Optical-phonon effects on the elastic constants of PdH_x and PdD_x

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A previous theory for the optical-phonon contribution to the elastic constants in PdH_x and PdD_x is extended to include effects due to the acoustic phonons. Additional terms are obtained which have a bearing on the interpretation of experimental results.

A detailed experimental and theoretical study of the elastic constants of PdH_x and PdD_x has been reported by Geerken *et al.*[1] The optical-phonon contribution to the bulk modulus was expressed in terms of different Grüneisen parameters, γ_l and γ_t, for the longitudinal and transverse optical phonons, respectively. An unusually large value of $|\gamma_l-\gamma_t|$ was found. On combining the elastic-constant measurements with thermal expansion[2,3] and neutron scattering[4] results, a negative value of γ_l was obtained. The optical Grüneisen constants are particularly interesting because of their connection to superconductivity[5] in PdH_x and PdD_x.

The purpose of this Brief Report is to extend the theory presented in Ref. 1 to take the acoustic phonons more fully into account. Additional terms are found in the expression for the bulk modulus which substantially affect the interpretation of the experimental results of Ref. 1.

The theory developed in Ref. 1 is first outlined with an emphasis on the bulk modulus. The internal energy is given by

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

where $\{\varepsilon_i\}$ is the strain in Voigt notation, $U_0(\varepsilon_i)$ is the frozen lattice energy, $\hbar\omega_q$ is the phonon energy, and the sum is over all phonon states q. The phonon occupancy is given by the Planck distribution function,

$$n_q=[\exp(\beta\hbar\omega_q)-1]^{-1} \;. \tag{2}$$

The adiabatic bulk modulus is defined by

$$B=V\left[\frac{\partial^2 U}{\partial V^2}\right]_S \;, \tag{3}$$

where V is the volume of the crystal and S is the entropy.

Two important Grüneisen parameters for the bulk modulus are

$$\gamma_q=-\frac{\partial\ln(\hbar\omega_q)}{\partial\ln V} \;, \tag{4}$$

and an average Grüneisen parameter defined by

$$\gamma=\frac{\sum_q(\beta\hbar\omega_q)^2 n_q(n_q+1)\gamma_q}{\sum_q(\beta\hbar\omega_q)^2 n_q(n_q+1)} \;. \tag{5}$$

The result found in Ref. 1 for the bulk modulus is

$$\begin{aligned}B=B_0&+\frac{1}{V}\frac{\partial\ln B_0}{\partial\ln V}\sum_q(n_q+\tfrac{1}{2})\hbar\omega_q\gamma_q\\&+V\sum_q(n_q+\tfrac{1}{2})\frac{\partial^2\hbar\omega_q}{\partial V^2}\\&-\frac{1}{\beta V}\sum_q(\beta\hbar\omega_q)^2 n_q(n_q+1)(\gamma_q-\gamma)^2 \;.\end{aligned} \tag{6}$$

Geerken *et al.*[1] assumed that the optical-phonon contribution to B could be adequately described by evaluating the sums of Eqs. (5) and (6) over the optical modes only. The coupling between the acoustic and optic modes induced by the last term in Eq. (6) was neglected. It will be shown below that the neglected terms are not small.

Two volume Grüneisen constants were assumed in Ref. 1, γ_l and γ_t, for the longitudinal optical and transverse optical phonons, respectively. In the present paper the results of Ref. (1) are extended by assuming a third volume Grüneisen constant, γ_a, for all the acoustic phonons, and carrying out the sums over the acoustic and optical modes. The result is

$$\begin{aligned}B=B_0&+\frac{1}{\beta V}\frac{\partial\ln B_0}{\partial\ln V}(F_1^a\gamma_a+F_1^l\gamma_l+2F_1^t\gamma_t)+\frac{1}{\beta V}[F_1^a\gamma_a(\gamma_a+1)+F_1^l\gamma_l(\gamma_l+1)+2F_1^t\gamma_t(\gamma_t+1)]\\&-\frac{1}{\beta V}\left[F_1^a\left\langle\frac{\partial\gamma_q}{\partial\ln V}\right\rangle_a+F_1^l\left\langle\frac{\partial\gamma_q}{\partial\ln V}\right\rangle_l+2F_1^t\left\langle\frac{\partial\gamma_q}{\partial\ln V}\right\rangle_t\right]-\frac{1}{\beta V}[F_2^a(\gamma_a-\gamma)^2+F_2^l(\gamma_l-\gamma)^2+2F_2^t(\gamma_t-\gamma)^2] \;,\end{aligned} \tag{7}$$

