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Hydrogen motion in single-crystal palladium hydride as studied ultrasonically

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The attenuation of ultrasonic waves has been investigated in single-crystal α'-phase palladium hydride ($PdH_{0.64}$) over the temperature range of 77—300 K. The longitudinal and two independent transverse waves were propagated along the [110] crystal axis. These correspond to the elastic constants $C_L=\frac{1}{2}(C_{11}+C_{12}+2C_{44})$, $C'=\frac{1}{2}(C_{11}-C_{12})$, and C_{44}. Attenuation peaks were observed for all three modes. At 10 MHz the maxima occurred at approximately 190 K for C_L and C', and 180 K for C_{44}. The peaks are attributed to a stress-induced ordering of hydrogen pairs and complexes, and vacancy pairs and complexes, on the hydrogen sublattice. The relative magnitudes of the peaks are well accounted for in terms of hydrogen-hydrogen, hydrogen-vacancy, and vacancy-vacancy interactions at nearest- and next-nearest-neighbor positions. A simple nearest-neighbor interaction is shown to be inadequate to explain the results. The gradients of the hydrogen-vacancy interaction energies at nearest- and next-nearest-neighbor sites are deduced, with the main uncertainty having to do with the selection of an anelastic critical temperature in the theoretical expression. Using 50 K for the critical temperature we find 5.4×10^{-11} and 3.8×10^{-11} N for the absolute value of the gradients at nearest- and next-nearest-neighbor sites, respectively. The three measured attenuation peaks were found to satisfy a Cauchy-type relationship. Such a relationship suggests a central-force description of the interactions among hydrogen atoms and vacancies. The existence of a hydrostatic mode of relaxation is shown for the first time for this system. The relaxation rate for this mode is approximately the same as that for C_L and C', while the C_{44} mode relaxes approximately twice as fast. Plots of the attenuation times the temperature versus inverse temperature are asymmetric. Such asymmetry was previously observed in internal-friction measurements and attributed to the existence of an anelastic critical temperature. Our data, taken at higher frequencies and thus higher temperatures, can be fitted using an anelastic critical temperature, but the value is considerably higher than that deduced from the internal-friction experiments. The difference suggests that the asymmetry is not due to a critical temperature, but has some other origin.

I. INTRODUCTION

Hydrogen in palladium is known to occupy the octahedral sites provided by the palladium atoms.[1-3] At room temperature PdH_x exists in two phases. There is a low-concentration α phase in which the lattice parameter deviates very little from that of pure palladium and a high concentration α' phase[4] with a lattice parameter which is substantially greater than that of pure palladium and which increases[5] with increasing x. Although there are interesting and important problems to be studied in the α phase and at the α-α' phase transition, the α' phase is of particular interest because of the superconductivity which occurs in this phase and the various ordering phenomena which occur at low temperature.[6-9] The octahedral sites are only partially occupied for $x<1$ and at low temperatures a superlattice is formed with the hydrogen atoms and vacancies becoming ordered on the fcc lattice. The problem is similar to that of a lattice gas and is closely related to the Ising model of antiferromagnetism as well as the ordering of binary alloys. The present case is somewhat simpler than the ordering of binary alloys in the sense that here the hydrogen atoms and vacancies themselves become ordered while in a binary alloy two types of atoms become ordered, usually as a result of a vacancy mechanism.

Short-range order persists to temperatures well above the order-disorder transformation described above. Moreover, internal-friction measurements[10-15] have been interpreted in terms of changes in short-range order produced by mechanical stress. The effect is similar to Zener relaxation in alloys, but in the case of PdH_x it is the hydrogen atoms and vacancies which undergo stress-induced ordering.

We present here the results of ultrasonic attenuation measurements on $PdH_{0.64}$. We interpret the attenuation as arising from stress-induced ordering as in the internal-friction experiments. Because the ultrasonic experiments are carried out at much higher frequencies than in the case of internal friction, the effects occur at correspondingly higher temperatures. Through the use of a single crystal and three independent ultrasonic modes we have been able to separate the effects into that due to two pure shear strains and that due to dilatation. The former we interpret as being due to changes in directional order while the latter we attribute to changes in the order parameter at definite neighbor shells, with the first-neighbor shell presumably giving the biggest effect and smaller contributions arising from more distant shells. With the somewhat restrictive assumption that only first- and second-neighbor shells are important, we are able to derive from our data the gradients of the hydrogen-vacancy ordering energy at these shells.

II. EXPERIMENTAL DETAILS

The palladium hydride sample was prepared from a single crystal of palladium as described previously.[16] The palladium single crystal in the form of a cylindrical rod with axis along the [110] crystalline direction was obtained from Materials Research Corporation. The sample on which the measurements were made was 1.2 cm long and approximately 1 cm in diameter. This specimen was prepared with flat and parallel end faces perpendicular to the [110] axis. Hydrogenation was carried out by absorption from the gas phase in a pressure cell and furnace. The temperature and pressure were varied so as to avoid the mixed α-α' phase region. The hydrogen content was determined by weight gain.

The longitudinal wave and two transverse waves polarized along [001] and $[1\bar{1}0]$ directions were propagated along the [110] axis. These modes correspond, respectively, to the elastic constants

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

$C=C_{44}$, and $C'=(\frac{1}{2})(C_{11}-C_{12})$. Most of the measurements were made at 10.8 MHz, although a few measurements were made at higher frequencies. The attenuation was measured by use of the standard pulse-echo technique. The heights of two echoes were monitored in order to minimize effects due to the bond between the quartz transducer and sample. Data were usually taken by cooling from room temperature to liquid-nitrogen temperature with a cooling rate of 1 K/min or slower. No appreciable hysteresis was noted on comparing heating and cooling runs at this rate.

