

Dependence of the Thermal Conductivity of Dilute Solid Mixtures of Orthohydrogen and Parahydrogen on Orthohydrogen Concentration

C. Ebner* and C. C. Sung†

Department of Physics, Ohio State University, Columbus, Ohio 43210

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The dependence on orthohydrogen ($o\text{-H}_2$) concentration c of the thermal conductivity of solid mixtures of $o\text{-H}_2$ and parahydrogen ($p\text{-H}_2$) is calculated in the single-mode relaxation-time approximation. The contribution of the phonon-phonon and phonon-boundary scattering to the relaxation time is determined phenomenologically from the experimental data on pure $p\text{-H}_2$ due to Bohn and Mate. The phonon- $o\text{-H}_2$ scattering is calculated from the statistical model of $o\text{-H}_2$ in $p\text{-H}_2$. The effect of zero-point motion is found to enhance interaction between the $o\text{-H}_2$ and phonons substantially. Our results are compared with experimental data, and qualitative agreement is obtained.

I. INTRODUCTION

There has been a revival of interest in solid mixtures of orthohydrogen and parahydrogen following experimental and theoretical work by Hatton and Rollin,¹ Hill and Ricketson,² and Nakamura.³ Mixtures of parahydrogen and very low concentrations of orthohydrogen have also received a considerable amount of attention, with numerous properties being measured.⁴ In particular, the thermal conductivity K of $p\text{-H}_2$ containing a few percent $o\text{-H}_2$ impurities has been measured earlier by Hill and Schneidmesser⁵ and recently by Bohn and Mate⁶ at temperatures $T < 6^\circ\text{K}$. We report in the present work a calculation of K in this temperature and concentration region.

The phonon scattering processes which are of interest to us here are boundary scattering, impurity ($o\text{-H}_2$) scattering, and various phonon-phonon effects. We shall combine these contributions within the familiar single-mode relaxation-time approximation as described in the review article by Carruthers.⁷

The contributions of the three scattering processes will be determined as follows: We are primarily interested in the effect of the $o\text{-H}_2$ impurities and so simply use the experimental results on nearly pure specimens of $p\text{-H}_2$ to determine the boundary and phonon-phonon scattering phenomenologically. The phonon lifetime for phonon- $o\text{-H}_2$ scattering $\Gamma_{\text{ph-}o}$ is found by employing the Hamiltonian of Ref. 3. The $o\text{-H}_2$ correlation functions needed to evaluate the scattering cross section are taken from Refs. 8 and 9. Because of the light mass of solid H_2 , He^3 , and He^4 , the usual lattice dynamics is not applicable. Attempts^{10,11} have been made to include this "quantum crystal" effect in the calculation of the thermal conductivity on the basis of Nosanow's theory.¹² This effect is also included in our computation as is done in the spirit

of Refs. 10 and 11.

$\Gamma_{\text{ph-}o}$ is evaluated in Sec. II; Sec. III contains the calculation of K and a discussion of the results. Section IV is a summary.

II. IMPURITY-PHONON SCATTERING

A. Hamiltonian

We are interested in computing the effect of $o\text{-H}_2$ on lattice conduction in the solid crystal of $p\text{-H}_2$. The interaction responsible for the phonon- $o\text{-H}_2$ scattering is the difference of interactions between the pair $p\text{-H}_2 + p\text{-H}_2$ and the pair $p\text{-H}_2 + o\text{-H}_2$. The strength and the form of this interaction have not been accurately determined. Nakamura discussed this problem and wrote the interaction as

$$H_{\text{int}} = \sum_{i=1}^{N_i} \sum_j \left[V \exp \frac{(-|\vec{r}_i - \vec{r}_j|)}{\rho} - \epsilon_d \left(\frac{a}{|\vec{r}_i - \vec{r}_j|} \right)^6 \right] \left[3 \left(\vec{J}_i \frac{(\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|} \right)^2 - 2 \right], \quad (1)$$

