperature, the thermal expansion due to optical phonons is smaller in $PdH_{0.65}$ than in $PdD_{0.66}$. Applying the scaling law (10) to the data of Fig. 1 we obtain that $\alpha = 1.51 \pm 0.02$ and thus

$$\frac{M_H \langle \omega_H \rangle^2}{M_D \langle \omega_D \rangle^2} = 1.14 \pm 0.03 \tag{11}$$

(c) *Bulk modulus*

The adiabatic bulk modulus measured in sound velocity experiments depends essentially on the *deviation* of the Grüneisen parameters $\gamma(\vec{q}, \nu)$ from their average value

$$\bar{\gamma} \equiv \frac{\sum (\beta \hbar \omega(\vec{q}, \nu))^2 n(\vec{q}, \nu)[n(\vec{q}, \nu) + 1]\gamma(\vec{q}, \nu)}{\sum (\beta \hbar \omega(\vec{q}, \nu))^2 n(\vec{q}, \nu)[n(\vec{q}, \nu) + 1]} \tag{12}$$

where $\beta = 1/(k_B t)$ (k_B is Boltzmann's constant). If one assumes that the deviation of the Grüneisen parameters in PdH_x is *proportional* to that in PdD_x then the contribution of optical phonons to the bulk modulus satisfies approximately the following scaling law

$$(B(\alpha T) - B_0)_H = \delta \cdot \alpha (B(T) - B_0)_D \tag{13}$$

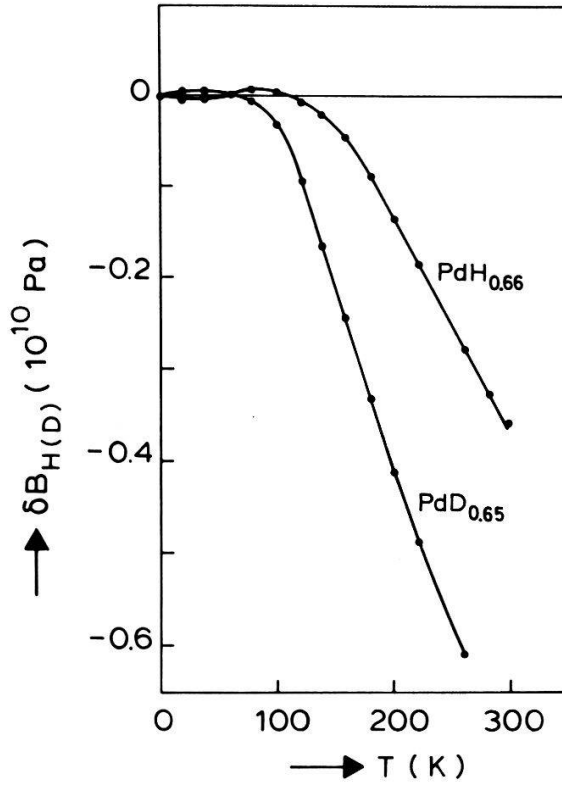By applying this relation to the bulk modulus data of Geerken et al. [23] shown in

Figure 2
Optical phonon contribution to the temperature variation of the adiabatic bulk modulus of $PdH_{0.66}$ and $PdD_{0.65}$.

Fig. 2 we obtain $\alpha = 1.48 \pm 0.04$ or equivalently

$$\frac{M_H \langle \omega_H \rangle^2}{M_D \langle \omega_D \rangle^2} = 1.09 \pm 0.06 \tag{14}$$

(d) *Point-contact spectroscopy*

All the results concerning $M_H \langle \omega_H \rangle^2/(M_D \langle \omega_D \rangle^2)$ presented so far in Section II(a), (b) and (c) (with the exception of the superconducting tunneling data given in Table 1) are strictly speaking only relevant to the anharmonicity of the proton (deuteron)-palladium potential. For a proper discussion of the origin of the inverse isotope effect in T_c one requires however the average

$$\langle \omega_{H(D)}^2 \rangle = \frac{\displaystyle\int [\alpha^2 F(\omega)]_{H(D)} \omega \, d\omega}{\displaystyle\int [\alpha^2 F(\omega)]_{H(D)} \frac{1}{\omega} \, d\omega} \tag{15}$$