III. EXPERIMENTAL RESULTS

Figure 1 shows the measured attenuation for 10.8-MHz longitudinal waves propagating along the [110] axis. The attenuation increases as the temperature is decreased, passes through a maximum at approximately 190 K, decreases and reaches a temperature-independent background at low temperature. If the attenuation at low temperature is subtracted as a background correction, then the height of the peak is 0.67 dB/cm. Figure 2 shows the attenuation for transverse waves polarized along $[1\bar{1}0]$ and propagating along the [110] axis. The attenuation is much higher than for the longitudinal wave, but otherwise the results are similar. Subtracting the low-temperature background gives a peak height of 6.4 dB/cm. Finally, Fig. 3 shows the attenuation of transverse waves polarized along [001] and propagating along [110]. There are two qualitative differences between the attenuation for this mode and that of the other two modes. First, there seems to be at least two processes involved for this mode: There is a well-defined peak as for the other modes, and there is another component which slowly increases with temperature. In order to extract the peak, the dashed line shown in Fig. 3 is used as a background. Only the peak will be analyzed in this paper. Second, the maximum in the attenuation occurs at a lower temperature for this mode than for the other two modes. The maximum in this case occurs at about 180 K. Using the dashed line in Fig. 3 as a background, the peak height is 1.3 dB/cm.

Also shown in Figs. 1–3 are attenuation measurements for pure palladium. As can be seen, no at-

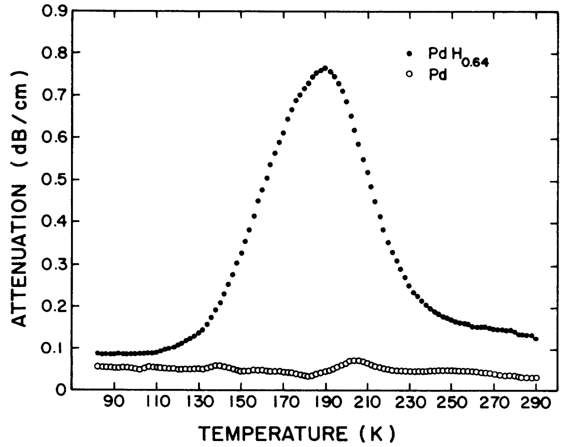

FIG. 1. Attenuation of 10.8-MHz longitudinal ultrasonic waves propagating along the [110] axis of single-crystal palladium and α'-phase palladium hydride ($PdH_{0.64}$).

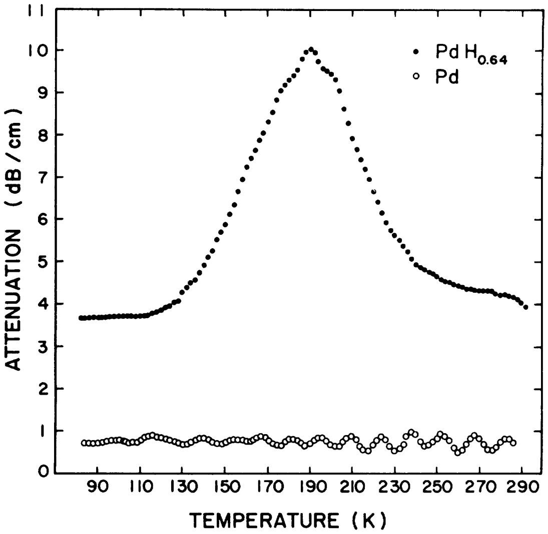

FIG. 2. Attenuation of 10.8-MHz transverse ultrasonic waves propagating along the [110] axis and polarized along the [1$\bar{1}$0] axis of single-crystal palladium and α'-phase palladium hydride.

tenuation peaks were observed in this case.

Some measurements were performed at frequencies up to 150 MHz. In all cases the maximum shifted to higher temperatures with increasing frequency.

The velocity was also measured carefully in the temperature range of the attenuation peaks. Although the largest effect was the normal temperature dependence of the velocity, small shifts were observed in the region of the peaks.

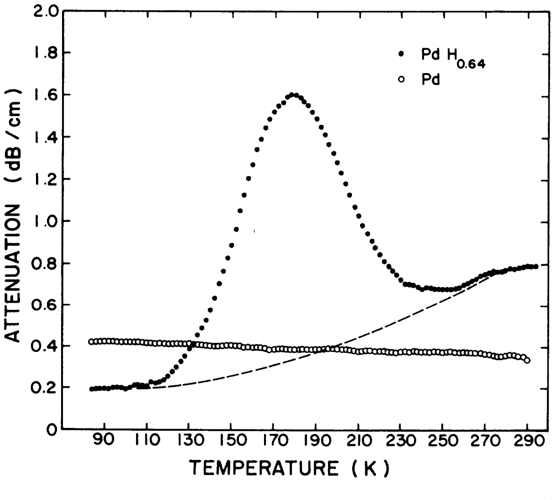

FIG. 3. Attenuation of 10.8-MHz transverse ultrasonic waves propagating along the [110] axis and polarized along the [001] axis in single-crystal palladium and α'-phase palladium hydride ($PdH_{0.64}$). The dashed line was used as a background in analyzing the hydride data.