where

$$V e^{-a/\rho} \approx -1.4 \times 10^{-16} \text{ erg}$$

and

$$\epsilon_d = 0.88 \times 10^{-16} \text{ erg};$$

\vec{r}_i is the position of the i th $o\text{-H}_2$ and \vec{r}_j that of its j th $p\text{-H}_2$ nearest neighbor. The equilibrium value of $|\vec{r}_i - \vec{r}_j| = a = 3.75 \text{ \AA}$ and $a/\rho \sim 20$.¹³ The sum on i is over all $o\text{-H}_2$ impurities while that on j is over the $p\text{-H}_2$ nearest neighbors of each impurity. \vec{J}_i is the angular momentum operator of the i th $o\text{-H}_2$. The sum on j in Eq. (1) is zero in a hexagonal close-packed structure when all atoms are at their equilibrium positions. However, when they are displaced from equilibrium positions for various

reasons, the average is nonzero and the Hamiltonian (1) contributes to the energy of the system.³ It has also been directly measured.⁴

Next, we consider the interaction between two o -H₂ molecules located at positions \vec{r}_i and \vec{r}_j , such that the molecules's axes are oriented at the angles $\Omega_i (= \theta_i, \phi_i)$ and Ω_j relative to the polar axes which we take as the direction of c axis. This is the electric quadrupole-quadrupole interaction^{3,14}

$$H_{ik} = \frac{4}{5}\pi \epsilon_1 (a/|r_{ik}|)^5 \left(\frac{280}{9}\pi\right)^{1/2} \times \sum_{mn} C(224mn) Y_2^m(\Omega_i) Y_4^{m+n}(\Omega_{ik}) Y_2^n(\Omega_k), \quad (2)$$

where $\epsilon_1 = 3.7 \times 10^{-16}$ erg and Ω_{ik} expresses the orientation of $\vec{r}_i - \vec{r}_k$ relative to the c axis of the hcp structure; the C 's are Clebsch-Gordan coefficients and the Y 's, spherical harmonics.

In calculations of the specific heat and nuclear magnetic relaxation times we need $\langle H_{int} \rangle$, the average of H_{int} over the nearest neighbors, which is almost zero because of the crystal symmetry and the angular dependence of Eq. (1), as mentioned earlier. In the calculation of the thermal conductivity, $\langle H'_{int} \rangle$ is needed. Here, H'_{ik} is the second derivative of H_{ik} in the expansion of lattice vibration. The complicated angular factor introduced in H'_{int} makes

$$\langle H'_{int} \rangle \gg [(a/\rho)^2/6 \times 5] \langle H'_{ik} \rangle,$$

where the factor $(a/\rho)^2/6 \times 5$ is introduced by taking the second derivative of H_{int} and H_{ik} . In addition, we deal with systems having low concentration of o -H₂ which will further reduce the effect of H_{ik} . Thus the scattering of a pair of o -H₂ is neglected. H_{ik} does play an important role, however, in that it introduces correlations between o -H₂ molecules and thus gives rise to phonon- o -H₂ scattering which is different from the usual static impurity scattering with regard to both concentration and momentum dependence.

We begin the evaluation of the phonon-impurity (o -H₂) interaction by expanding H_{int} in terms of the operators $A_{\vec{k}}^\dagger$ and $A_{\vec{k}}$, which create and destroy phonons of wave vector \vec{k} . (In this section we include the polarization index in the specification of phonon momentum.) Also, we transform into a coordinate system such that the z axis is parallel to the crystal's c axis, thus obtaining, e. g.,

$$\delta(\vec{r}_i - \vec{r}_j)^m = \sum_n D_{nm}^1(\Omega_{ij}) S_{ij}^n, \quad (3)$$

where

$$S_{ij}^m = \left(\frac{\hbar}{2M}\right)^{1/2} \sum_k A_{\vec{k}}^\dagger \epsilon_{\vec{k}}^m \omega_{\vec{k}}^{-1/2} [e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} - 1], \quad (4)$$

and $\delta(\vec{r}_i - \vec{r}_j)^m$ is the m 'th component of the difference of the instantaneous displacements of the i th

and j th molecules from their equilibrium positions; M is the crystal mass; D_{nm}^1 is the rotation-operator matrix element from the direction of $\vec{r}_i - \vec{r}_j$ to that of the z axis; and $\epsilon_{\vec{k}}^n$ is the n th component of the phonon (unit) polarization vector.