Presently available superconducting tunneling data have not been inverted to provide the Eliashberg function $\alpha^2 F(\omega)$ for PdH_x and PdD_x. Dumoulin et al. [18] have only used the position of the minima in the d^2I/dV^2 characteristics of tunnel junctions to determine ω_H/ω_D and found 14% anharmonicity in the force constants.

In the last few years a new method, point-contract spectroscopy, has been shown to be a powerful tool in the investigation of the electron–phonon interaction in noble metals, simple and transition metals. In the rest of this section we

shall briefly describe this new type of spectroscopy and, from measurements on PdH_x and PdD_x, evaluate $\langle\omega_H^2\rangle$ and $\langle\omega_D^2\rangle$.

Point-contact spectroscopy has mainly been developed by Jansen, Van Gelder and Wyder [24]. It is based on the existence of alinearities in the current (I)–voltage (V) characteristic of a tiny electrical contact between two *normal* metals at low temperatures. The resistance of such a microcontact depends on the ratio of electron-mean free path l and the diameter $2a$ of the contact. In the Knudsen limit i.e. if $a/l \ll 1$, the current through the contact is to first order given by

$$I = \frac{3\pi}{4}\frac{a^2}{\rho l}\cdot V \tag{16}$$

where ρ is the resistivity of the metal. Equation (16) is usually used to estimate the contact diameter which is of the order of $100\,\text{Å}$ for a contact resistance of about $10\,\Omega$.

The non-linear behaviour of the I–V characteristic arises from higher order (in a/l) contributions to the current due to electron-phonon collisions.

Kulik et al. [25] and Van Gelder [26] have shown that for a small constriction between two pieces of normal metal with a spherical Fermi surface the second derivative d^2I/dV^2 of the I–V curve the point-contact spectrum is directly proportional to the point-contact electron–phonon coupling function according to

$$d^2I/dV^2 = -\frac{4\pi e^3}{\hbar}N(E_F)\Omega_{\text{eff}}\alpha_p^2 F(\omega) \tag{17}$$

where $N(E_F)$ is the density of states of electrons of one spin at the Fermi level and Ω_{eff} is the effective volume for phonon generation by the injected "hot" electrons. The point-contact coupling function $\alpha_p^2 F(\omega)$ is defined by

$$\alpha_p^2 F(\omega) = \frac{V}{(2\pi)^3\hbar}\frac{\displaystyle\int\frac{dS}{v_{\vec{k}}}\int\frac{dS}{v_{\vec{k}}}\sum_\nu |g(\vec{k},\vec{k}',\nu)|^2 K(\vec{k},\vec{k}')\delta(\omega-\omega(\vec{q},\nu))}{\displaystyle\int\frac{dS}{v_{\vec{k}}}} \tag{18}$$

This function is very similar to the Eliasberg electron–phonon coupling function given by equation (3) except for the Kulik weighting factor $K(\vec{k},\vec{k}')$. This factor favours heavily the backscattering of electrons since the alinearities of the I–V curve are associated with a backflow of electrons through the contact orifice.

Using a special procedure for the preparation of point-contacts between two pieces of PdH_x or PdD_x Caro et al. [27] succeeded recently in measuring for the first time the $\alpha_p^2 F$ function in a metal-hydrogen (deuterium) system.

The point-contact spectrum of $PdH_{0.63}$ at 1.5 K is presented in Fig. 3(a). The large peak at low energies is associated with the acoustic vibrations of the palladium lattice. The peak at $57\,\text{meV}$ is due to the optical phonons. This peak shifts clearly to lower energy ($39\,\text{meV}$) if hydrogen is replaced by deuterium as can be seen from Fig. 3(b).

