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# Contribution of optical phonons to the elastic moduli of $PdH_x$ and $PdD_x$

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Sound-velocity and ultrasonic-attenuation measurements were carried out on dilute $\alpha$-phase and concentrated $\alpha'$-phase $PdH_x$ and $PdD_x$ alloys between 10 and 300 K. Both the bulk modulus $B$ and the angular shear modulus $C_{44}$ of $\alpha'$-$PdH_x(PdD_x)$ are lower than those of pure Pd, as expected from the lowering of the acoustic-phonon branches at the Brillouin-zone boundary observed in neutron scattering experiments. The tetragonal shear modulus $C'$, on the other hand, increases with hydrogen or deuterium concentration. As a consequence, at 0 K the Debye temperatures of $PdD_{0.652}$ and $PdH_{0.66}$ are almost equal to that of Pd ($\Theta^D=276$ K). A marked isotope effect is found in the temperature variation of all elastic moduli, the temperature coefficients $dC_{ij}/dT$ being significantly more negative for the deuterides. This isotope effect, which is due to the different energies of the optical phonons in $PdH_x$ and $PdD_x$, is well described by a quasiharmonic model in which the transverse- and longitudinal-optical phonons are treated as Einstein oscillators with different Grüneisen parameters $\gamma_t$ and $\gamma_l$. The Einstein temperatures are $\Theta_t^H=650$ K, $\Theta_l^H=910$ K in $PdH_{0.66}$, and $\Theta_t^D=450$ K, $\Theta_l^D=640$ K in $PdD_{0.652}$. Our analysis implies that $|\gamma_l-\gamma_t|$ is large compared to the average optical-phonon Grüneisen parameter $\bar{\gamma}=\frac{1}{3}(\gamma_l+2\gamma_t)$ determined from thermal-expansion measurements. For the longitudinal mode $C_L$ the ultrasonic attenuation exhibits a maximum around 220 K which is interpreted as being due to a reorientation of pairs or clusters of vacancies in the hydrogen sublattice under uniaxial strain. For the shear modes the increase in attenuation is approximately 1 order of magnitude higher than in $C_L$. This strong temperature dependence of the attenuation has, however, no measurable influence on the $C_{ij}$.

## I. INTRODUCTION

An accurate description of the proton—host-metal ion potential is required for a good understanding of the properties of metal hydrides, many of them exhibiting remarkable isotope effects. Most of our knowledge of this potential comes from neutron scattering measurements of the frequency of the hydrogen (or deuterium) vibration in a lattice. Additional information on the proton—host-metal ion potential has also been derived from measurements of the thermal expansion or elastic moduli, or from the hydrogen (deuterium) concentration dependence of the equilibrium lattice spacing of the host metal. For all the transition-metal hydrides investigated so far the absorption of H or D produces a substantial dilation of the host lattice. Since the mode-Grüneisen parameters are normally positive, this dilation of the lattice is expected to result in a lowering of the phonon frequencies. For $PdH_x$ (and $PdD_x$), however, neutron scattering experiments show that the frequency $\omega_t^H$ (or $\omega_t^D$) of the transverse-optical phonons remains constant for alloys in the $\alpha'$ phase. As shown in Fig. 1., data obtained from superconducting tunneling seem to indicate that a decrease in $\omega_t^H$ (and $\omega_t^D$) occurs only above 90 at. % H or D in Pd. Two characteristic features of Fig. 1, namely, the ~16% higher transverse frequency for the dilute $\alpha$-PdH(D) phase compared to that of the concentrated $\alpha'$-PdH(D) phase, and the slightly anharmonic ratio $\omega_t^H/\omega_t^D=1.04\sqrt{2}$ of transverse-optical-phonon frequencies, has been confirmed furthermore by Rush,[17] who recently obtained $\omega_t^H=68.5$ meV and $\omega_t^D=46.5$ meV for $\alpha$-PdH(D), and $\omega_t^H=59$ meV and $\omega_t^D=40$ meV for $\alpha'$-PdH(D).

The constancy of $\omega_t$ in $\alpha'$-$PdH_x$ and $PdH_x$ could be due to an anomalously small Grüneisen

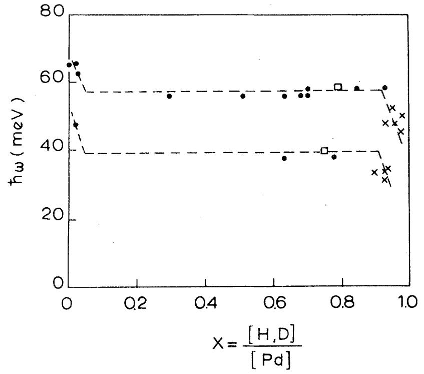

FIG. 1. Hydrogen (deuterium) concentration dependence of the transverse-optical-phonon frequencies in $PdH_x$ and $PdD_x$ [●, inelastic neutron scattering (Refs. 1–10), ×, superconducting tunneling (Refs. 11–15) □, Raman scattering (Ref. 16).]

constant or to a fortuitous cancellation of volume-dilation effects and concentration dependence of the proton-palladium interaction. In order to determine the strain dependence of the proton-palladium potential, we have investigated the temperature dependence of the elastic moduli $C_{ij}$ of both $\alpha$- and $\alpha'$-phase $PdH_x$ and $PdD_x$ alloys. Measurements of the bulk modulus $B$ are particularly interesting since the temperature derivative $dB/dT$ is proportional to $(\gamma_l - \gamma_t)^2$, where $\gamma_{l(t)}$ is the Grüneisen parameter of the longitudinal-(transverse-) optical phonons.

In addition to sound velocity we also measured ultrasonic attenuation in order to study the dynamic behavior of H or D in the metal lattice. A maximum in ultrasonic absorption is expected to occur when the mean-residence time $\tau$ of a proton (or a deuteron) is equal to the inverse sound frequency $\omega^{-1}$. In our experiment the condition $\omega\tau \cong 1$ is satisfied at approximately 220 K in $\alpha'$-phase $PdH_x$ or $PdD_x$.

This paper is organized as follows. A brief description of the experimental procedure is given in Sec. II. The experimental results presented in Sec. III are discussed in Sec. IV. The quasiharmonic model developed to analyze the data is described in Sec. V A. The various fitting procedures used to determine the Einstein temperatures and the Grüneisen parameters of longitudinal and optical phonons which enter this theoretical model are given in Sec. VB. Conclusions are given in Sec. VI.

## II. EXPERIMENTAL PROCEDURE

Two ultrasonic methods are used in this work. The absolute value of the elastic moduli are determined at room- and/or liquid-nitrogen temperature by means of a continuous-wave technique.[18] The frequency of the ultrasonic wave is varied around 30 MHz and the elastic moduli are determined with a precision of typically 1% from the frequency intervals between consecutive resonances of standing waves. The relative changes of the elastic moduli with temperature are measured by comparing the phase of a short pulse which has been reflected several times at the sample boundaries with that of the excitation signal. The accuracy is typically 0.02%. The different waves are generated by 10-MHz $X$- and $Y$-cut quartz transducers with glycerol used as a bonding agent. For comparison we also used more-permanent glues such as Loctite or UHU glue. The temperature is varied between 10 and 300 K with the use of an Oxford Instruments continuous-flow cryostat.

The cylindrical single crystals of 99.999%-pure palladium have been grown by means of a floating-zone method. They are oriented by means of Laue backscattering to within 1° in the [110] crystallographic direction and cut to a length of 20 mm by means of a low-damage spark-erosion technique. The samples are 10 mm in diameter. Their end faces are carefully polished and parallel within $10^{-4}$ of the sample length.

The alloying of palladium with hydrogen (deuterium) into the $\alpha'$ phase is carried out by absorption from the gas phase in a high-pressure cell at temperatures $\sim 25\,^\circ\mathrm{C}$ above the critical temperature $T_c$ in order to avoid segregation in $\alpha$ and $\alpha'$ phases. The hydrogen (deuterium) gas pressure is gradually increased to 30 (40) atm. The sample is kept for several hours at $T_c + 25\,^\circ\mathrm{C}$ and 30 (40) atm for proper homogenization. After this, the temperature is reduced to room temperature at a rate of 15 °C per hour. Finally, the pressure is released and the sample is electrolytically coated with a thin gold layer to prevent hydrogen (deuterium) from leaking out of the metal. Between runs the samples are stored in liquid nitrogen. The hydrogen-to-metal concentration ratio $x = [H]/[Pd]$ is determined gravimetrically with an accuracy better than 0.05 at. % by means of a microgram balance and is rechecked between runs. After each (de)hydrogenation cycle the end faces are repolished and the length of the sample is measured with a precision of $\Delta l / l \sim 10^{-4}$. The density $\rho$ of the $\alpha'$-PdH(D) samples is calculated using

$d\ln V/dx = 19\times 10^{-4}$ for the lattice expansion associated with the solution of H(D) in Pd. The thermal expansion of the alloys investigated in this work is evaluated from the results of Abbenseth and Wipf[19] on $PdH_x$ and $PdD_x$ with $0.6 \leq x \leq 0.8$.