The expansion of H_{int} to second order in the displacement of the molecules from equilibrium will contain zeroth, first, and second derivatives with respect to intermolecular distance.¹⁵ Each of these derivatives brings a factor of $a/\rho \approx 20$ into the interaction relative to the derivatives corresponding to angular distortion of the lattice and so in lowest order we may keep only terms involving second derivatives with respect to intermolecular distance. In this approximation we find

$$V'' = \frac{1}{2} \epsilon \sum_{n=0,1,2} \sum_{mm'} E_{ni} D_{om}^2(\Omega_{ij}) D_{om}^1(\Omega_{ij}) D_{om'}^1(\Omega_{ij}) S_{ij}^m S_{ij}^{m'}, \quad (5)$$

where

$$\epsilon = V e^{-a/\rho} / \rho^2, \quad E_0 = (3J_z^2 - 2),$$

$$E_{\pm 1} = \sqrt{\frac{3}{2}} (J_z J_{\pm} + J_{\pm} J_z), \quad E_{\pm 2} = \sqrt{\frac{3}{8}} J_{\pm}^2.$$

The J_{\pm} are the usual raising and lowering operators $J_{\pm} = (J_x \pm iJ_y)$ and all operators J refer to the specific index i .

The average represented by \sum_j is taken as $(12/4\pi) \int d\Omega_{ij}$ in Eq. (5). For example, we cite

$$\begin{aligned} & \sum_j D_{oo}^2 D_{om}^1 D_{om'}^1 S_{ij}^m S_{ij}^{m'} \\ &= \frac{12}{4\pi} \sum_{\vec{k}, \vec{k}'} \int d\Omega D_{oo}^2 D_{om}^1 D_{om'}^1 P_1(\theta_{ij}) P_1(\theta_{ij'}) \\ & \times k k' (\omega_{\vec{k}} \omega_{\vec{k}'})^{-1/2} A_{\vec{k}}^\dagger A_{\vec{k}'} \epsilon_{\vec{k}}^m \epsilon_{\vec{k}'}^{m'} + \text{H. c.} \end{aligned} \quad (6)$$

B. Quantum Crystal Effect

The molecular mass of hydrogen is small, leading to large quantum-mechanical zero-point motion of the molecules around their equilibrium lattice positions. Consequently, it is not a valid approximation to evaluate the various interactions between molecules as though they were fixed at the lattice sites. Rather, an average over the zero-point motion should be introduced. Noolandi and Van Kranendonk, and Harris⁹ gave such a treatment of interactions in solid hydrogen, based upon the quantum crystal theory of Nosanow.¹² Nosanow found that molecules behave as though they interacted via an effective potential $v_{\text{eff}}(\vec{R})$ which is obtained by averaging the bare interaction $v(\vec{r})$:

$$\begin{aligned} & V_{\text{eff}}(\vec{R}_1 - \vec{R}_2) \\ &= \int d\vec{r}_1 d\vec{r}_2 \phi^2(|\vec{r}_1 - \vec{R}_1|) \phi^2(|\vec{r}_2 - \vec{R}_2|) f^2(r_{12}) V(r_{12}) \end{aligned}$$

$$\times \left[\int d\vec{r}_1 d\vec{r}_2 \phi^2(|\vec{r}_1 - \vec{R}_1|) \phi^2(|\vec{r}_2 - \vec{R}_2|) f^2(r_{12}) \right]^{-1},$$

where ϕ and f are from the trial wave function for the quantum crystal ψ :

$$\psi = \prod_i \phi(|\vec{r}_i - \vec{R}_i^0|) \prod_{ij} f(r_{ij}).$$

\vec{r}_i is the position of the i th molecule and \vec{R}_i^0 its equilibrium position, $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$. The functions ϕ and f were taken to be of the form

$$f(r) = \exp\{-K[(\sigma/r)^{12} - (\sigma/r)^6]\},$$

$$\phi(r) = (A/\pi)^{3/4} \exp(-\frac{1}{2}Ar^2).$$

Nosonow determined the parameters A and K by minimizing the ground-state energy, finding $Aa^2 = 46.5$ and $k = 0.2406$, where a is the nearest-neighbor distance.