By means of the spectra in Figs. 3(a) and (b) and equation (15) in which the Eliashberg function is replaced by the point-contact electron–phonon coupling function $\alpha_p^2 F(\omega)$ one finds that

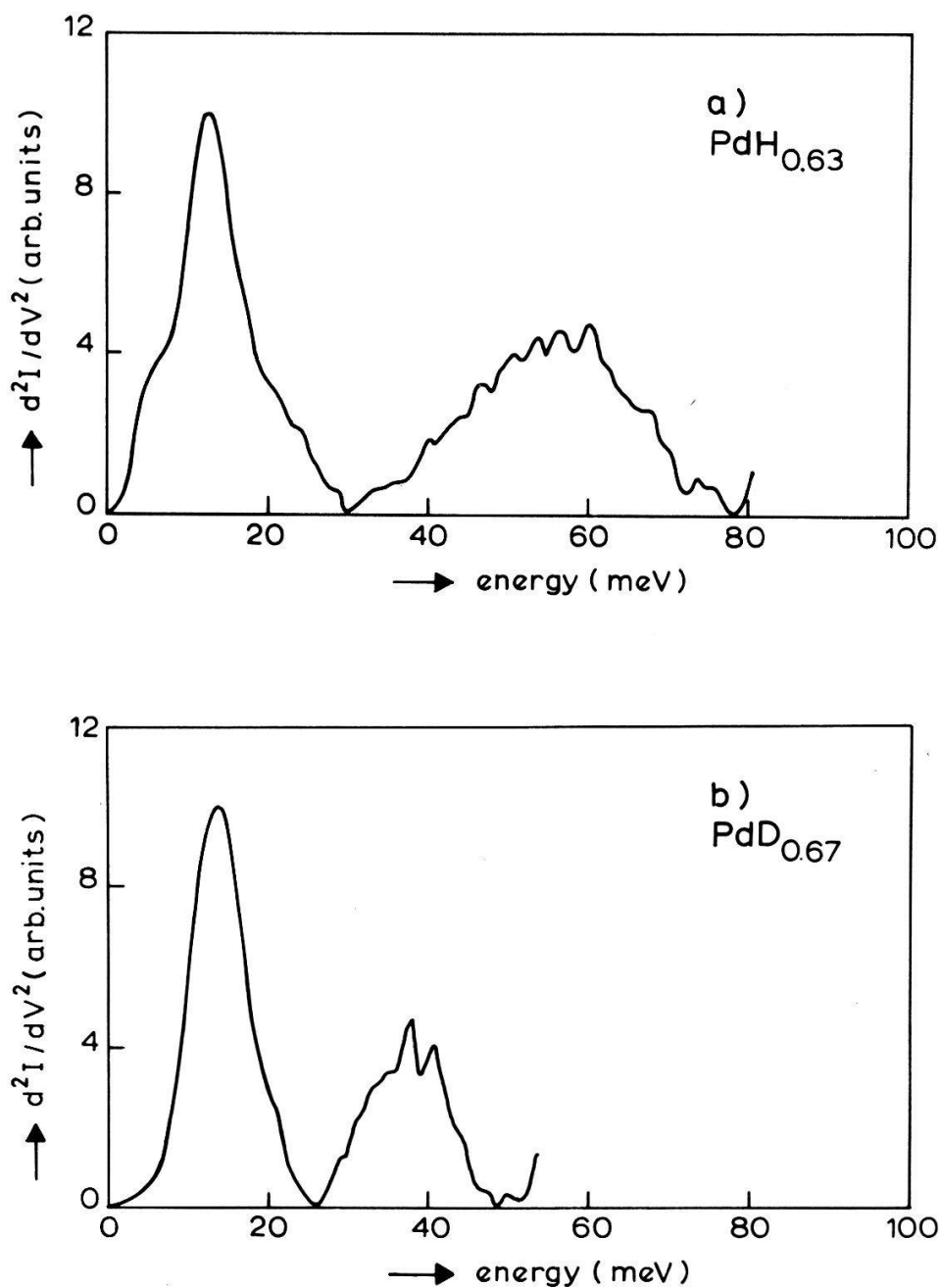$$\frac{M_H\langle\omega_H^2\rangle_p}{M_D\langle\omega_D^2\rangle_p} = 1.07 \pm 0.05 \tag{19}$$

Figure 3
Point-contact spectra of (a) $PdH_{0.63}$ and (b) $PdD_{0.67}$.