where

$$V\frac{\partial^2\hbar\omega_q}{\partial V^2}=\frac{\hbar\omega_q}{V}\left[\gamma_q(\gamma_q+1)-\frac{\partial\gamma_q}{\partial\ln V}\right] \tag{8}$$

has been used,

$$F_1^i=\sum_i(n_q+\tfrac{1}{2})\beta\hbar\omega_q \tag{9}$$

and

$$F_2^i = \sum_i n_q(n_q+1)(\beta\hbar\omega_q)^2 , \tag{10}$$

with $i=a,l,t$. The sum over a is over all the acoustic modes, while the sum over t is over half the transverse optical modes with a compensating factor of 2 used in Eq. (7) as was the case in Ref. 1. F_1 and F_2 differ slightly from the definitions used previously. In Ref. 1 the optical phonons were approximated as Einstein oscillators of energy $\hbar\omega_l$ ($\hbar\omega_t$), in which case,

$$F_1^{l(t)} = Nx(n_{l(t)}+\tfrac{1}{2})\beta\hbar\omega_{l(t)} , \tag{11}$$

$$F_2^{l(t)} = Nxn_{l(t)}(n_{l(t)}+1)(\beta\hbar\omega_{l(t)})^2 , \tag{12}$$

with

$$n_{l(t)} = [\exp(\beta\hbar\omega_{l(t)})-1]^{-1} , \tag{13}$$

where N is the total number of palladium atoms in the crystal and x is the H or D to Pd ratio. Combining the first four terms of Eq. (7) in a manner similar to that of Ref. 1, and using Eq. (5) to rewrite the last term of Eq. (7), B can be expressed as

$$B = B_0 + \frac{1}{\beta V}\left[(F_1^a+F_1^l+2F_1^t)A + \left[\frac{2F_1^lF_1^t}{F_1^a+F_1^l+2F_1^t} - \frac{2F_2^lF_2^t}{F_2^a+F_2^l+2F_2^t} \right](\gamma_l-\gamma_t)^2 + \left[\frac{F_1^aF_1^l}{F_1^a+F_1^l+2F_1^t} - \frac{F_2^aF_2^l}{F_2^a+F_2^l+2F_2^t} \right](\gamma_a-\gamma_l)^2 + \left[\frac{2F_1^aF_1^t}{F_1^a+F_1^l+2F_1^t} - \frac{2F_2^aF_2^t}{F_2^a+F_2^l+2F_2^t} \right](\gamma_a-\gamma_t)^2 \right] \tag{14}$$

with

$$A = \bar{\gamma}\frac{\partial \ln B_0}{\partial \ln V} + \bar{\gamma}(\bar{\gamma}+1) - \frac{F_1^a\left\langle \frac{\partial \gamma_q}{\partial \ln V}\right\rangle_a + F_1^l\left\langle \frac{\partial \gamma_q}{\partial \ln V}\right\rangle_l + 2F_1^t\left\langle \frac{\partial \gamma_q}{\partial \ln V}\right\rangle_t}{F_1^a+F_1^l+2F_1^t} , \tag{15}$$

and

$$\bar{\gamma} = \frac{F_1^a\gamma_a+F_1^l\gamma_l+2F_1^t\gamma_t}{F_1^a+F_1^l+2F_1^t} . \tag{16}$$

These results are derived under the assumption that the phonon populations maintain equilibrium with the ultrasonic wave.

The results of Ref. 1 are recovered by setting $F_1^a=F_2^a=0$. *However*, F_1^a is roughly comparable to F_1^l and F_1^t over the temperature range of the experiments. Further, $F_2^a > F_2^t, F_2^l$. (F_2^i is, within a factor of the Boltzmann constant, just the heat capacity of phonons of type i.) If $(\gamma_l-\gamma_t)^2 \gg (\gamma_a-\gamma_l)^2, (\gamma_a-\gamma_t)^2$ then, of course, the term involving $(\gamma_l-\gamma_t)^2$ could dominate. Even in that case the F_1^a and F_2^a factors would need to be taken into account.

Obviously, one could not hope to obtain all the various parameters in Eq. (14) by fitting that expression to the experimental results. It might be possible to estimate F_1^i, F_2^i, and γ_a from other types of experiments, and then use Eq. (14) to extract γ_l and γ_t from the bulk modulus data. It would be interesting to see if such an approach would give values of γ_l and γ_t different from those found in Ref. 1.

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[1]B. M. Geerken, R. Griessen, L. M. Huisman, and E. Walker, Phys. Rev. B **26**, 1637 (1982).

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

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

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

[5]B. N. Ganguly, Phys. Rev. B **14**, 3848 (1976).