The elastic moduli $C_{ij}$ are obtained from sound-velocity measurements by means of the following standard relations:

$$\rho v_l^2 = \tfrac{1}{2}(C_{11}+C_{12}+2C_{44}) \equiv C_L \, ,$$

$$\rho v_{t_1}^2 = C_{44} \, ,$$

$$\rho v_{t_2}^2 = \tfrac{1}{2}(C_{11}-C_{12}) \equiv C' \, ,$$

where $v_l$, $v_{t_1}$, and $v_{t_2}$ are the velocities of the longitudinal and the two nondegenerate transverse modes of a sound wave propagating in the [110] direction.

## III. EXPERIMENTAL RESULTS

Figures 2, 3, and 4 show the temperature dependence of $C_L$, the tetragonal shear modulus $C'$, and the angular shear modulus $C_{44}$ for pure palladium and various $PdH_x$ and $PdD_x$ alloys. The temperature dependence of the bulk modulus

$$B = C_L - C_{44} - \tfrac{1}{3}C'$$

is shown in Fig. 5. All elastic moduli of Pd and the $C_L$ and $B$ of $PdH_{0.66}$ agree within about 1% with those of Hsu and Leisure.[20] The deviations of the $C_{44}$ and $C'$ of $PdH_{0.66}$ are slightly larger.

One general feature of the curves shown in Figs. 2–5 is that the temperature variation of the elastic moduli is markedly larger for the concentrated hydrides and deuterides than for pure palladium. At 250 K, for example, the absolute value of the temperature coefficient $d\ln B/dT$ of the bulk modulus of pure palladium is approximately 2 times smaller than that of $PdH_{0.66}$ and almost 3 times smaller than that of $PdD_{0.652}$. For the other elastic moduli the differences between pure palladium and the interstitial alloys are even more noticeable. Above ~100 K the temperature coefficient $d\ln C_{44}/dT$ of Pd is opposite to that of $\alpha'$-PdH(D). The minimum around 100 K in the $C_{44}(T)$ curve of palladium has disappeared and the angular shear modulus of $\alpha'$-PdH(D) alloys exhibits a "normal" decrease with temperature. A similar behavior is found for the tetragonal shear constant $C'$. The point of inflexion in the $C'(T)$ curve of palladium does not show up in the hydrides and deuterides.

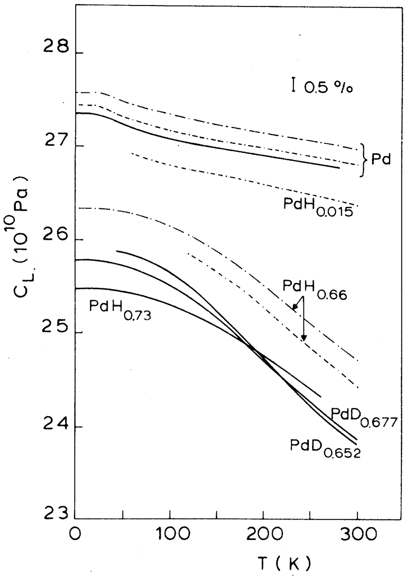

FIG. 2. Temperature dependence of $C_L$ in Pd, $PdH_{0.73}$, and $PdD_{0.652}$ (solid lines). The results are compared with previously obtained data (Ref. 50) (· — — · — —) and those of Hsu and Leisure (Ref. 20) (— · — · — ·). The estimated absolute error is indicated in the upper right corner while the relative error for the temperature dependence itself is at least 1 order smaller.

In spite of the small range of concentrations corresponding to homogeneous phases in $PdH_x$ or $PdD_x$, it is nevertheless possible to see that the temperature coefficients of the volume-conserving

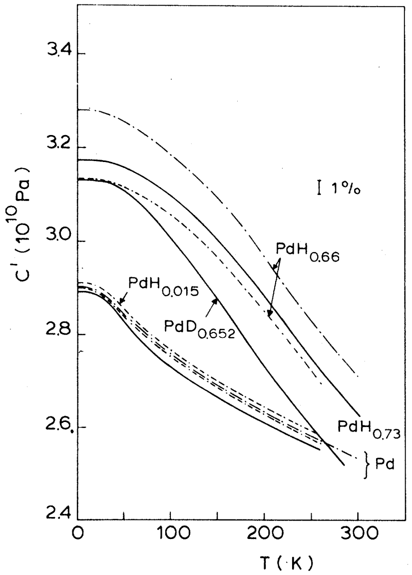

FIG. 3. As in Fig. 2, but for $C'$.

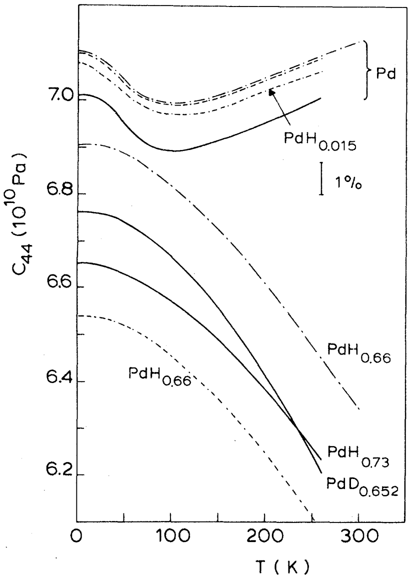

FIG. 4. As in Fig. 2, but for $C_{44}$.

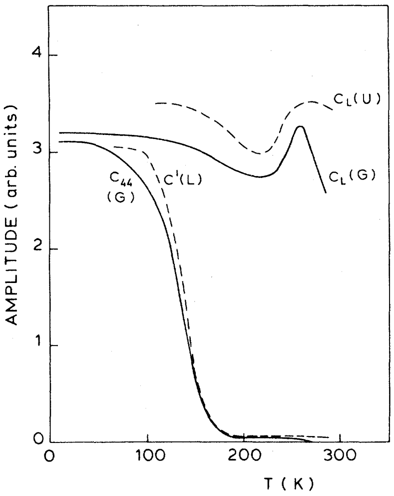

FIG. 6. Temperature dependence of the amplitude of the ultrasonic waves corresponding to different elastic moduli of $\alpha'$-PdD using boundings such as glycerol (G), Loctite (L), and one-component UHU (U).

shear deformations hardly depend on the hydrogen concentration, in contrast to that of $C_L$ and $B$ above approximately 100 K (compare $PdH_{0.66}$ and $PdH_{0.73}$ in Figs. 2 and 5). Another clear difference between the shear modes and the longitudinal mode is illustrated in Fig. 6 where some typical curves of the temperature dependence of the *amplitude* of the first ultrasonic echo are shown. The longitudinal-mode amplitude has a weak minimum around 220 K. In order to make sure that this temperature variation is not due to the bonding material (glycerol) used to couple the transducer to the crystal, the same experiments were repeated with bonding materials that do not soften around room temperature, such as Loctite and one-component UHU glue. Figure 6 shows that the bonding material has almost no effect on the dip around 220 K. Above 250 K, however, the softening of the glycerol bond causes rapid decrease of the amplitude with temperature. This amplitude reduction is not observed when UHU is used as bonding agent. For clarity, only the amplitude of the first echo has been shown in Fig. 6. The minimum at 220 K is, however, a general feature which is even stronger in higher-order echoes. The $\alpha'$-PdH results are the same as those of $\alpha'$-PdD, within experimental accuracy.

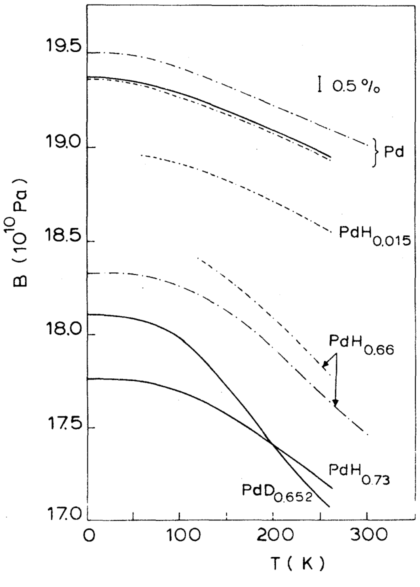

FIG. 5. As in Fig. 2, but for $B$.