The values given in Table 1 and in eqs. (11), (14) and (19) all indicate that the proton-palladium potential is slightly stiffer than the deuteron-palladium potential. In the average one finds that the ratio of the force constants is 1.12 ± 0.05. (In fact the value given in equation (19) which is based on the correct definition of the force constant even points to a smaller anharmonicity.)

This 12% anharmonicity would lead to $\lambda_D/\lambda_H = 1.12$ and thus to an approximately two times too weak inverse isotope effect if the only effect of zero-point motion of H (or D) would be to influence the force constants of the interstitial-host potential. In the next section we show that the electron-optical phonon enhancement parameters are also significantly influenced by the zero-point motion via Debye–Waller factors.

III. Effects of Debye–Waller factor on $\lambda_{H(D)}$.

The 12% anharmonicity found in Section II is due to the relatively large zero-point motion amplitude of H and D in palladium. Anharmonicity will influence the strength of the electron-optical phonon interaction via a change of the phonon frequencies themselves and via many-phonon scattering processes. Furthermore large vibration amplitudes lead to the appearance of Debye–Waller factors in the electron–phonon matrix elements (even for a harmonic potential). All these effects are proportional to the ratio $\langle u^2 \rangle / a^2$ where $\langle u^2 \rangle$ is the average square displacement of H (or D) from its equilibrium position and a is the lattice constant of palladium. In turns out [28], however, that the principal effects are due to the renormalization of the phonon frequencies in one phonon processes (which leads to a difference in the force constant $M_{H(D)} \langle \omega^2_{H(D)} \rangle$ and to the Debye–Waller factor).

In order to evaluate the importance of Debye–Waller terms in λ we assume that the Bloch states of PdH (and PdD) near the Fermi energy are adequately described by a pseudowave function

$$\Phi_{\vec{k}}(\vec{r}) = \sum_j a_j(\vec{k}) |\vec{k} + \vec{G}_j\rangle \tag{20}$$

where $|\vec{k} + \vec{G}_j\rangle$ is a normalized planewave of wave vector $\vec{k} + \vec{G}_j$, and $\vec{G}_j$ are reciprocal lattice vectors. The coupling function $g(\vec{k}, \vec{k}', \nu)$ in equation (3) can then be written as

$$g(\vec{k}, \vec{k}, \nu) = -i \left(\frac{\hbar}{2MN\omega(\vec{q}, \nu)} \right)^{1/2} \sum_{j, 1} a_j^*(\vec{k}') a_l(\vec{k}) e^{-M_{il}(\vec{k}', \vec{k})}$$
$$\times \vec{e}(\vec{q}, \nu) \cdot (\vec{k}' - \vec{k} + \vec{G}_j - \vec{G}_l) \langle \vec{k}' + \vec{G}_j| W |\vec{k} + \vec{G}_l\rangle \tag{21}$$

where $\langle \vec{k}'| W |\vec{k}\rangle$ is the pseudopotential form factor. The quantity $M_{il}(\vec{k}', \vec{k})$ in the Debye-Waller factor in equation (21) is given by (at $T = 0$ K),

$$M_{il}(\vec{k}', \vec{k}) = \frac{\hbar^2}{4MN} \sum_{q,\nu} \frac{|\vec{e}(\vec{q}, \nu) \cdot (\vec{k}' - \vec{k} + \vec{G}_j - \vec{G}_l)|^2}{\hbar\omega(\vec{q}, \nu)} \tag{22}$$

where the summation is over the $3N$ optical modes. If the optical phonon dispersion curves in PdH and PdD are modelled by Einstein oscillators of energy $\hbar\omega_H$ and $\hbar\omega_D$ then

$$M_{il}(\vec{k}', \vec{k})_{H(D)} = \frac{\hbar}{4M_{H(D)}\hbar\omega_{H(D)}} (\vec{k}' - \vec{k} + \vec{G}_j - \vec{G}_l)^2 \tag{23}$$