IV. THEORY

We interpret the attenuation peaks in terms of relaxation effects involving the motion of hydrogen atoms. When relaxation is present the stress and strain are, in general, not in phase with each other and the theory of anelasticity must be applied.[17] In this case the relationship between stress and strain may be expressed in terms of a complex elastic constant c^*. For the case of a single relaxation time, c^* is given by

$$c^*(\omega)=c^R+\delta c\frac{i\omega\tau}{1+i\omega\tau}\ , \tag{1}$$

where ω is the angular frequency of the ultrasonic wave, τ is the relaxation time at constant strain, c^R is the relaxed elastic constant measured at $\omega\tau \ll 1$ so that the hydrogen atoms have time to fully respond, and $\delta c = c^U - c^R$ with c^U being the unrelaxed elastic constant measured at $\omega\tau \gg 1$. In general, the complex elastic constant is related to the ultrasonic attenuation and the ultrasonic velocity v by

$$\alpha_c=\frac{\omega}{2v}\operatorname{Im}\left[\frac{c^*(\omega)-c^R}{c^R}\right] \tag{2a}$$

and

$$\frac{\delta v}{v}=\frac{1}{2}\operatorname{Re}\left[\frac{c^*(\omega)-c^R}{c^R}\right]\ , \tag{2b}$$

where α_c is the amplitude attenuation coefficient corresponding to the elastic constant c, and $\delta v = v(\omega) - v(0)$. These equations are valid if $(c^U - c^R)/c^R \ll 1$, which is usually the case. Combining Eqs. (1) and (2), we have

$$\alpha_c=\frac{\omega}{2v}\frac{\delta c}{c^R}\frac{\omega\tau}{1+\omega^2\tau^2} \tag{3a}$$

and

$$\frac{\delta v}{v}=\frac{\delta c}{2c^R}\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\ . \tag{3b}$$

Equations (3) give a Debye-type response for the attenuation and velocity. In many cases τ is expressible as

$$\tau=\tau_0\exp(W/kT)$$

where τ_0^{-1} is an attempt frequency and W is the activation energy. It is the strong dependence of τ on temperature which gives the peak in the attenuation. Since the peak occurs when $\omega\tau=1$, measurement of the peak temperature at several different frequencies makes it possible to extract W.

Because of the symmetry of the octahedral site occupied by the hydrogen in palladium, no relaxation occurs for an isolated hydrogen interstitial.

However, relaxation effects have been observed in PdH_x by internal-friction experiments and attributed to the stress-induced rearrangement of H pairs or clusters. More recently ultrasonic attenuation measurements have been similarly interpreted.[18,19] This type of relaxation was first proposed by Zener[20] to explain relaxation effects in alloys. As has been pointed out,[12] for the range of H concentration considered here, it is simpler to speak of vacancy pairs or clusters, rather than H pairs or clusters.

We ascribe the attenuation peaks observed in the present study to Zener relaxation. For example, Mazzolai *et al.*[15] observed in $PdH_{0.64}$ a Zener internal-friction peak at 114 K with a measuring frequency of 3.2 kHz. At the same concentration we observed a peak at 190 K with a measuring frequency of 10.8 MHz. Comparing these two measurements under the assumption that they are due to the same mechanism yields an activation energy of 0.20 eV, a value within the range usually quoted for H motion in Pd.[21]

A number of papers[22–25] have developed both the thermodynamic and kinetic aspects of the theory of Zener relaxation for isolated pairs of solute atoms. In the present case 64% of the sites in the hydrogen sublattice are occupied, leaving 36% vacant. Thus, the concept of an isolated hydrogen pair or vacancy pair does not appear to be applicable.

For an account of the thermodynamics of the present experiments we turn to the theory of Zener relaxation in concentrated binary alloys as developed by LeClaire and Lomer,[26] and Welch and LeClaire.[27] In these theories the concept of isolated pairs is replaced by that of directional short-range order parameters. For the case at hand, the binary alloy is composed of hydrogen atoms and vacancies on the hydrogen fcc sublattice. The free energy can be written in terms of hydrogen-hydrogen, hydrogen-vacancy, and vacancy-vacancy interaction terms, short-range order parameters, and a configurational entropy term. It is assumed that order parameters along different directions are capable of changing independently of the others in response to strain. c^U and c^R are calculated, respectively, by taking derivatives of the free energy with respect to strain by freezing the order parameters, and by allowing the order parameters to change continually to maintain equilibrium in response to strain. The result is

$$\frac{\delta c}{c^R} = -\left[\frac{N}{V}\right]\frac{x(1-x)}{c^R}\sum_{i=1}^{\infty}\sum_{j=1}^{z_i/2}\left[\frac{d\alpha_i^j}{d\epsilon}\frac{dV_i^j}{d\epsilon}\right] , \tag{4}$$

where N/V is the number of lattice sites per unit volume, x is the concentration of hydrogen atoms, and c^R is the elastic constant corresponding to the particular strain mode ϵ. The index i refers to particular neighbor shells, nearest neighbors, second-nearest neighbors, etc., relative to some particular lattice site chosen as origin. z_i is the number of atoms within the shell i, and j refers to the $z_i/2$ positive directions within the shell. The α_i^j are the Warren-Cowley short-range order parameters which describe the probability of occupation of various lattice sites by hydrogen atoms and vacancies. V_i^j is the ordering energy for the site in shell i, along direction j, relative to the origin:

$$V_i^j = V_{i\text{HH}}^j + V_{iVV}^j - 2V_{i\text{H}V}^j , \tag{5}$$

where $V_{i\text{HH}}^j$, V_{iVV}^j, and $V_{i\text{H}V}^j$ refer to interaction energies between two hydrogen atoms, two vacancies, and a hydrogen atom and a vacancy. (This definition of V_i^j differs by a factor of 2 from that used in Ref. 27.) In the lattice-gas approximation $V_i^j = V_{i\text{HH}}^j$.