Following Harris,⁹ we perform the average of the interaction Hamiltonian H_{int} . The angular dependence of the interaction is not changed by this procedure, and so the net effect is that the averaged interaction is some constant multiple of the bare interaction evaluated at the nearest-neighbor distance $\langle v \rangle = \xi v(R_0)$.

To calculate the phonon coupling, we really need the second derivatives of H_{int} . There is some question whether it is more nearly correct to take the second derivative before or after performing the zero-point-motion average.¹¹

For its first term, or valence part of H_{int} , it turns out that if the derivatives are performed after averaging, the result is some three times smaller than for the other procedure. Following Refs. 10 and 11, we perform the average after taking the second derivative. The result is that for the valence part, $\xi_v = 2.8$; while for the second term, or dispersion part of H_{int} , $\xi_d = 1.5$.

C. Phonon Lifetime

As a result of the averaging performed in Sec. II B, Eq. (5) should be written with a new coupling constant $\bar{\epsilon} = \xi_v \epsilon$;

$$V''(t) = \frac{1}{2} \bar{\epsilon} \sum_{i,n=0,1,2} \sum_{\vec{k}, \vec{k}'} E_{ni}(\omega_{\vec{k}} \omega_{\vec{k}'})^{-1/2} C_{\vec{k}\vec{k}'}^n A_{\vec{k}}^\dagger A_{\vec{k}'}. \quad (7)$$

by completing the various summations and averages; E_{ni} is a time-dependent operator because of both nuclear magnetic field effects and the interaction H_{ik} between o -H₂ molecules. The magnetic energy is far smaller than the thermal energies of interest here and may be neglected; however, the interaction H_{ik} provides internal energy levels for the o -H₂ and so gives rise to important inelastic scattering of phonons.

The transition probability of phonons for the process $\vec{k} \rightarrow \vec{k}'$ is given by the golden rule

$$P_{\vec{k}\vec{k}'}(t) = (2\pi/\hbar) |\langle k' | \int_{-\infty}^t dt' V''(t') | k \rangle|^2, \quad (8)$$

and the inverse lifetime of a phonon in state k is in the limit of large t ¹⁶:

$$\Gamma_{\text{ph}-0}^{-1}(k) = \frac{d}{dt} \sum_{k'} P_{kk'}(t) = [n_i (\frac{1}{2} \bar{\epsilon})^2 / 16\pi^2 m^2] \times \sum_{n=1,2} \int d\vec{k}' J_n(\omega_k - \omega_{k'}) (\omega_k \omega_{k'})^{-1/2} |C_{kk'}^n|^2. \quad (9)$$

Here n_i is the impurity number density while m is the total mass density and $J_n(\omega)$ is the correlation function of operators E_n . They can be expressed in terms of

$$J_n(\omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\omega t} J_n(t). \quad (10)$$

The correlation functions J_n are¹⁷

$$\begin{aligned} J_1(t) &= \langle J_z^2(t), J_z^2(0) \rangle = \frac{2}{3} \exp(-c \cdot 4.63 |\epsilon' t / \hbar|^{3/5}), \\ J_2 &= \langle J_z(t) J_x(t), J_x(0) J_z(0) \rangle \\ &= \frac{2}{3} \exp(-c \cdot 7.10 |\epsilon' t / \hbar|^{3/5}), \end{aligned} \quad (11)$$

where $\epsilon' = 1.89 \times 10^{-16}$ erg, and c is the fractional o -H₂ concentration. The brackets in Eq. (11) indicate the average over all states of angular momentum. Of course, the high-temperature approximation is implicitly assumed. Also, ω_k is the energy of a phonon of wave vector k (and polarization λ). Note that if correlations were neglected, $J_n(t)$ would be constant and $J_n(\omega) = \delta(\omega)$, so that Eq. (9) would be the usual⁷ expression for scattering by static impurities.

Direct evaluation of the sums in Eq. (5) gives the averages

$$T_n = \int d\Omega_{k'} |C_{kk'}^n|^2.$$

Retaining only leading terms, we find

$$T_1 = \frac{1}{3} \pi \left(\frac{8}{35}\right)^2 \cos^2 \theta_k, \quad T_2 = \pi \left(\frac{2}{35}\right)^2 (1 + \cos^2 \theta_k),$$

where θ_k is the angle between k and the crystal c axis.