The main contributions to $\alpha^2 F(\omega)$ come from large angle normal scattering processes and Umklapp processes. These processes involve large momentum changes and are strongly influenced by the Debye–Waller factor. In a single OPW-approximation the Fermi surface is a sphere, $a_j(\vec{k}) = \delta_{j,0}$ and for normal processes

$$M_{00} \cong \frac{2E_F}{\hbar\omega_{H(D)}} \cdot \frac{m}{M_{H(D)}} \tag{24}$$

where m is the mass of the electron. For Umklapp processes involving a

reciprocal lattice vector $\vec{G}$ (i.e. $\vec{k}' - \vec{k} = \vec{q} + \vec{G}$)

$$M_{00} \cong \frac{\hbar^2 G^2}{4 M_{H(D)} \hbar \omega_{H(D)}} \qquad (25)$$

In the case of stoichiometric PdH (and PdD) the Fermi surface [29] is similar to that of copper but has larger necks at the [111]-faces of the Brillouin zone. Umklapp processes which give the major contribution to $\alpha^2 F(\omega)$ will therefore involve mainly G_{200} reciprocal lattice vectors. As a rough approximation one expects that $\alpha^2 F(\omega) \propto \exp(-(1/3) G_{200}^2 \langle u_{H(D)}^2 \rangle)$ and consequently that

$$\left(\frac{\lambda_D}{\lambda_H}\right)_{\text{Debye-Waller}} \cong \exp\left(\frac{8\pi^2 \hbar^2}{a^2 M_H \hbar \omega_H}\left(1 - \frac{\omega_H}{2\omega_D}\right)\right) \qquad (26)$$

In *PdH* and *PdD* the lattice constant is $a \cong 4.13\text{Å}$ and the optical phonon energies are $\hbar\omega_H = 53\,\text{meV}$ and $\hbar\omega_D \cong 35\,\text{meV}$ [18]. The inverse isotope effect with the Debye-Waller factor is thus $(\lambda_D/\lambda_H)_{\text{Debye-Waller}} \cong 1.09$. Combining this result with the effect of anharmonicity described in Section II one obtains finally

$$\frac{\lambda_D}{\lambda_H} \cong 1.09 \times 1.12 = 1.22 \qquad (27)$$

in fair agreement with $\lambda_D/\lambda_H = 1.25$ required to reproduce the relative inverse isotope effect $\Delta T_c/T_c = 0.24$.

IV. Conclusions

The anharmonicity $M_H \omega_H^2 / M_D \omega_D^2$ of the $H(D)$-Pd potential is found to be 1.12 by averaging experimental results for neutron scattering, electrical resistivity, superconducting tunneling, Raman scattering, thermal expansion, elastic moduli and point-contact spectroscopy.

The large vibration amplitude of the interstitials in PdH_x and PdD_x makes it necessary to include Debye–Waller factors in the electron-phonon coupling functions. The ratio of the Debye-Waller factors for the electron-optical phonon processes which contribute most to $\alpha^2 F(\omega)$ (mainly Umklapp scattering involving second nearest neighbour reciprocal lattice vectors) is 1.09.

Assuming that the renormalization of phonon frequencies (as the result of anharmonicity) and the presence of Debye–Waller factors in the coupling function $g(\vec{k}, \vec{k}', \nu)$ are the main consequences of the large vibration amplitudes of H and D in palladium we estimate that $\lambda_D/\lambda_H = 1.22$. Together with $T_c(Pd) = 9\,\text{K}$, this ratio of the optical phonon contributions to λ would lead to a superconducting transition temperature of $11.2\,\text{K}$ for stoichiometric PdD in reasonable agreement with the experimental value of $11.5\,\text{K}$.