In contrast to the weak temperature dependence of the amplitude of the longitudinal-mode echoes, the corresponding curves for the shear modes show a pronounced reduction in the amplitude of the echo pattern around 150 K. Above 200 K the amplitude remains very low (but large enough for sound-velocity measurements). Even with Loctite or UHU bonds the amplitude does not increase when approaching room temperture. A similar behavior is reported by Fisher *et al.*[21] for Nb-Ta-H and Nb-V-H alloys. For alloys with [H]/[*M*] $>0.03$ the echoes even fall under the detection limit of their ultrasonic apparatus.

## IV. DISCUSSION OF EXPERIMENTAL RESULTS

### A. Concentration dependence of the elastic moduli at $T=0$ K

By extrapolating the measured $C_{ij}$(T) curves to 0 K, one obtains the concentration dependence of the elastic moduli presented in Fig. 7. The moduli $B$, $C_L$, and $C_{44}$ are lower in $PdH_x$ and $PdD_x$ than in pure palladium while $C'$ increases with H(D) content. This behavior is just opposite to that observed for the elastic moduli of the group-V transition-metal hydrides where $C'$ decreases upon hydrogenation and $B$, $C_L$, and $C_{44}$ are reported to be concentration independent by some authors,[22] or to increase with increasing hydrogen content by others.[23–26]

The difference between $PdH_x$ and the group-V metal hydrides is due to a different $d$-band filling in these alloys. As shown by Ducastelle,[27] the bulk modulus $B$ of transition metals of the same row of the Periodic Table exhibits a parabolic dependence on the number of $d$ electrons. $B$ is maximum for five electrons in the $d$ band. As addition of H(D) increases the electron-to-atom ratio, one concludes, within the framework of this model, that $B$, $C_L$, and $C_{44}$ behave "normally" since $V$, Nb, and Ta have a less than half-filled $d$ band and Pd has almost ten $d$ electrons.

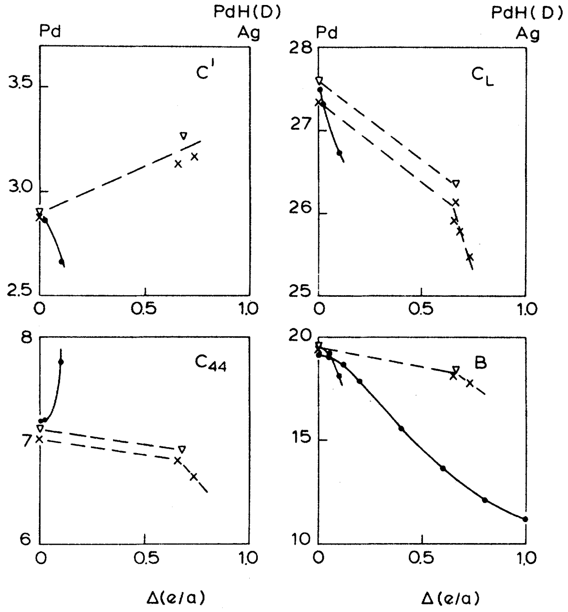

FIG. 7. Concentration dependence of the elastic moduli of $PdH_x(D_x)$ (× this work and ∇ Ref. 20) compared to that of the substitutional alloys $Pd_{1-y}Ag_y$ (●, Refs. 51 and 52) in units of $10^{10}$ Pa. The dashed lines serve as a guide to the eye.

If band filling were the only relevant parameter, one would expect the same concentration dependence of $C_{ij}$ in $PdH_x$ and in the isoelectronic $Pd_{1-x}Ag_x$ substitutional alloys. In Fig. 7 one observes, however, that $B(\alpha'\text{-PdH(D)})$ is significantly larger than $B(Pd_{0.3}Ag_{0.7})$. This difference in bulk modulus cannot result from a volume effect since the Pd-Pd interatomic distance in $PdH_x$ is larger than in $Pd_{1-x}Ag_x$. The isotropic compression needed to reduce the equilibrium volume of $PdH_x$ to that of $Pd_{1-x}Ag_x$ would even increase this difference as $d\ln B/d\ln V<0$. This quantitative disagreement is likely to be of electronic origin. The band structures of $Pd_{1-x}Ag_x$ and $PdH_x$ are known to be quite different. In addition to an upwards shift of the Fermi energy relative to the top of the $d$ band upon adding hydrogen to palladium, the palladium states with $s$ symmetry at the octahedral site are lowered in energy, forming a low-lying Pd—H bonding band.[28] As a result, the hybridization contribution to the cohesive energy[29] is larger in $PdH_x$ than in $Pd_{1-x}Ag_x$. One would expect then a smaller atomic volume for the hydride but instead, one finds that the lattice constant of $PdH_x$ is larger than that of $Pd_{1-x}Ag_x$. This indicates that the repulsive contribution is stronger in the hydride as well. This increased repulsion results then in the observed larger bulk modulus in the hydride, as it is well known[27,29,30] that $B$ is dominated by the repulsive term in the cohesive energy.

In both the group-V metal hydrides and palladium hydride, the concentration dependence of $C'$ behaves abnormally in terms of the $d$-band filling model mentioned above. While for bcc metal hydrides it is conceivable that in the temperature range where the experiments have been carried out the anomalous concentration dependence of $C'$ is due to a relaxation effect (e.g., Snoek effect), such an explanation is not applicable to $PdH_x$ and $PdD_x$ for which $C'$ is anomalous even at $T=0$ K.

### B. Debye temperatures and acoustic-phonon spectra

From thermal-expansion data below 10 K, Smith and White[31] found that the lattice contribution to the linear thermal-expansion coefficient $\alpha=(1/l)(dl/dT)$ was approximately the same in $PdH_{0.66}$ and pure palladium. The same conclusion was reached by Mackliet and Schindler[32] from their measurements of the specific heat at low temperatures. This is confirmed by the present measurements of $C_{ij}$ which lead to $\Theta_D(\mathrm{Pd})=276\pm2$ K, $\Theta_D(\mathrm{PdH_{0.66}})=278\pm2$ K, and $\Theta_D(\mathrm{PdD_{0.652}})=280\pm2$ K for the Debye temperatures determined by means of the Launay's[33] method. The constancy of $\Theta_D$ is the result of an almost perfect cancellation of the increase in $C'$ and the decrease in $C_L$ and $C_{44}$ upon hydrogenation. The increase in $C'$ implies that in the *long-wavelength limit* the lowest transverse-acoustic branch $T_1$ of $\mathrm{PdD_{0.652}}$ lies *above* that of Pd (see also Rowe[34]). Neutron scattering data show, however, that the phonon frequencies at the *boundary* of the Brillouin zone are 15–20% lower in the deuteride than in pure Pd. This leads to a strongly temperature-dependent Debye temperature.

The large difference in the hydrogen concentration dependence of the acoustic-phonon frequencies at the center and at the Brillouin-zone boundaries can be qualitatively understood by means of a simple spring model for a fcc lattice. In such a model, $B$, $C_L$, $C_{44}$, and the phonon frequencies at the Brillouin-zone boundary are essentially determined by the first-nearest-neighbor force constant $\mathrm{K}_1$, while $C'$ depends sensitively on the second-nearest-neighbor force constant $\mathrm{K}_2$ (for example, $B\sim\mathrm{K}_1-\mathrm{K}_2$, $C_L\sim\mathrm{K}_1-(\frac{4}{5})\,\mathrm{K}_2$, $C_{44}\sim\mathrm{K}_1$, but $C'\sim\mathrm{K}_1+4\,\mathrm{K}_2$). The dilation of the lattice upon H(D) absorption results in a weakening of $\mathrm{K}_1$. The presence of an interstitial between a given Pd ion and its second-nearest neighbor, on the other hand, leads to a hardening of $\mathrm{K}_2$. For $C'$ the increase in $K_2$ is strong enough to compensate the first-nearest-neighbor force-constant weakening, and consequently, $C'$ increases with increasing concentration of interstitials (see Fig. 7).

## C. Temperature dependence of elastic moduli

As mentioned in Sec. III there is a clear isotope effect in the temperature coefficients $dC_{ij}/dT$ of $\mathrm{PdH}_x$ and $\mathrm{PdD}_x$ alloys. The isotope effect is most apparent in the temperature variation of the bulk modulus of $\mathrm{PdH_{0.66}}$ and $\mathrm{PdD_{0.652}}$ shown in Fig. 5. The slope of the $B(T)$ curve for $\mathrm{PdD_{0.652}}$ is significantly steeper than that of the corresponding hydride, and in $\mathrm{PdD_{0.652}}$ a weak point of inflexion is observed around 180 K.