The result for the impurity scattered phonon lifetime is thus

$$\begin{aligned} \Gamma_{\text{ph}-0}^{-1}(\vec{k}) &= (3/\pi)^2 (\frac{1}{2} \bar{\epsilon})^2 n_i / 16\pi^2 m^2 \int \frac{k'^2 dk'}{\omega_k \omega_{k'}} k'^2 a^2 k^2 a^2 \\ &\times \left\{ \frac{1}{3} \pi \left(\frac{8}{35}\right)^2 \cos^2 \theta_k [9 J_1(\omega_k - \omega_{k'}) - 4\delta(\omega_k - \omega_{k'})] \right. \\ &\left. + 4\pi \left(\frac{2}{35}\right)^2 (1 + \cos^2 \theta_k) J_2(\omega_k - \omega_{k'}) \right\}. \end{aligned} \quad (12)$$

III. THERMAL CONDUCTIVITY

Following Carruthers,⁷ we treat the thermal conductivity in the single-mode relaxation-time approximation:

$$K = (2\pi)^{-3} \sum_{\lambda} \int d^3k S_{\lambda}^2 C_{\text{ph}}(\omega_{k\lambda}) \cos^2\theta_k \Gamma(k\lambda), \quad (13)$$

where $C_{\text{ph}}(\omega)$ is the heat capacity per normal mode,

$$C_{\text{ph}}(\omega) = k_B (\beta \hbar \omega)^2 c^{\beta \hbar \omega} (c^{\beta \hbar \omega} - 1)^{-2}, \quad (14)$$

$\Gamma(k, \lambda)$ is the phonon lifetime, S_{λ} is the phonon velocity, and $\beta = k_B T$, k_B being the Boltzmann constant. For lack of more detailed information, we assume a linear dispersion relation $\omega_{k\lambda} = S_{\lambda} k$, which should be a valid assumption for $k \ll k_D$, the Debye wave number. We are interested mainly in such phonons, since we are considering $T \ll \theta_D$, where θ_D is the Debye temperature; k_D and θ_D are related by $\hbar k_D S = k_B \theta_D$, where S is some suitable average of the velocities of transverse and longitudinal phonons. This S is evaluated by analyzing the T^3 part of the low-temperature specific heat of solid parahydrogen; such an analysis¹⁸ gives $S = 1.3 \times 10^5$ cm/sec. Also, k_D may be found from the molecular number density n of solid parahydrogen since $k_D = (6\pi^2 n)^{1/3}$; combining these results we find $\theta_D = 114^\circ \text{K}$.

Combining Eqs. (13) and (14) and defining $x = \hbar S k / k_B T$, we have

$$K = 9k_B S^2 n (T/\theta_D)^3 \times \int_0^{\infty} \frac{x^4 dx e^x}{(e^x - 1)^2} \frac{1}{2} \int_{-1}^1 d \cos\theta_k \cdot \cos\theta_k \Gamma(x, \lambda), \quad (15)$$

In order to arrive at Eq. (14) we had to approximate S_{λ} by S for all three phonon polarizations.

The inverse lifetime $1/\Gamma(k, \lambda)$ is made up of three additive contributions. First, at very small T and c , the effective mean free path of the phonons will be limited only by the boundaries of the sample, thus giving a constant contribution which we write as

$$\Gamma_b^{-1} = S/L, \quad (16)$$

where L is a length of the order of the size of samples. In general, L may be much less because of complicated polycrystal structures.

Next, in the high-temperature region, phonon-phonon scattering⁷ will be important. Both normal and Umklapp process can occur; however, theoretical treatment of such scattering is beyond the

scope of this work. Furthermore, it is not clear how all these contributions can properly be included. Instead, we simply introduce a term into $\Gamma^{-1}(x, \lambda)$:

$$\Gamma_v^{-1} = A_v e^{-\theta_v/T}, \quad (17)$$

of the approximate form that one expects for Umklapp scattering and then fit this term to the high- T and low- c experimental data. There is no particular reason for not including a normal-scattering term also; it is just that the term (17) is sufficient for our purposes.