Comparing Eqs. (3a) and (4) shows that a measurement of the attenuation maximum (occurring when $\omega\tau = 1$) allows an experimental determination of the double sum in Eq. (4); however, to get a more detailed picture the authors of Refs. 26 and 27 make certain approximations in order to develop the theory further. It is assumed that the hydrogen interactions may be described by central forces. V_i^j then depends only on the interatomic spacing r_i^j so that $dV_i^j/d\epsilon$ may be written as $(dV_i^j/dr_i^j)(dr_i^j/d\epsilon)$. Next, it is necessary to relate the order parameters to the ordering energy. LeClaire and Lomer take into account only ordering energies for nearest neighbors and use the quasichemical approach to relate α_i^j to V_i^j. The result is

$$\frac{\delta c}{c^R} = \frac{Nx(1-x)[x+(1-x)\alpha_1][(1-x)+x\alpha_1](1-\alpha_1)}{c^R VkT(1+\alpha_1)}\left[\frac{dV_1}{dr_1}\right]^2\sum_{j=1}^{z_1/2}\left[\frac{dr_1^j}{d\epsilon}\right]^2 , \tag{6}$$

where it has been assumed that for the low values of strains commonly used in internal-friction and ultrasonic experiments, the α_1^j do not depend strongly on j and can be replaced by α_1, the order parameter for the nearest-neighbor shell, and similarly that dV_1^j/dr_1^j can be replaced by dV_1/dr_1, the gradient of the ordering energy at first-neighbor sites.

Equation (6) shows that δc differs for different acoustic modes only through the summation term, a purely geometric factor. We give here the fcc lattice results for the three acoustic modes used in the present experiments. The sums are

$$\sum_{j=1}^{6}\left[\frac{dr_1^j}{d\epsilon}\right]^2=\frac{5a_0^2}{8},\quad c=C_L \tag{7a}$$

$$\sum_{j=1}^{6}\left[\frac{dr_1^j}{d\epsilon}\right]^2=\frac{a_0^2}{4},\quad c=C_{44} \tag{7b}$$

$$\sum_{j=1}^{6}\left[\frac{dr_1^j}{d\epsilon}\right]^2=\frac{a_0^2}{8},\quad c=C' \ . \tag{7c}$$

Here a_0 is the lattice constant. The notation at the right gives the acoustic mode considered. The last two results were given in the paper by LeClaire and Lomer, although their results are stated in terms of the nearest-neighbor distance rather than the lattice constant.

Welch and LeClaire[27] have included more distant-neighbor shells in their calculations. Although it is not possible to give an analytical expression for the relaxation strength in the general case, they do give an analytical expression for the high-temperature limit. This limit corresponds to the short-range order parameters being very small, i.e., the distribution of hydrogen atoms and vacancies on the fcc sublattice is nearly random. As the peak attenuation occurs near 200 K while the temperature for self-ordering in this system is in the vicinity of 50 K, it may be reasonable to use the high-temperature limit here. The calculation of Bond and Ross[9] also indicates that $\alpha_1 \ll 1$ for our case. The high-temperature limit equation is

$$\frac{\delta c}{c^R}=\frac{Nx^2(1-x)^2}{Vc^RkT}\sum_{i=1}^{\infty}\sum_{j=1}^{z_i/2}\left[\frac{dV_i^j}{d\epsilon}\right]^2 \ . \tag{8}$$

The double summation may be replaced as before, except that now there will be geometric factors and gradients of ordering energies for each shell. We have computed the above sums for the three acoustic modes used in our experiment and for an fcc lattice out to the fifth-neighbor shell. Using $N/V=4/a_0^3$ for the fcc lattice the results may be written as

$$\frac{\delta C_L}{C_L}=\frac{4x^2(1-x)^2}{a_0C_LkT}\left[\frac{5w_1}{8}+\frac{w_2}{2}+\frac{15w_3}{4}+\frac{5w_4}{2}+\frac{109w_5}{20}+\cdots\right], \tag{9a}$$

$$\frac{\delta C}{C}=\frac{4x^2(1-x)^2}{a_0CkT}\left[\frac{w_1}{4}+\frac{3w_3}{2}+w_4+\frac{9w_5}{10}+\cdots\right], \tag{9b}$$

$$\frac{\delta C'}{C'}=\frac{4x^2(1-x)^2}{a_0C'kT}\left[\frac{w_1}{8}+\frac{w_2}{2}+\frac{3w_3}{4}+\frac{w_4}{2}+\frac{73w_5}{20}+\cdots\right], \tag{9c}$$

where the distinction between c^U and c^R has been dropped in the denominator since $\delta c/c \ll 1$. Here, $w_i \equiv (dV_i/dr_i)^2$, the square of the gradient of the ordering energy for shell i. Although these equations give the relaxation strengths for three independent acoustic modes, an inspection shows that these equations are not linearly independent. They are related by

$$\delta C_L = 2\,\delta C + \delta C' \ . \tag{10}$$

With only two independent equations we can determine only two of the w_i, but we can use the third equation to check for self-consistency.

When Eq. (10) is written in terms of the usual two-index elastic constants, the result is $\delta C_{12}=\delta C_{44}$. This equation is similar to the Cauchy relationship for the elastic constants of cubic crystals which is $C_{12}=C_{44}$. The Cauchy relationship depends on the existence of central forces between atoms. The fact that $dV_i^j/d\epsilon$ was written as $(dV_i^j/dr_i^j)(dr_i^j/d\epsilon)$ means that two-body central forces were assumed for the hydrogen-vacancy ordering energy. Thus, Eq. (10), which is a Cauchy relationship for the δc's may have been expected. An experimental violation of Eq. (10) would seem to indicate that central forces cannot be used to describe the interactions among the hydrogen atoms and vacancies.