Three experimental facts must be taken into consideration to identify the origin of the strong temperature dependence of the $C_{ij}$ and their dependence on the isotope mass of the interstitials.

### *1. The 50-K transition*

It is well known that around 50 K a partial ordering of the interstitials in a $\mathrm{Ni_4Mo}$ structure takes place in $\mathrm{PdH}_x$ alloys.[36,37] In an experimental study of internal friction in thin foils of $\mathrm{PdH}_x$ with $0.62\le x\le0.89$, Zimmermann[38] found that below ~50 K the temperature dependence of the Young modulus $E$ is weak (essentially that of pure Pd), but that above a certain characteristic temperature, $dE/dT$ increases abruptly to much more negative values. In spite of the much higher resolution of ultrasonic techniques compared to low-frequency beam-bending techniques, no such anomaly has been observed in our measurements. This may be due to the difference in samples (polycrystalline foils and bulk single crystals) and in hydrogen loading (electrolytic charging across the mixed-phase region in the case of Zimmermann).

### *2. Relaxation processes*

The experiments of Zimmermann showed also that there is a clear relation between a large peak at 110 K in the internal friction of $\mathrm{PdH}_x$ alloys and a "modulus defect" at approximately the same temperature in the Young modulus. Since we have also observed a strong absorption in the measurements of some of the elastic moduli (see Fig. 6) it is necessary to see whether the large $dC_{ij}/dT$ may be explained by means of relaxation effects taking place when an ultrasonic wave propagates through the sample.

According to Mazzolai *et al.*[39] the large internal-friction peak observed in $\alpha'$-PdH is due to stress-induced reorientation of pairs or clusters of vacancies with noncubic strain fields in the hydrogen sublattice. The reorientation of a pair requires a jump (or several jumps for clusters of vacancies) of an individual hydrogen. According to the standard theory of anelasticity[40] one expects a maximum in the absorption and a steplike elastic modulus defect when the angular frequency $\omega$ of the periodic stresses (or strains) applied to the sample is approximately equal to the jump frequency $\omega_p$ of the protons (more precisely when $\omega/10<\omega_p<10\omega$). We can evaluate the temperature $T_m$ for which the absorption has its maximum value and the interval $\Delta T$ over which an anelastic contribution occurs by assuming that $\omega_p\sim1/\tau$ where $\tau$ is the mean residence time. $\tau$ can be evaluated from the reduced diffusion constant $D_r$ because $\tau$ is equal to $b^2/6D_r$, where $b$ is the jump length. With the use of the experimental data of Mazzolai and Züchner[41] for the diffusion constant of concentrated $PdH_x$ alloys and $b = 2.87$ Å for the octahedral-octahedral site separation, we find $T_m = 220$ K and $\Delta T \approx 50$ K for the frequency $\omega = 30$ MHz used in our measurements (in Zimmermann's experiment $\omega = 300$ Hz and thus $T_m = 110$ K and $\Delta T \approx 20$ K, in agreement with the data shown in Fig. 3 of Ref. 38). These values agree very well with the data shown in Fig. 6 for $PdD_x$.

As mentioned in Sec. III, the maximum in the absorption for $PdH_x$ occurs at approximately the same temperature as for $PdD_x$. This is not surprising since $\tau = \tau_0 e^{E_a/kT}$ varies over many decades between cryogenic and room temperature as a result of the relatively large activation energy $E_a = 0.22$ eV for a jump from one octahedral site to another.

It would be natural at this point to attribute the large differences between $dB/dT$ in Pd and in $PdH_{0.66}$ (and $PdD_{0.652}$) to some relaxation process in the sample. The corresponding modulus defect would then approximately be given by

$$\delta B_{H(D)}(T) = B_{Pd}(T) - B_{PdH_x(D_x)}(T) - \left[ B_{Pd}(0) - B_{PdH_x(D_x)}(0) \right] , \quad (2)$$

and from

$$T_m(PdH_x) \cong T_m(PdD_x) ,$$

it would follow that $\delta B_H(T)$ should be proportional to $\delta B_D(T)$. However, as shown in Fig. 8 quite a different behavior is observed, the $PdD_x$ curve being *shifted* towards lower temperatures by a factor of $\sim 1.45$ relative to the $PdH_x$ curve. Such a large *shift* cannot be understood within a relaxation model.

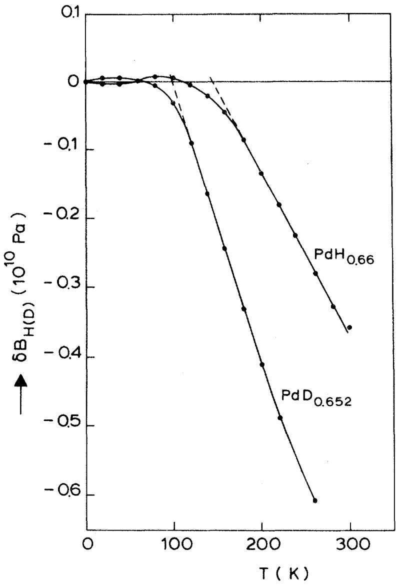

FIG. 8. Temperature variation of the bulk moduli differences $\delta B$ for $PdH_{0.66}$ (Ref. 20) and $PdH_{0.652}$ according to Eq. (2).

In the following we shall therefore assume that, in spite of the large ultrasonic absorption in $C_{44}$ and $C'$ (and to some extent in $C_L$), the temperature variation of the elastic moduli $C_{ij}(T)$ is *not* influenced by a stress-induced rearrangement of H ions. This conclusion is supported by the Young modulus measurements of Zimmermann,[38] where the modulus defect associated with the strain-induced relaxation of H vacancies is clearly superimposed onto a *strongly* temperature-dependent background.

### 3. *Optical phonons*

Neutron scattering experiments show that the optical phonons in $PdH_x$ and $PdD_x$ are well separated in energy from the top of the acoustic-phonon branches. The dispersion of the longitudinal-optical phonons is large as a result of the strong proton-proton interaction and the nonstoichiometry of the alloys. The transverse-optical-phonon branches, on the other hand, are rather narrow.[3] The phonon density of states has, therefore, a peak at 650 K in $PdH_x$ (450 K in $PdD_x$) with a high-energy shoulder whose top reaches about 1100 K in $PdH_x$ (750 K in $PdD_x$). The position of the density-of-states peak is approximately independent of the concentration of interstitials (see Fig. 1).

Above $\sim 100$ K (70 K) a significant number of optical phonons are excited in $PdH_x$ ($PdD_x$) and their effect on the electrical conductivity[42,43] and thermal expansion[19] has been clearly put in evidence. Figure 8 suggests that also for the elastic moduli a large contribution to $dC_{ij}/dT$ arises from the gradual excitation of optical phonons with increasing temperature. The fact that $\delta B(PdH_{0.66})$ deviates from zero at a 1.45 times higher temperature than $\delta B(PdD_{0.652})$ indicates that $M_H \omega_H^2 \approx 1.05 M_D \omega_D^2$, i.e., $\omega_H/\omega_D \approx 1.03\sqrt{2}$. In the following section we derive expressions for the contribution of optical phonons to elastic moduli.

## V. QUASIHARMONIC MODEL OF THE CONTRIBUTION OF OPTICAL PHONONS TO THE ELASTIC MODULI

### A. Theory

The difference in the temperature dependence of the elastic moduli of $PdH_x$ and $PdD_x$ is assumed to arise from the difference in the energy of the optical phonons in these alloys. In ultrasonic experiments, such as those carried out here, one measures the adiabatic elastic moduli $C_{ij}$, defined by[44]:

$$C_{ij}=\frac{1}{V}\left[\frac{\partial^2 U}{\partial\epsilon_i\partial\epsilon_j}\right]_S , \tag{3}$$

where $\{\epsilon_i\}$ is the six-component strain vector, $U$ the internal energy given by

$$U=U_0(\epsilon_i)+\sum_q(n_q+\tfrac{1}{2})\hbar\omega_q , \tag{4}$$

and $S$ the entropy, defined by

$$S=k_B\sum_q[(n_q+1)\ln(n_q+1)-n_q\ln n_q] , \tag{5}$$

with

$$n_q=(e^{\beta\hbar\omega_q}-1)^{-1} ,$$

and

$$\beta=(k_BT)^{-1} .$$

The summations are over all the phonon states and $\hbar\omega_q$ is the energy of a phonon with wave vector $q$. The frozen lattice energy $U_0$ depends only on the strain vector $\{\epsilon_i\}$. The bulk modulus $B$ is defined analogously to $C_{ij}$ with

$$(1/V)\left[\frac{\partial^2}{(\partial\epsilon_i\partial\epsilon_j)}\right]$$

replaced by

$$V\left[\frac{\partial^2}{\partial V^2}\right] .$$

In order to calculate the temperature dependence of the elastic moduli, we assume, in the spirit of the quasiharmonic approximation, that the $\omega_q$ are functions of the strain vector $\{\epsilon_i\}$, with

$$\frac{\partial\ln\hbar\omega_q}{\partial\epsilon_i}=-\gamma_q^i \tag{6}$$

or

$$\frac{\partial\ln\hbar\omega_q}{\partial\ln V}=-\gamma_q ,$$

where $\gamma_q^i$ and $\gamma_q$ are the Grüneisen parameters associated with the $C_{ij}$ and $B$, respectively. $U$ and $S$ depend on temperature explicitly through $\beta$ and implicitly through the volume dependence (thermal expansion) of $U_0$. They also depend on temperature through the volume dependence of the $\omega_q$, but that dependence is of second order in the thermal expansion[44] and can be neglected.