Finally, there is also the impurity scattering contribution as given in Eq. (11); by introducing some dimensionless variables, we may rewrite it as

$$\Gamma_{\text{ph}-0}^{-1}(\vec{k}) = \left(\frac{24}{35}\right)^2 \left(\frac{\bar{\epsilon}}{2}\right)^2 \frac{(a/S)^4}{(2M)^2} \frac{xc\omega_D}{2\pi} \times \int_0^1 x'^3 dx' \{ \cos^2\theta_k [9J_1(x-x') - 4\delta(x-x')] + \frac{3}{4}(1 + \cos^2\theta_k) J_2(x-x') \}, \quad (18)$$

where

$$J_1(x) = (2/3\pi) \int_0^{\infty} dy \cos xy e^{-0.321cy^{3/5}} \quad (19)$$

and J_2 is the same as J_1 with 0.492 replacing 0.321 in the exponent. Also, $x = k/k_D$, $x' = k'/k_D$, and $y = \omega_D t$, $\omega_D (= S k_D)$ is the Debye frequency. With the help of the identity

$$\int_0^{\infty} dy \cos xy e^{-\alpha y^{3/5}} = \pi \delta(x) + \int_0^{\infty} dy \cos xy [\exp(\alpha y^{3/5}) - 1] \quad (20)$$

we may arrive at a final expression for $\Gamma_{\text{ph}-0}^{-1}(k)$:

$$\Gamma_{\text{ph}-0}^{-1}(\vec{k}) = \left(\frac{24}{35}\right)^2 \frac{(a/S)^4}{(2M)^2} \left(\frac{\bar{\epsilon}}{2}\right)^2 \times \frac{\omega_D c}{\pi} \{ \cos^2\theta_k [x^4 + 3xI_1(x, c)] + \frac{1}{4}(1 + \cos^2\theta_k) [x^4 + xI_2(x, c)] \}, \quad (21)$$

where

$$I_1(x, c) = \frac{1}{\pi} \int_0^{\infty} dy [\exp(-0.321cy^{3/5}) - 1] \times \{ 3y^{-2}(1 - 2y^{-2}) \cos(1-x)y + y^{-1}(1 - 6y^{-2})$$

$$\times \sin(1-x)y + 6y^{-4} \cos xy \} \quad (22)$$

and I_2 is the same as I_1 except that 0.492 replaces 0.321 in the exponent.

This form is convenient because, upon evaluating I_2 and I_1 numerically, it turns out that, to about 2% accuracy, they are proportional to c for $c \lesssim 0.10$ and, consequently, they are proportional to each other. For small x , I_1 and I_2 are well represented by $I_2 = 0.0467c(1+3x)$ and $I_1 = 0.654I_2$. There is no point in including higher-order corrections in x as they would be of the same order as the ignored deviations from a linear phonon-dispersion relation.

We note that Eq. (21) contains the usual cx^4 or ck^4 terms corresponding to static scattering by the impurities; however, it also contains terms which for small k are proportional to c^2x and will give rise to thermal conductivity $K \sim T^2c^{-2}$.

The total inverse phonon lifetime is thus

$$\Gamma^{-1}(\vec{k}) = S/L + \Gamma_{\text{ph}-0}^{-1}(\vec{k}) + A_v e^{-\theta_v/T}. \quad (23)$$

This expression is substituted into Eq. (15) and the integration completed numerically for various T and c . The parameters $A_v = 2.2 \times 10^{12}$ and $\theta_v = \theta_D/2.2$ in Eq. (23) are determined from the data at T near 6 °K. Also, L is chosen to fit the data from the purest sample at $T \approx 1.5$ °K. This gives $L = d/17$ where d is the diameter of the sample. Finally, the parameter $\bar{\tau}$ which determines the magnitude of $\Gamma_{\text{ph}-0}^{-1}$ is chosen to give the best overall fit¹⁹ of theory to experiment at all o -H₂ concentrations. The value obtained is a factor of 3 larger than that found from the theoretical numbers following Eq. (1), a discrepancy which is reasonable in view of the large uncertainty in V and a/ρ . The theoretical curves in Fig. 1 are computed with these fixed parameters. A comparison of the theory with experimental data is given in Ref. 6.