Implicit in the derivation of Eq. (10) is the assumption that the δc's are all measured at the same temperature. As mentioned earlier, the attenuation curve for mode C peaked at a slightly lower temperature than for C' and C_L. Thus, in comparing experimental results to Eq. (10), a T^{-1} dependence can be used to correct for the different peak temperatures. The correction will be a small one in the present case.

Before determining the experimental values of the δc's from Eq. (3a) one further consideration is necessary. With a single relaxation time, the function $\omega\tau/(1+\omega^2\tau^2)$ has the value $\frac{1}{2}$ at the attenuation peak, but this value is reduced if there is a distribution of relaxation times. As will be shown later, there is evidence for a spectrum of relaxation times in our experiments. Nowick and Berry[17] have considered this problem. They have tabulated a function $f_2(0,\beta)$ which characterizes the peak height in this case. β is the halfwidth of the Gaussian distribution in $\ln(\tau/\tau_m)$, τ_m being the mean value. The *maximum* value of the attenuation is then given by

$$\alpha_{\max}=\frac{\omega}{2v}\frac{\delta c}{c}f_2(0,\beta)\ . \tag{11}$$

Internal-friction peaks[15] in palladium hydride are asymmetric and this asymmetry has been attributed to an order-disorder transition on the hydrogen sublattice. This situation can be described[15,17] by replacing the T^{-1} dependence of $\delta c/c$ in Eqs. (9) with a $(T-T_S)^{-1}$ dependence where T_S is an anelastic critical temperature. The anelastic critical temperature arises from the temperature dependence of $d\alpha_i^j/d\epsilon$ in Eq. (4). This temperature dependence was only partially taken into account in Eq. (8). Welch and LeClaire[27] investigated this problem for the case of only nearest-neighbor interactions and found that T_S may be different for different acoustic modes. They also investigated second-nearest-neighbor interactions, but only for a restricted set of parameters not applicable to the present problem.

V. INTERPRETATION

A. Peak heights—gradients of ordering energy

In this section we compare our experimental results for the attenuation peak heights to the theory outlined in the preceding section. We first use Eq. (11) to calculate the experimental values of $\delta c/c$ from $\alpha_{\max}$ for each mode. We then interpret the experimental values of $\delta c/c$ in terms of Eqs. (6) and (9). The difference between these equations is that the former is restricted to nearest-neighbor interactions but is not restricted in temperature, while the latter includes more distant-neighbor interactions but is restricted to the high-temperature limit. As mentioned earlier, the high-temperature approximation seems likely to be a good one in the present case. Values of $\alpha_{\max}$ (in units of Np/cm), $\delta c/c$, and δc are given in Table I for the three acoustic modes investigated. Also listed are the values of β and $f_2(0,\beta)$ used. The previously measured[16] sound velocities and elastic constants were used in the calculation.

We first compare our experimental results for δc with Eqs. (6) and (7) of the LeClaire-Lomer theory. Using the δc's from Table I we find experimentally the ratios

$$\delta C_{\mathrm{L}}:\delta C:\delta C'=2.5:0.7:1.0\ .$$

The predictions for these ratios given by Eqs. (6) and (7) are 5:2:1. Thus, our results for palladium hydride are in strong disagreement with the predictions of this theory. (Seraphim and Nowick[28] previously found that their internal-friction measurements on Ag-Zn and Li-Mg alloys disagreed with the LeClaire-Lomer theory.) The most likely cause for the disagreement would seem to be either the assumption that V_l^j depends only on the interatomic spacing along direction j, or the restriction of the interaction to nearest neighbors only. We show below that we can give a reasonable account of our results by including second-nearest-neighbor interactions.

Before making a detailed interpretation of our results in terms of the Welch-LeClaire theory, we first check to see if Eq. (10) is obeyed experimentally. Using the measured values of δC and $\delta C'$, and correcting for the fact that δC was measured at 180 K, we calculate from Eq. (10) $\delta C_{\mathrm{L}}=6.9\times10^8$ N/m^2 at 190 K. The measured value at this temperature is 7.2×10^8 N/m^2. This difference is within experimental error. This agreement serves as a check of the Welch-LeClaire theory and hence of the assumption of central forces, without any restriction as to the range of the interaction.

Equations (9) give theoretical expressions for the δc's in terms of the w_i's. As stated earlier we can only hope to determine two of the w's and thus we assume the simplest case, namely that only first- and

TABLE I. Parameters for the attenuation peaks in α'-phase palladium hydride ($PdH_{0.64}$). δC was measured at 180 K; the other modes at 190 K. C_B is the bulk modulus.

	C_L	C	C'	C_B
$\alpha_{\max}$ (cm^{-1})	0.077	0.15	0.74	0.086
β	1.20	1.63	1.40	1.20
$f_2(0,\beta)$	0.39	0.35	0.37	0.39
$(\delta c/c)$[a]	2.8×10^{-3}	3.1×10^{-3}	9.8×10^{-3}	2.7×10^{-3}
(δc) (N/m^2)[a]	7.2×10^{8}	2.1×10^{8}	2.9×10^{8}	4.8×10^{8}
$(\delta c/c)$[b]	2.7×10^{-3}	3.2×10^{-3}	1.0×10^{-2}	2.2×10^{-3}
$(\delta c/c)$[c]	2.7×10^{-3}	3.2×10^{-3}	9.9×10^{-3}	2.2×10^{-3}

[a] Determined from Figs. 1—4.