Under adiabatic conditions $\delta S=0$ and

$$\sum_q\beta\hbar\omega_q\left[\frac{\partial n_q}{\partial\epsilon_i}\right]_S=0 . \tag{7}$$

This equation relates the strain dependence of the temperature to the strain dependence of the phonon frequencies by

$$\left[\frac{\partial\ln T}{\partial\epsilon_i}\right]=\frac{\sum_q(\beta\hbar\omega_q)^2n_q(n_q+1)\gamma_q^i}{\sum_q(\beta\hbar\omega_q)^2n_q(n_q+1)}$$

$$\equiv\gamma^i . \tag{8}$$

Because $T$ is a scalar, the average Grüneisen constant $\gamma^i$ vanishes for a pure shear in a cubic crystal.[45] The average Grüneisen constant $\gamma$, corresponding to the bulk modulus, is defined analogously, with $\partial/\partial\epsilon_i$ replaced by $\partial/\partial\ln V$. It varies with temperature, except when all the phonon frequencies are equal (pure Einstein model) or when all the $\gamma_q$ are equal.

With the use of the adiabatic condition (Eq. 7), the elastic moduli $C_{ij}$ can be written as

$$C_{ij}=\frac{1}{V}\frac{\partial^2U_0}{\partial\epsilon_i\partial\epsilon_j}+\frac{1}{V}\sum_q\left[n_q+\frac{1}{2}\right]\frac{\partial^2\hbar\omega_q}{\partial\epsilon_i\partial\epsilon_j}$$

$$-\frac{1}{V\beta}\sum_q(\beta\hbar\omega_q)^2n_q(n_q+1)$$

$$\times(\gamma_q^i-\gamma^i)(\gamma_q^j-\gamma^j) . \tag{9}$$

The first term on the right-hand side of this equation depends implicitly on the phonons through the zero-point motion and thermal expansion because it has to be evaluated at the actual volume $V(T)$ given by

$$V(T)=V_0\left[1+\frac{1}{B_0}\sum_q(n_q+\tfrac{1}{2})\frac{\hbar\omega_q}{V_0}\gamma_q\right] , \tag{10}$$

where $V_0$ and $B_0$ are the volume and the bulk modulus of the crystal at $T=0$ K and in the absence of zero-point motion. We find

$$\frac{1}{V}\frac{\partial^2 U_0}{\partial\epsilon_i\partial\epsilon_j}=C_{ij}^0+[V(T)-V_0]\frac{\partial}{\partial \mathrm{V}}C_{ij}^0$$

$$=C_{ij}^0+\frac{C_{ij}^0}{B_0\mathrm{V}_0}\frac{\partial \ln C_{ij}^0}{\partial \ln V}\sum_q\left[n_q+\frac{1}{2}\right]\hbar\omega_q\gamma_q\ . \tag{11}$$

The expressions for the bulk modulus are analogous to those for $C_{ij}$, with $\gamma_q^i$ and $\gamma^i$ replaced by $\gamma_q$ and $\gamma$, respectively, $(1/V)[\partial^2/(\partial\epsilon_i\partial\epsilon_j)]$ replaced by $V(\partial^2/\partial \mathrm{V}^2)$, and $C_{ij}^0$ by $B_0$.

One often makes the additional assumption[46,47] that the occupation numbers $n_q$ themselves do not depend on the strain state of the crystal. This is equivalent to assuming that all the Grüneisen constants $\gamma_q^i$ or $\gamma_q$ are equal to their average ($\gamma^i$ or $\gamma$, respectively), and consequently, vanish for pure shears. Also, the terms proportional to $n_q(n_q+1)$ vanish identically when the $\gamma_q$ are equal. These terms describe the redistribution in the occupancy of the phonon states[48] due to the relative shifts of the phonon energies, as is shown by the fact that these terms depend only on the *deviation* of the Grüneisen constants from their average value. As will become clear in Sec. V B, they are, however, essential for the explanation of the experimental data.

The elastic moduli $C_{ij}$ can be written as

$$C_{ij}=C_{ij}^0+C_{ij}^{\mathrm{ac}}+C_{ij}^{\mathrm{opt}}\ , \tag{12}$$

where $C_{ij}^0$ is the contribution of the frozen lattice, and $C_{ij}^{\mathrm{ac}}$ and $C_{ij}^{\mathrm{opt}}$ that of the acoustic and optical phonons, respectively. The bulk modulus has a fourth contribution, $B^{\mathrm{mix}}$, which describes the redistribution between the acoustic- and optical-phonon modes, due to the compression of the lattice. This term, however, is small and will be neglected.

In order to obtain tractable expressions, we assume here that the optical-phonon dispersion curves can be described by two Einstein oscillators with frequencies $\omega_t$ (transverse phonons) and $\omega_l$ (longitudinal phonons). We cannot assume that there are only two optical *shear* Grüneisen constants, one for the longitudinal modes and one for the transverse modes, because the sum of $\gamma_q^i$ over the star of $q$ has to vanish for a pure shear.[45] We will assume, however, that there are only two *volume* Grüneisen constants, denoted by $\gamma_l$ and $\gamma_t$.

The optical contribution to the $C_{ij}$ can now be written as

$$C_{ij}^{\mathrm{opt}}=\frac{Nx}{\beta}\left[F_1^l\left[\gamma_l\frac{C_{ij}^0}{B_0V_0}\frac{\partial\ln C_{ij}^0}{\partial\ln V}+\left\langle\frac{1}{\hbar\omega}\frac{\partial^2\hbar\omega}{\partial\epsilon_i\partial\epsilon_j}\right\rangle_l\right]\right.$$

$$+2F_1^t\left[\gamma_t\frac{C_{ij}^0}{B_0V_0}\frac{\partial\ln C_{ij}^0}{\partial\ln V}+\left\langle\frac{1}{\hbar\omega}\frac{\partial^2\hbar\omega}{\partial\epsilon_i\partial\epsilon_j}\right\rangle_t\right]$$

$$\left.-F_2^l\langle(\gamma^i)^2\rangle_l-2F_2^t\langle(\gamma^i)^2\rangle_t\right] \tag{13}$$

with

$$F_1^{l(t)}=(n_{l(t)}+\tfrac{1}{2})\beta\hbar\omega_{l(t)}\ , \tag{14}$$

$$F_2^{l(t)}=n_{l(t)}(n_{l(t)}+1)(\beta\hbar\omega_{l(t)})^2\ , \tag{15}$$

$$n_{l(t)}=(e^{\beta\hbar\omega_{l(t)}}-1)^{-1}\ , \tag{16}$$

and

$$\langle f\rangle_l=\frac{1}{Nx}\sum_q f_q\ ,$$

$$\langle f\rangle_t=\frac{1}{2Nx}\sum_q f_q\ , \tag{17}$$

where the sum is over the longitudinal (transverse) modes only. $x$ is the concentration of H or D, and $Nx$ is the number of protons or deuterons in the crystal. It is equal to the number of longitudinal-optical modes and equal to half the number of transverse-optical modes.