The appearance of Debye–Waller factors in λ_H and λ_D which are large enough to account for approximately half the observed inverse isotope effect in T_c raises the question whether Debye–Waller factor effects should be observable or not in other physical quantities, such as electron-impurity scattering or Fermi surface dimensions. A qualitative answer to this question can be obtained from the

following expression of the electron self-energy $\sum (k, E_F)$ [30]

$$\sum (\vec{k}, E_F) = -\frac{2\pi\hbar^2 xN}{mk_F V} \sum_{l=0}^{\infty} (2l+1)\langle F_l(\vec{k})\rangle e^{i\delta_l} \sin \delta_l \qquad (28)$$

where k_F is the Fermi wave vector and δ_l the l-phase shift of the H (or D)-scattering potential. The quantity $F_l(\vec{k})$ depends on the pseudo-wave coefficients $a_j(\vec{k})$ (see equation (20)) and on the displacement $\vec{u}$ of H (or D) from the octahedral interstitial site at $\vec{R}_0$ in the following way

$$\langle F_l(\vec{k})\rangle = \sum_{j,m} a_j^*(\vec{k})a_m(\vec{k})P_l(\cos \theta_{jm}) \exp [i(\vec{G}_j - \vec{G}_m)\vec{R}_0]$$
$$\times \exp \left[\frac{-1}{6}(\vec{G}_j - \vec{G}_m)^2\langle u^2\rangle\right] \qquad (29)$$

where θ_{jm} is the angle between $\vec{k} - \vec{G}_j$ and $\vec{k} - \vec{G}_m$ and P_l are Legendre polynomials. The main difference between the Debye–Waller factor in equation (29) and that in equation (21) is that for the self-energy the Debye–Waller factor is identically equal to one for a spherical Fermi surface while $e^{-M_{jm}(\vec{k}',\vec{k})} < 1$ for electron–phonon scattering. This is of course not surprising since the electron self-energy cannot depend on the position of the impurity immersed in a *homogeneous* electron gas. Debye–Waller effects in $\sum (\vec{k}, E_F)$ are thus only present for metals with distorted Fermi surfaces. Even then the effects are quite small. Recent de Haas–van Alphen experiments by Bakker et al. [12] on dilute PdH_x and PdD_x have shown that for the Γ-centered electron sheet there were (within experimental errors) no isotope effects in the dimension of this sheet and in the electron relaxation time. Since these two quantities are directly related to the real part and imaginary part of $\sum (\vec{k}, E_F)$ these data indicates that Debye–Waller factor effects are at most a few percent. The same conclusion holds for concentrated PdH_x and PdD_x alloys since the Γ-sheet is the only sheet of the Fermi surface of Pd which does not vanish when the hydrogen (deuterium concentration) is increased.

Note added in proof: The conclusions concerning the magnitude of the anharmonicity in the force constants i.e. $M_H\omega_H^2/(M_D\omega_D^2) = 1.12$ have recently been confirmed by a new analysis of neutron scattering data [32].

Acknowledgements

REFERENCES

[1] B STRITZKER and W. BUCKEL, Z. für Phys. *257*, 1 (1972).
[2] V. B GINODMAN and L. N. ZHERIKHINA, Sov. J. Low Temp. Phys. *6*, 278 (1980) (Fiz. Nizk. Temp. *6*, 582 (1980)).
[3] B N. GANGULY, Z. für Phys. *265*, 433 (1973).
[4] B. N GANGULY, Phys. Rev. B *14*, 3848 (1976).

[5] D A. PAPACONSTANTOPOULOS and B. M. KLEIN, Phys. Rev. Letters *35*, 110 (1975).

[6] B M. KLEIN, E. N. ECONOMOU and D. A. PAPACONSTANTOPOULOS, Phys. Rev. Letters *39*, 574 (1977).