[b] Calculated from the parameters of column 1 of Table II and Eqs. (9).

[c] Calculated from the parameters of column 2 in Table II and Eqs. (9) with T^{-1} replaced by $(T-T_S)^{-1}$.

second-neighbor interactions are important. We have three experimental measurements to determine the two parameters w_1 and w_2. We chose w_1 and w_2 using a least-squares procedure such that the sum of the squares of the percentage differences between the measured δc's and the δc's calculated from Eq. (9) was minimized. The results are given in column 1 of Table II in terms of the $|dV_i/dr_i|$.

If we ignore hydrogen-vacancy and vacancy-vacancy interactions, then the dV_i/dr_i are just the forces between hydrogen atoms. It is interesting to note that our results are of the same order of magnitude as those determined for nearest- and next-nearest D-D forces in $\mathrm{PdD}_{0.63}$ from neutron scattering experiments.[29,30]

It is clear from Table II that forces beyond nearest neighbors are quite important. Of course, what is really measured in our experiment is the sum of the interaction terms indicated by Eqs. (9). Although we obtain a good fit to our data using only interactions out to second-nearest neighbors, we cannot be sure that more distant neighbors do not also make a contribution.

Listed in row 6 of Table I are the values of $\delta c/c$ calculated using the $|dV_i/dr_i|$ of the first column of Table II. The close agreement between calculated and measured quantities is a measure of the self-consistency of the procedure used.

B. Hydrostatic term

The theories of LeClaire and Lomer, and Welch and LeClaire predict an effect for hydrostatic stress. For example, when Eq. (8) is developed for hydrostatic stress the result is

$$\frac{\delta C_B}{C_B}=\frac{4x^2(1-x)^2}{a_0C_BkT}\left[\frac{w_1}{3}+\frac{w_2}{3}+2w_3+\frac{4w_4}{3}+\frac{10w_5}{3}+\cdots\right], \tag{12}$$

where C_B is the bulk modulus. The fact that we have obtained a self-consistent description for three independent acoustic modes implies that the hydrostatic component is present, but we now examine this term more explicitly. The modes C and C' are pure shear modes involving no volume changes, but the C_L mode can be regarded as a combination of shears and pure volume changes. Using $C_L=C_B+(\frac{1}{3})C'+C$ [Eq. (2a)] and $v\sim c^{1/2}$, it is easily shown that

$$\alpha_{C_B}=\left[\frac{C_L}{C_B}\right]^{3/2}\alpha_{C_L}-\frac{1}{3}\left[\frac{C'}{C_B}\right]^{3/2}\alpha_{C'}-\left[\frac{C}{C_B}\right]^{3/2}\alpha_C\ , \tag{13}$$

where α_{C_B} is an attenuation coefficient associated with hydrostatic stresses. With the data in Figs. 1—3, we computed α_{C_B} from Eq. (13). (The background attenuation was subtracted from Figs. 1—3.) The results are shown in Fig. 4. The hydrostatic term exhibits a well-defined peak, similar in nature to the other modes. The peak occurs at about 190 K, approximately the same temperature as for the C_L and C' modes. From the height of the peak we can calculate $\delta C_B/C_B$. The results are given in Table I. The relaxation strength is seen to be comparable to those of the other modes. Also shown in row 6 of Table I is the value of $\delta C_B/C_B$ calculated from the dV_i/dr_i of column 1 in Table II. Considering that the data for the hydrostatic mode are obtained by taking differences of the data for the other modes, the measured and calculated values are in reasonable agreement.

The full hydrostatic peak in Zener relaxation does not appear to have been previously displayed as in Fig. 4, although its presence was demonstrated by internal-friction measurements on a single-crystal bcc Li-Mg alloy.[28] Measurements of the orientation dependence of the relaxation strengths of Young's modulus and the shear modulus indicated the existence of a dilatational component.

TABLE II. Gradients (in newtons) of the hydrogen-vacancy ordering energies at nearest- and next-nearest-neighbor sites determined using various values for the anelastic critical temperature T_S.

	$T_S=0$	$T_S=50$ K	$T_S=150$ K (C_L), $T_S=140$ K (C,C')
$\left\lvert\frac{dV_1}{dr_1}\right\rvert$	6.3×10^{-11}	5.4×10^{-11}	2.7×10^{-11}
$\left\lvert\frac{dV_2}{dr_2}\right\rvert$	4.5×10^{-11}	3.8×10^{-11}	2.1×10^{-11}

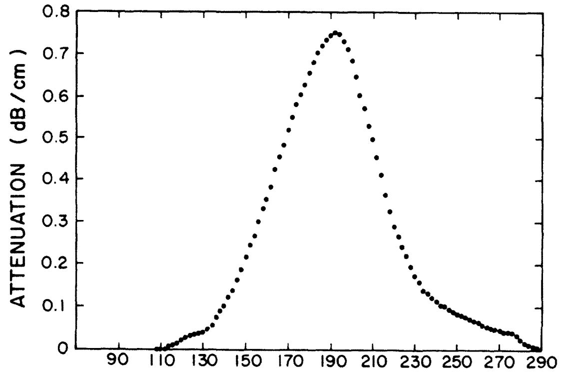

FIG. 4. Attenuation corresponding to the hydrostatic mode in $PdH_{0.64}$. These data were obtained from the data of Figs. 1—3 as explained in the text. The background attenuation was first subtracted from Figs. 1—3.