The bulk modulus is conveniently written as

$$B^{\mathrm{opt}}=\frac{Nx}{\beta V}\left[(F_1^l+2F_1^t)A\right.$$

$$\left.+\left[\frac{2F_1^lF_1^t}{F_1^l+2F_1^t}-\frac{2F_2^lF_2^t}{F_2^l+2F_2^t}\right](\gamma_l-\gamma_t)^2\right]\ , \tag{18}$$

with

$$A=\bar{\gamma}\frac{\partial\ln B_0}{\partial\ln V}+\bar{\gamma}(\bar{\gamma}+1)$$

$$-\frac{F_1^l\left\langle\frac{\partial\gamma}{\partial\ln V}\right\rangle_l+2F_1^t\left\langle\frac{\partial\gamma}{\partial\ln V}\right\rangle_t}{F_1^l+2F_1^t}\ , \tag{19}$$

and

$$\bar{\gamma}=\frac{F_1^l\gamma_l+2F_1^t\gamma_t}{F_1^l+2F_1^t}\ . \tag{20}$$

The advantage of writing $B^{\mathrm{opt}}$ this way is that the coefficient $A$ depends only weakly on temperature if $\gamma_l$ and $\gamma_t$ are temperature independent. $\bar{\gamma}$ varies then between

$$(\gamma_l+2\omega_t\gamma_t/\omega_l)/(1+2\omega_t/\omega_l)$$

at $T=0$ K and $(\gamma_l+2\gamma_t)/3$ at $T=\infty$. The temperature dependence of $B$ arises therefore, almost entirely from the factors in front of $A$ and $(\gamma_l-\gamma_t)^2$.

### B. Fit to the experimental data

As mentioned in Sec. IV B the Debye temperature determined from low-temperature data is significantly higher than that derived from the total acoustic-phonon spectrum. This implies that the contribution of optical phonons cannot be obtained by substracting from the $C_{ij}$ the acoustic contribution of a Debye model fitted to the low-temperature ($T<80$ K) part of the $C_{ij}(T)$ curves. Under these circumstances it is better to consider the differences

$$\Delta C_{ij}(T)=C_{ij}(T,\mathrm{PdH}_x)-C_{ij}(T,\mathrm{PdD}_x)-[C_{ij}(0,\mathrm{PdH}_x)-C_{ij}(0,\mathrm{PdD}_x)]\ , \tag{21}$$

which are independent of the acoustic modes. The $\Delta C_{ij}$ obtained from the experimental data in Figs. 3, 4, and 5 are shown in Fig. 9. For all three moduli, $\Delta C_{ij}$ is very small at low temperatures, as expected from the variation of the functions $F_1$ and $F_2$ which are essentially zero for $T\lesssim\Theta_E/6$ (the Einstein temperature $\Theta_E$ is approximately 450 K for the optical-transverse phonons in $\mathrm{PdD}_x$).

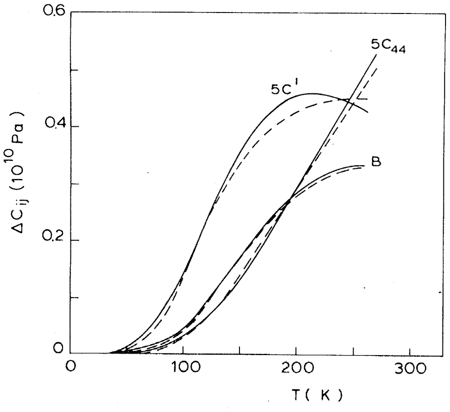

FIG. 9. Elastic moduli differences $\Delta C_{ij}(T)$ according to Eq. (21). The experimental data are represented by full lines and the fits are given by dotted lines.

The most striking feature of the curves in Fig. 9 is, however, the large difference in the temperature variation of $\Delta C_{ij}$ for the shears. $\Delta C'(T)$ increases much more rapidly than $\Delta C_{44}$ and reaches a maximum around 200 K. $\Delta C_{44}$, on the other hand, is a smoothly increasing function without maximum or point of inflexion. The curve for $\Delta B(T)$ shows an intermediate variation.

We shall show now that the differences in $\Delta C_{ij}(T)$ can be fitted by means of the expressions derived in the preceeding section. The purpose of such a fit is (i) to obtain information on the strain dependence of the optical phonons, and (ii) to show that optical phonons are indeed responsible for the large temperature dependence of $C_{ij}$. The fit procedure is as follows:

*(i) Bulk modulus.* Equation (18) shows that $\Delta B(T)$ can be cast in the form

$$\Delta B(\mathrm{T})=f(T,\Theta_l^{\mathrm{H}},\Theta_t^{\mathrm{H}},\Theta_l^{\mathrm{D}},\Theta_t^{\mathrm{D}})A+g(T,\Theta_l^{\mathrm{H}},\Theta_t^{\mathrm{H}},\Theta_l^{\mathrm{D}},\Theta_t^{\mathrm{D}})(\gamma_l-\gamma_t)^2\ , \tag{22}$$

if the contribution of $B^{\mathrm{mix}}$ is negligible and if $\gamma^i(\mathrm{PdH}_x)=\gamma^i(\mathrm{PdD}_x)$. $\Theta_l^{\mathrm{H(D)}}$ is the Einstein temperature of the longitudinal-optical phonons, in $\mathrm{PdH}_x(\mathrm{PdD}_x)$ and $\Theta_t^{\mathrm{H(D)}}$ the Einstein temperature of the transverse-optical phonons. To reduce the number of fitting parameters we assume that $\Theta^{\mathrm{H}}=\sqrt{2}\Theta^{\mathrm{D}}$ both for the longitudinal and transverse phonons. The remaining parameters $\Theta_t^{\mathrm{H}}$, $\Theta_l^{\mathrm{H}}$, $A$, and $(\gamma_l-\gamma_t)^2$ are not independent since they determine the value of $B(\mathrm{PdH}_x)-B(\mathrm{PdD}_x)$ at zero temperature. Within experimental errors no isotope effect has been found at $T=0$ K and thus, from Eq. 18 it follows that

$$A=-\frac{2\Theta_l^{\mathrm{H}}\Theta_t^{\mathrm{H}}}{(\Theta_l^{\mathrm{H}}+2\Theta_l^{\mathrm{H}})^2}(\gamma_l-\gamma_t)^2\ . \tag{23}$$

Replacing $A$ in Eq. (22) by its value in Eq. (23) we obtain finally an expression of the following form for $\Delta B$:

$$\Delta B=h(T,\Theta_l^{\mathrm{H}},\Theta_t^{\mathrm{H}})(\gamma_l-\gamma_t)^2\ , \tag{24}$$

i.e., the function $\Delta B/h$ should be independent of temperature for the proper choice of $\Theta_l^{\mathrm{H}}$ and $\Theta_t^{\mathrm{H}}$. It turns out, in fact, that the quality of the fit depends strongly on $\Theta_l^{\mathrm{H}}$, but only weakly on $\Theta_t^{\mathrm{H}}$. From neutron scattering data one knows, however, that $\Theta_t^{\mathrm{H}}=650$ K. The function $\Delta B/h$ versus temperature obtained with this value for $\Theta_t^{\mathrm{H}}$ is indicated in Fig. 10 for several values of $\Theta_l^{\mathrm{H}}$. As a consequence of the sensitivity of the curves to $\Theta_l^{\mathrm{H}}$ it is possible to derive an accurate value for the Einstein temperature of the longitudinal phonons. One finds $\Theta_l^{\mathrm{H}}=910\pm10$ K corresponding to $\hbar\omega=78.5$ meV, in good agreement with the incoherent neutron scattering spectra of Ross *et al.*[3] for $\mathrm{PdH}_{0.70}$. From this fit we also obtain that

$$|\gamma_l-\gamma_t|=12.3\pm0.3 \tag{25}$$

and

$$\bar{\gamma}\left[\frac{\partial \ln B_0}{\partial \ln V}\right]+\bar{\gamma}(\bar{\gamma}+1)-\left\langle\frac{\partial\gamma}{\partial \ln V}\right\rangle=-37\ . \tag{26}$$