[7] D. A. PAPACONSTANTOPOULOS, B. M. KLEIN, E. N. ECONOMOU and L. L. BOYER, Phys. Rev. B *17*, 141 (1978).

[8] D. A. PAPACONSTANTOPOULOS, B. M. KLEIN, J. S. FAULKNER and L. L. BOYER, Phys. Rev. B *18*, 2784 (1978).

[9] R. J. MILLER and C. B. SATTERTHWAITE, Phys. Rev. Letters *34*, 144 (1975).

[10] C. B. SATTERTHWAITE, Phys. Stat. Sol. (a) *43*, K147 (1977).

[11] W. J. VENEMA, thesis (Vrije Universiteit Amsterdam) 1980.

[12] H. L. M. BAKKER, R. FEENSTRA, R. GRIESSEN, L. M. HUISMAN and W. J. VENEMA, Phys. Rev. B *26*, 5321 (1982).

[13] A. RAHMAN, K. SKÖLD, C. PELIZZARI, S. K. SINHA and H. FLOTOW, Phys. Rev. B *14*, 3630 (1976).

[14] J. M. ROWE, J. J. RUSH, H. G. SMITH, MARK MOSTOLLER and H. E. FLOTOW, Phys. Rev. Letters *33*, 1297 (1974).

[15] J. M. ROWE and J. J. RUSH, *Neutron Inelastic Scattering* 1977, PtII, Vienna, Austria, 17–21 Oct. 1977, (OAEA 1978), p. 303.

[16] C. J. GLINKA, J. M. ROWE, J. J. RUSH, A. RAHMAN, S. K. SINHA and H. E. FLOTOW, Phys. Rev. B *17*, 488 (1978).

[17] R. SHERMAN, H. K. BIRNBAUM, J. A. HOLY and M. V. KLEIN, Phys. Letters *62A*, 353 (1977).

[18] L. DUMOULIN, P. NÉDELLEC, C. ARZOUMANIAN and J. P. BURGER, Phys. Stat. Sol. b *90*, 207 (1978).

[19] B. STRITZKER and H. WÜHL, *Hydrogen in Metals II*, ed. G. Alefeld and J. Völkl, Springer-Verlag 1978, p. 243.

[20] J. J. RUSH, private communications.

[21] P. NÉDELLEC, L. DUMOULIN, C. ARZOUMANIAN and J. P. BURGER, J. de Physique C6, *39*, 432 (1978).

[22] H. HEMMES, B. M. GEERKEN and R. GRIESSEN, to be published.

[23] B. M. GEERKEN, R. GRIESSEN, L. M. HUISMAN and E. WALKER, Phys. Rev. B *26*, 1637 (1982).

[24] A. G. M. JANSEN, A. P. VAN GELDER and P. WYDER, J. Phys. C:Sol. St. Phys. *13*, 6073 (1980).

[25] I. O. KULIK, A. N. OMEL'YANCHUK and R. I. SHEKHTER, Sov. J. Low Temp. Phys. *3*, 740 (1977) (Fiz. Nizk. Temp. *3*, 1543 (1977)).

[26] A. P. VAN GELDER, Sol. St. Comm. *25*, 1097 (1978).

[27] J. CARO, D. G. DE GROOT and R. GRIESSEN, to be published.

[28] A. E. KARAKOZOV and E. G. MAKSIMOV, Sov. Phys. JETP *47*, 358 (1978) (Zh. Eksp. Teor. Fiz. *74*, 681 (1978)).

[29] M. GUPTA and A. J. FREEMAN, Phys. Rev. B *17*, 3029 (1978).

[30] R. SORBELLO, Sol. St. Comm. *39*, 487 (1981).

[31] R. A. BOND and D. K. ROSS, J. Phys. F:Met. Phys. *12*, 597 (1982).

[32] L. E. SANSORES, J. TAGÜENA-MARTINEZ and R. A. TAHIR-KHELI, J. Phys. C: Sol. St. Phys. *15*, 6907 (1982).