C. Peak shapes and widths

We now turn to a discussion of the widths and shapes of the attenuation peaks. We have investigated these peaks at frequencies up to 30 MHz for C', 60 MHz for C, and 150 MHz for C_L. An Arrhenius plot of the frequency versus the inverse of the peak temperatures yields an activation energy of approximately 0.20 eV for each mode, although the temperature range spanned is too narrow to permit accurate values to be determined. The peaks in Figs. 1—3 are too broad to be accounted for by a single relaxation time and an activation energy of this value. We take this extra width as evidence for a distribution of relaxation times. In the case of a Gaussian distribution of relaxation times, Nowick and Berry[17] give a table relating the width of the peak to the parameter β which describes the width of the Gaussian distribution. Although we will show below that the distribution does not appear to be Gaussian, we will as a first approximation use the results for a Gaussian distribution to analyze our data. The parameter β in Table I is obtained using the widths of the experimental curves at the half-height points, Table 4-2 of Nowick and Berry, and an activation energy of 0.20 eV. It should be noted that the function $f_2(0,\beta)$ listed in Table I and involved in the determination of the dV_i/dr_i, does not deviate strongly from the value of 0.5 which it would have for a single relaxation time ($\beta=0$). Thus our results for the w_i do not depend sensitively on the analysis of the widths and shapes of the peaks.

When the quantity αT is plotted versus T^{-1} for each peak an asymmetric curve is obtained. In each case the curve falls off most steeply on the high-temperature side. A similar situation was found by Mazzolai *et al.*[15] and attributed to a Curie-Weiss type of behavior.

Following the procedure of Mazzolai *et al.* we plotted $\alpha(T-T_S)$ vs T^{-1} and adjusted the value of T_S in an attempt to find a symmetrical curve. We were able to find values of T_S to symmetrize the plots as shown in Fig. 5 for the longitudinal mode. Plots for the C and C' modes were qualitatively similar. The T_S values are approximately 140 K for the two shear modes and 150 K for the longitudinal mode. These values are surprisingly high, as will be discussed below.

From the widths of the symmetrized curves we extracted β values as before. These values as well as other parameters associated with these curves are listed in Table III. It will be seen that $\delta c/c$ differ slightly from those of Table I, because the function $f_2(0,\beta)$ differs slightly. It is encouraging that these

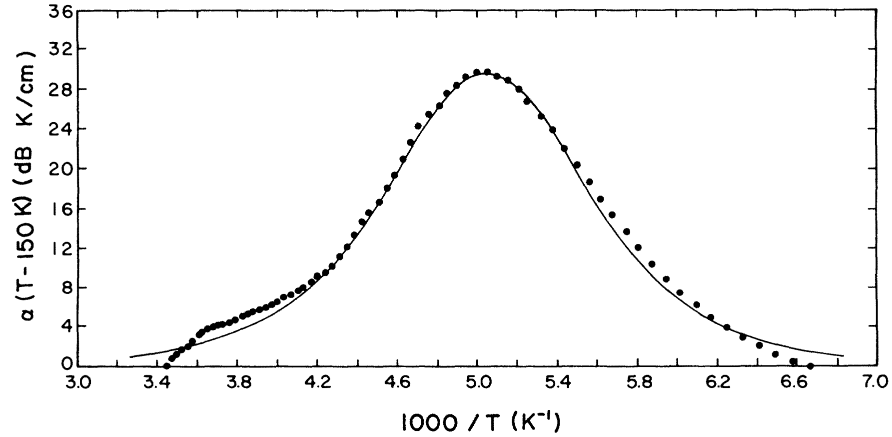

FIG. 5. Symmetrized plot of $\alpha(T-T_S)$ vs T^{-1} for the data of Fig. 1 with $T_S=150$ K. The dots represent the data, the solid line represents a theoretical fit for a distribution of relaxation times with $\beta=0.45$.

TABLE III. Parameters for the attenuation peaks in α'-phase palladium hydride ($PdH_{0.64}$) using the T_S values shown. δC was measured at 180 K; δC_L and $\delta C'$ at 190 K.

	C_L	C	C'
α_{max} (cm^{-1})	0.077	0.15	0.74
T_S (K)	150	140	140
β	0.45	1.05	0.85
$f_2(0,\beta)$	0.48	0.41	0.45
$(\delta c/c)^a$	2.3×10^{-3}	2.7×10^{-3}	8.0×10^{-3}
$(\delta c)^a$ (N/m^2)	5.9×10^{8}	1.8×10^{8}	2.4×10^{8}
$(\delta c/c)^b$	2.5×10^{-3}	2.6×10^{-3}	7.8×10^{-3}

[a] Determined from Figs. 1–3.

[b] Calculated from the parameters in Table II for $T_S \neq 0$, and Eq. (9) with T^{-1} replaced by $(T-T_S)^{-1}$.

two different ways of analyzing the data do not change the values of $\delta c/c$ significantly.

We used the response function for a Gaussian distribution computed by Nowick and Berry to fit the symmetrized curves. The results for the longitudinal mode are shown as the solid line in Fig. 5. As can be seen, the fit is reasonably good. Similar results were obtained for the C and C' modes. This means that the shapes of the curves are well described by the values of T_S and β listed in Table III.

In order to determine values for the dV_i/dr_i with the assumption of the T_S, we use the values of $\delta c/c$ from Table III, and Eqs. (9) with T^{-1} replaced by $(T-T_S)^{-1}$. The results are shown in column 3 of Table II. Naturally, the values of the dV_i/dr_i derived in this case are substantially different from those derived assuming that $T_S=0$.