With $\bar{\gamma}=3.6$, and taking

$$\frac{\partial \ln B_0}{\partial \ln V}=-5\pm2$$

as for most transition metals, we find

$$\left[\frac{\partial\gamma}{\partial \ln V}\right]=34\pm6\ .$$

*(ii) Shear elastic moduli.* The difference $\Delta C_\xi(T)$ can be written in the form

$$\begin{aligned}\Delta C_\xi(T)=&f(T,\Theta_l^{\mathrm{H}},\Theta_l^{\mathrm{D}})A_l+f(T,\Theta_t^{\mathrm{H}},\Theta_t^{\mathrm{D}})A_t\\&+g(T,\Theta_l^{\mathrm{H}},\Theta_l^{\mathrm{D}})\langle(\gamma^\xi)^2\rangle_l\\&+2g(T,\Theta_t^{\mathrm{H}},\Theta_t^{\mathrm{D}})\langle(\gamma^\xi)^2\rangle_t\ ,\end{aligned} \tag{27}$$

with

$$A_i=\gamma_i\frac{C_\xi^0}{B_0}\frac{\partial \ln C_\xi^0}{\partial \ln V}+\left\langle\frac{1}{\hbar\omega}\frac{\partial^2\hbar\omega}{\partial\xi^2}\right\rangle_i\ , \tag{28}$$

if it is assumed that $A_i$, $\gamma_i$, and $\gamma_i^\xi$ do not depend on the mass of the interstitial. For a tetragonal shear, the shear parameter $\xi$ is related to the components of the strain vector through $\epsilon_1=\epsilon_2=-\xi/2$, $\epsilon_3=\xi$, $\epsilon_4=\epsilon_5=\epsilon_6=0$, and for an angular shear through $\epsilon_1=\epsilon_2=\epsilon_3=0$ and $\epsilon_4=\epsilon_5=\epsilon_6=\xi$. From a fit of Eq. (27) to the difference curves in Fig. 9, using the Einstein temperatures from the bulk-modulus fit, one obtains the following values:

$$\begin{aligned}&\langle(\gamma')^2\rangle_l=5\pm5\ ,\quad A_l'\cong0\ ,\\&\langle(\gamma')^2\rangle_t=15\pm2\ ,\quad A_t'\cong0\end{aligned} \tag{29}$$

for the tetragonal shear (corresponding to $C'$) and

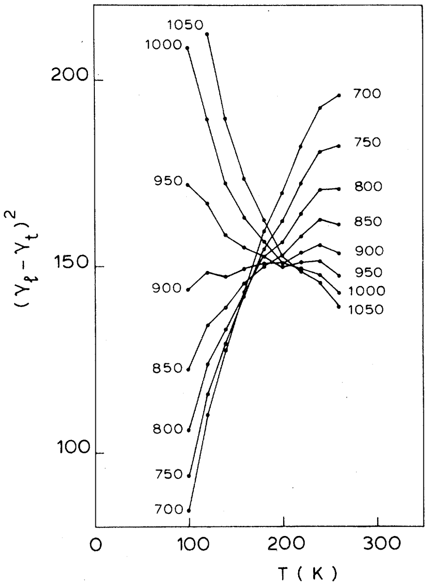

FIG. 10. Temperature variation of $(\gamma_l-\gamma_t)^2$ for different Einstein temperatures $\Theta_l^{\mathrm{H}}$ of the longitudinal-optical-phonon branch according to Eq. (24).

$$\begin{aligned}&\langle(\gamma^{44})^2\rangle_l\cong0\ ,\quad A_l^{44}=25\pm10\ ,\\&\langle(\gamma^{44})^2\rangle_t\cong0\ ,\quad A_t^{44}=13\pm2\end{aligned} \tag{30}$$

for the angular shear (corresponding to $C_{44}$). With these values for the fitting parameters, the calculated $\Delta C_{ij}$ agree within 10% with the experimental results (see Fig. 9).

One of the most surprising results of the fits described above is the very large value found for $|\gamma_l-\gamma_t|$. In order to show that this is not an artifact of the fitting procedure let us assume, as in Fig. 8, that $B^{\mathrm{opt}}(T)$ is approximately given by $\delta B(T)$ in Eq. (2), i.e., by subtracting the temperature-dependent part of the bulk modulus of $\mathrm{PdH}_x$ (or $\mathrm{PdD}_x$) from that of pure Pd. For each alloy, separately, one can then determine $|\gamma_l-\gamma_t|$ by fitting Eq. (24) to $\delta B(T)$. For $\mathrm{PdH}_{0.66}$ we obtain

$$|\gamma_l-\gamma_t|_{\mathrm{H}}=7.6\pm0.5\ , \tag{31}$$

and for $\mathrm{PdD}_{0.652}$

$$|\gamma_l-\gamma_t|_{\mathrm{D}}=10.0\pm0.5\ . \tag{32}$$

No allowance for a difference in $|\gamma_l-\gamma_t|$ between $\mathrm{PdH}_x$ and $\mathrm{PdD}_x$ was made in the fit of the difference $\Delta B$. This is the reason why the values in Eqs. (31) and (32) do not agree within experimental errors with the value of 12.3 [Eq. (25)] obtained from a fit where *a priori* $\gamma_l$ and $\gamma_t$ are assumed to be independent of the isotopic mass. The important point is, however, that for both fit procedures $|\gamma_l-\gamma_t|$ is significantly larger than the average value

$$\tfrac{1}{3}(\gamma_l+2\gamma_t)_{\mathrm{H,D}}\cong 3.3\pm 0.4 \qquad (33)$$

obtained from thermal-expansion measurements[19,31] on $PdH_x$ and $PdD_x$.

Taking $|\gamma_l-\gamma_t|=10\pm 2.5$ as an average of the values in Eqs. 25, 31, and 32, and the average $\gamma$ value of Eq. 33, we obtained two sets of possible values for $\gamma_l$ and $\gamma_t$ depending on the sign of $\gamma_l-\gamma_t$. For $\gamma_l-\gamma_t=-10$ the corresponding volume Grüneisen parameters are (i) $\gamma_l=-3.3\pm 2.1$ and $\gamma_t=6.7\pm 1.2$, and for $\gamma_l-\gamma_t=+10$ they are (ii) $\gamma_l=10\pm 2.1$ and $\gamma_t=0.0\pm 1.2$. Although the small value of $\gamma_t$ in the second set (ii) would provide us with a simple explanation of the insensitivity of the frequency of the transverse-optical phonons to changes in hydrogen or deuterium concentration, the values of set (i) have to be prefered because the value $\gamma_t=6.7$ of the first set (i) agrees reasonably well with the Grüneisen parameters determined by Blaschko *et al.*[49] for a few transverse-optical-phonon modes in $PdD_{0.71}$ (in Fig. 1 of Ref. 49, $4<\gamma_t<6$). The constancy of $\omega_t$ in $\alpha'$-$PdH_x$ and $PdD_x$ is thus probably due to a cancellation of volume-dilation effects and the concentration dependence (at constant volume) of the proton-palladium interaction potential.

So far we have only considered fits to the bulk modulus. For an angular shear it follows from simple symmetry considerations that for the phonon frequencies at point $\Gamma$ of the Brillouin zone $\partial\omega/\partial\xi_{44}\equiv 0$. The same holds for all phonon branches along the $\langle 100\rangle$ directions. The average $|\gamma_l^{44}|$ and $|\gamma_t^{44}|$ will thus be small for such deformations, in agreement with the experimental results in Eq. (30). This is also supported by the observation that for an angular shear the H-Pd separation remains unchanged for eight nearest neighbors, while in a tetragonal shear all distances between nearest neighbors are modified. Furthermore, for a tetragonal shear along [001] the degeneracy $\omega_l=\omega_t$ in the vicinity of point $\Gamma$ is lifted in such a way that

$$\gamma_l(q)=-2\gamma_t(q) \quad \text{for } \vec{q}\,||[001]$$

and

$$\begin{aligned}\gamma_l(q)&=\gamma_{t_1}(q)\\ &=-\tfrac{1}{2}\gamma_{t_2}(q) \quad \text{for } \vec{q}\,||[100]\ .\end{aligned}$$

For the average over the Brillouin zone one expects that

$$\langle\gamma^2\rangle_l\simeq\langle\gamma^2\rangle_t\neq 0\ ,$$

in qualitative agreement with the results in Eq. (29). The values obtained for the parameter $A_i$ cannot be discussed in terms of simple models as they depend on second derivatives of the phonon frequencies.

## VI. CONCLUSIONS

The sound-velocity measurements described in the previous sections have shown that the bulk modulus and the angular shear modulus $C_{44}$ decrease with increasing hydrogen or deuterium content as expected on the basis of a simple d-band-filling model. The tetragonal shear modulus $C'$, on the other hand, increases with increasing interstitial concentration. For all moduli the temperature coefficients $dC_{ij}/dT$ are significantly more negative for $PdH_x$ (or $PdD_x$) than for pure palladium. This stronger temperature variation of $C_{ij}$ is not due to a relaxation process, as one might conclude from the large ultrasonic absorption occuring around 220 K, but is due to the gradual excitation of the optical phonons. This interpretation is confirmed by the fact that the decrease in the $C_{ij}(T)$ of $PdH_x$ starts at a temperature which is approximately 1.45 times higher than in $PdD_x$. This implies that $M_{\mathrm{H}}\omega_{\mathrm{H}}^2\simeq 1.05 M_{\mathrm{D}}\omega_{\mathrm{D}}^2$.