The T_S values required to fit the data are significantly higher than the temperature for self-ordering which for the hydrogen concentration used here is about 50 K. There is no reason to expect that the anelastic critical temperatures found in ultrasonic and internal-friction experiments will coincide with the order-disorder transition temperature, and indeed Mazzolai *et al.* found temperatures considerably higher than the order-disorder transition temperatures for the high H concentration range. However, for the concentrations used here, Mazzolai *et al.* fitted their internal-friction data with T_S values of about 50 K. Thus, our results for T_S disagree strongly with both the usual determinations of the order-disorder temperature and the internal-friction results of Mazzolai *et al.* It seems significant that our high-frequency results which peak at a higher temperature than the internal-friction results, require a correspondingly higher T_S to fit the data. This discrepancy is disturbing and raises the question as to whether or not the asymmetry in the αT vs T^{-1} plot is due to Curie-Weiss behavior or to some other reason. The most obvious alternative explanation is an asymmetric distribution of relaxation times. However, there are some similarities here to the case of ultrasonic attenuation[31] in superionic conductors where an explanation involving excitation of correlated states[32] has been invoked. This alternative explanation for the widths and shapes of the attenuation peaks is not expected to affect significantly the main conclusions of this paper which have to do with the heights of the peaks.

As noted earlier, the different ways of analyzing the data do not yield markedly different values of $\delta c/c$. The main uncertainty in the $|dV_i/dr_i|$ then arises from the uncertainty in T_S. The values in columns 1 and 3 in Table II may be regarded as two extreme values. If we simply use $T_S=50$ K (the approximate temperature for self-ordering in this system) in Eqs. (9), we get the $|dV_i/dr_i|$ listed in the second column of Table II. The $\delta c/c$ were taken from Table I for this analysis. We observe small anomalies in the sound velocity near 50 K which are probably associated with the order-disorder transition. Thus the $|dV_i/dr_i|$ listed in column 2 of Table II are probably the most reliable.

D. Relaxation rates

The kinetics of Zener relaxation in concentrated binary alloys have been investigated by Welch.[33] He considered a vacancy mechanism for relaxation which may not be applicable to the present problem. For the case in which only nearest-neighbor interactions are important, he found that the relaxation times for all modes are the same. In contrast, we find that the C mode relaxes faster than the other modes. Using the approximate value of 0.20 eV for the activation energy of the C mode and the fact that the peak occurred at 180 K as compared to 190 K for the other two modes, we find that the relaxation rate for the C mode is approximately twice that of the other modes. This discrepancy may be a reflection of the importance of more distant-neighbor interactions. We have shown above that such interactions must be taken into account in order to explain the relative magnitudes of the attenuation peaks. It is interesting to note that a *C*-type strain changes first-neighbor distances, but does not change second-neighbor distances, while the strain associated with the other modes involve changes in both first- and second-neighbor distances. With the assumption that only nearest- and next-nearest-neighbor interactions are important, the *C* peak is then due to changes in the directional order parameters in the first-neighbor shell only, the *C'* peak is due to changes in directional order parameters at first- and second-neighbor shells, while the hydrostatic peak is due to changes in the ordinary order parameters at first- and second-neighbor shells. The C_L peak is due to a combination of the above effects. Since interactions beyond the first-neighbor shell are important, then it seems reasonable that the *C* mode will behave differently from the other modes. A satisfactory theory for the kinetics of the present problem is not available.

VI. CONCLUSION

Ultrasonic attenuation measurements in single-crystal $PdH_{0.64}$ as a function of temperature show well-defined peaks for each of the three independent acoustic modes. We attribute these peaks to a stress-induced ordering of pairs or clusters of hydrogen atoms and vacancies on the hydrogen sublattice. Using the theories of LeClaire and Lomer, and Welch and LeClaire for Zener relaxation in alloys, we can give a good description of the relative magnitudes of the peaks by taking into account nearest- and next-nearest-neighbor hydrogen-hydrogen hydrogen-vacancy, and vacancy-vacancy interactions. Nearest-neighbor interactions alone are clearly inadequate for an explanation of the results in the context of these theories.

We obtain a good fit to the peak heights in terms of the gradients of the hydrogen-vacancy ordering energies at nearest- and next-nearest-neighbor sites. The main uncertainty in determining the values of these gradients concerns the anelastic critical temperature T_S. Although we obtain a good fit to the shapes of the peaks using T_S values in the range of 140–150 K, these numbers seem unrealistically high. The best values are probably those obtained using $T_S = 50$ K, approximately the temperature for self-ordering in this system. With this value for T_S we find the absolute value of the gradients to be 5.4×10^{-11} N and 3.8×10^{-11} N at first- and second-neighbor sites, respectively. The results do not depend sensitively on the value of T_S in the range 0–50 K.

We find experimentally a Cauchy-type relationship for the δc's. This relationship is consistent with the assumption of a central-force description of the interactions among hydrogen atoms and vacancies.

We have shown for the first time the existence of a hydrostatic mode of relaxation in this system. Further, this mode relaxes at approximately the same rate as the *C'* shear mode. Each of these modes relaxes at approximately one-half the rate of the *C* shear mode. There seems to be no theory available at present capable of explaining these rates.

Plots of αT vs T^{-1} were asymmetric about the maximum. Such asymmetry was observed previously in internal-friction measurements and taken as evidence for the existence of an anelastic critical temperature. The values of T_S needed to explain the internal-friction asymmetry were reasonable, especially for the lower concentrations. The present measurements were made at much higher temperatures than the internal-friction measurements and, as expected, the loss peaks shifted to higher temperatures. Surprisingly, the values of T_S needed to explain the asymmetry shifted by approximately the same amount. Thus, we believe that the asymmetry shown by the present data has some other origin than an anelastic critical temperature.

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