A quasiharmonic model in which the transverse- and longitudinal-optical phonons are treated as Einstein oscillators with different Grüneisen parameters $\gamma_t$ and $\gamma_l$ is found to give a good description of the differences

$$\begin{aligned}\Delta C_{ij}(T)=C_{ij}(T,\mathrm{PdH}_x)-C_{ij}(T,\mathrm{PdD}_x)\\ -[C_{ij}(0,\mathrm{PdH}_x)-C_{ij}(0,\mathrm{PdD}_x)]\ ,\end{aligned}$$

which are independent of the acoustic-phonon modes. In this model the redistribution in the occupancy of the phonon states due to the relative shifts of the longitudinal- and transverse-phonon energies corresponding to the strain state under investigation is explicitly taken into account. This contribution, which is proportional to $(\gamma_l-\gamma_t)^2$ for the bulk modulus, is essential for the explanation of the measured values. Quantitative agreement with the data for all $C_{ij}$ is obtained by taking $\Theta_t^{\mathrm{H}}=650$ K, $\Theta_l^{\mathrm{H}}=910$ K, $\Theta_t^{\mathrm{D}}=450$ K, and $\Theta_l^{\mathrm{D}}=640$ K for the Einstein temperatures of the optical phonons in $PdH_{0.66}$ and $PdD_{0.652}$. The large value $|\gamma_l - \gamma_t| = 10 \pm 2.5$ determined from the various fits to the $B(T)$ curves of $PdH_{0.66}$ and $PdD_{0.652}$ indicates that the volume dependence of the longitudinal-optical phonons is *very different* from that of the transverse phonons. By combining the present results with those of neutron scattering and thermal-expansion measurements we obtain $\gamma_l = -3.3 \pm 2.1$ and $\gamma_t = 6.7 \pm 1.2$ . The constancy of the frequency $\omega_t$ in neutron scattering experiments thus results from the cancellation of two effects: a lowering of $\omega_t$ due to the dilation of the lattice upon hydrogen or deuteron absorption and a hardening of the proton-palladium potential.

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[1] J. M. Rowe, J. J. Rush, H. G. Smith, M. Mostoller, and H. E. Flotow, Phys. Rev. Lett. 33, 1297 (1974).

[2] W. Drexel, A. Murani, D. Tocchetti, W. Kley, I. Sosnowska, and D. K. Ross, J. Phys. Chem. Solids 37, 1135 (1976).

[3] D. K. Ross, P. F. Martin, N. A. Oates, and R. Khoda Bakhsh, Z. Phys. Chem. Neue Folge 114, 221 (1979).

[4] K. Sköld and G. Nelin, J. Phys. Chem. Solids 28, 2369 (1967).

[5] D. G. Hunt and D. K. Ross, J. Less-Common Met. 49, 169 (1976).

[6] A. Rahman, K. Sköld, C. Pelizzari, S. K. Sinha, and H. E. Flotow, Phys. Rev. B 14, 3630 (1976).

[7] J. D. Jorgensen, K. Sköld, A. Rahman, C. A. Pelizzari, H. E. Flotow, R. J. Miller, R. Standley, and T. O. Brun, *Proceedings of the Conference on Neutron Scattering, Gatlinburg,* 1976 (unpublished).

[8] J. Bergsma and J. A. Goedkoop, Physica (Utrecht) 26, 744 (1960).

[9] M. R. Chowdhury and D. K. Ross, Solid State Commun. 13, 229 (1973).

[10] O. Blaschko, R. Klemencic, P. Weinzierl, and L. Pintschovius, Phys. Rev. B 24, 1552 (1981).

[11] A. Eichler, H. Wühl, and B. Stritzker, Solid State Commun. 17, 213 (1975).

[12] H. Wühl, see T. Springer, Z. Phys. Chem. Neue Folge 115, 141 (1979).

[13] P. J. Silverman and C. V. Briscoe, Phys. Lett. 53A, 221 (1975).

[14] R. C. Dynes and J. P. Garno, Bull. Am. Phys. Soc. 20, 422 (1975).

[15] P. Nédellec, L. Dumoulin, C. Arzoumanian, and J. P. Burger, J. Phys. (Paris) 39, C6-432 (1978).

[16] R. Sherman, H. K. Birnbaum, J. A. Holy, and M. V. Klein, Phys. Lett. 62A, 353 (1977).

[17] J. J. Rush, private communication.

[18] R. Truell, Ch. Elbaum, and B. B. Chick, *Ultrasonic Methods in Solid State Physics* (Academic, New York, 1969).

[19] R. Abbenseth and H. Wipf, J. Phys. F 10, 353 (1980).

[20] D. K. Hsu and R. G. Leisure, Phys. Rev. B 20, 1339 (1979).

[21] E. S. Fisher, J. F. Miller, H. L. Alberts, and D. G. Westlake, J. Phys. F 11, 1557 (1981).

[22] C. R. Ko, K. Salama, and J. M. Roberts, J. Appl. Phys. 51, 1014 (1980).

[23] A. Magerl, B. Berre, and G. Alefeld, Phys. Status Solidi A 36, 161 (1976).

[24] O. Buck, L. A. Ahlberg, L. J. Graham, G. A. Alers, C. A. Wert and M. Amano, in *Conference on Internal Friction and Ultrasonic Attenuation in Solids, Tokyo, 1977* (unpublished).

[25] E. S. Fisher and J. F. Remark, J. Appl. Phys. 51, 927 (1979).

[26] W. L. Stuart, J. M. Roberts, N. G. Alexandropolous, and K. Salama, J. Appl. Phys. 48, 75 (1977).

[27] F. Ducastelle, J. Phys. (Paris) 31, 1055 (1970).

[28] A. C. Switendick, Ber. Bunsenges. Phys. Chem. 76, 535 (1972).

[29] C. D. Gelatt, H. Ehrenreich, and R. E. Watson, Phys. Rev. B 15, 1613 (1977).

[30] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[31] T. F. Smith and G. K. White, J. Phys. F 7, 1029 (1977).

[32] C. A. Mackliet and A. Schindler, Phys. Rev. 146, 463 (1966).

[33] J. de Launay, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1956), Vol. 2, p. 219.

[34] J. M. Rowe, J. Phys. F 8, L7 (1978). Significant deviations from linearity in the long-wavelength limit of the dispersion such as those reported by Magerl, *et al.*[35] in $NbH_x$ do not seem to happen in $PdH_x$ or $PdD_x$ since the elastic moduli from neutron scattering experiments agree within 10% with the values found in this work.

[35] A. Magerl, W. D. Teuchert, and R. Scherm, J. Phys. C 11, 2175 (1978).

[36] I. S. Anderson, C. J. Carlile, and D. K. Ross, J. Phys. C 11, L381 (1978).

[37] O. Blaschko, R. Klemencic, P. Weinzierl, O. J. Eder, and W. Just, J. Phys. F 11, 2015 (1981).

[38] G. J. Zimmermann, J. Less-Common Met. 49, 49 (1976).

[39] F. M. Mazzolai, P. G. Bordoni, and F. A. Lewis, J. Phys. F 11, 337 (1981).

[40] A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids,* Academic, New York 1972), p. 53.

[41] F. M. Mazzolai and H. Züchner, Z. Phys. Chem. Neue Folge 124, 59 (1981).

[42] D. S. MacLachlan, R. Mailfert, J. P. Burger, and B. Souffaché, Solid State Commun. 17, 281 (1975).

[43] A. Gorska, A. M. Gorski, J. Igalson, A. J. Pindor, and L. Sniadower, in *Proceedings of Hydrogen in Metals Conference* (Pergamon, Paris, 1977), Sec. 2 A 10.

[44] J. A. Garber and A. V. Granato, Phys. Rev. B 11, 3990 (1975).

[45] A. M. Gray, D. M. Gray, and E. Brown, Phys. Rev. B 11, 1475 (1975).

[46] E. A. Stern, Phys. Rev. 111, 786 (1958).

[47] G. Leibried and W. Ludwig, in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1961), Vol. 12, p. 275.

[48] T. H. K. Barron, Phys. Rev. 137A, 487 (1956).

[49] O. Blaschko, J. P. Burger, R. Klemencic, and G. Pépy, J. Phys. F 11, 2015 (1981).

[50] B. M. Geerken, A. M. Hoefsloot, R. Griessen, and E. Walker, in *Physics of Transition Metals,* edited by P. Rhodes (IOP, London, 1981), Vol. 55, p. 595.

[51] O. Belmahi, M. Merck, E. Perréard, M. Peter, E. Walker, and J. R. Schrieffer, Helv. Phys. Acta. 39, 338 (1966).

[52] E. Walker, J. Ortelli, and M. Peter, Phys. Lett. A 31, 240 (1970).