The value L seems to be rather small compared with the sample dimension. We refer the discussion of experimental concern to the companion paper.

We note that the strong concentration dependence of K , which is computed on the basis of theory explaining NMR experiments, is observed experimentally. However, there might be a discrepancy between theory and experiment with regard to the temperature dependence in this region. The theory predicts essentially a T^2 dependence, whereas the experiments show stronger temperature dependence in the region $1.4 < T < 2.4$ at all concentrations rather than only in the zero-concentration limit where a T^3 dependence should arise because of boundary scattering. If this discrepancy persists in the low-temperature region, it indicates that

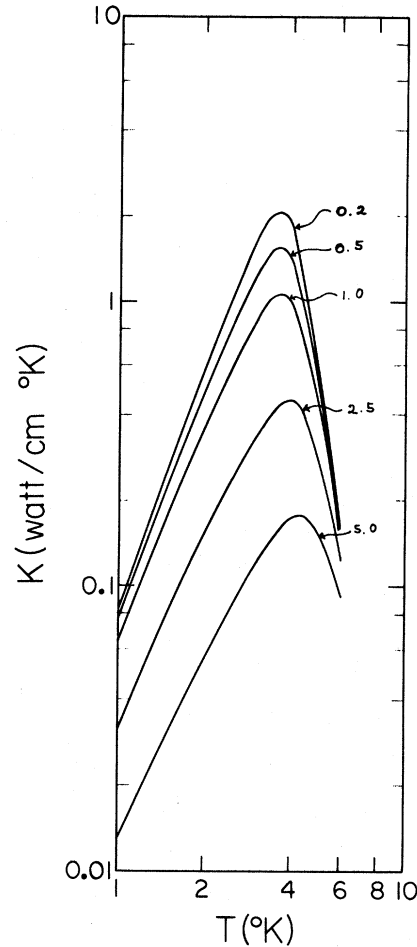


FIG. 1. Theoretical curves of thermal conductivity of various concentrations of orthohydrogen in parahydrogen.

boundary scattering is related to c in a complicated way. It is difficult to understand the strong concentration dependence of the measured thermal conductivity unless there is some connection between the o -H₂ concentration and the formation of boundaries. One way to clarify the situation would be to check the reproducibility of the data with other samples; effects associated with the presence of boundaries would vary from sample to sample. We also should mention in this connection similar difficulty in the thermal conductivity of KI with U centers.²⁰

IV. SUMMARY

The contributions of phonon-boundary and phonon-phonon scattering were determined phenomenologically by analysis of the experimental measurements. The scattering by the o -H₂ impurities, on the other hand, was calculated by expanding the

valence part of the o -H₂- p -H₂ interaction in terms of phonon creation and annihilation operators for small displacements of the molecules from their equilibrium positions. The final expression for the scattering cross section involves o -H₂ angular momentum correlation functions which have been previously evaluated. The thermal conductivity was then found by combining the three scattering effects listed above within the single-mode relaxation-time approximation. Comparison of the cal-

culated K with measurements shows general qualitative agreement. A possible discrepancy in the temperature dependence remains to be clarified in the low-temperature region.

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The calculated value of K using the usual formalism is about 10 times larger than the experimental data.

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¹⁴The spherical harmonics are normalized in the usual way: $\int d\Omega |Y_{lm}(\Omega)|^2 = 1$.

¹⁵For simplicity, only the valence part of H_{int} is retained here; inclusion of the dispersion part turns out to alter the phonon- o -H₂ coupling by a negligible amount.

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¹⁷The constant ϵ' obtained in Ref. 8 is different from that in Ref. 9 by approximately a factor of 2. We find that this difference does not seriously affect the T and c dependence of the conductivity. See also Ref. 19.

¹⁸R. W. Hill and O. W. Lounasmaa, Phil. Mag. 4, 785 (1959).

¹⁹If the value of ϵ' used were that given in Ref. 9, $\bar{\epsilon}$ would be correspondingly different; we stress, however, that the temperature and concentration dependence of K would remain the same.

²⁰See, for example, L. G. Radosovich and C. T. Walker, Phys. Rev. 156, 1030 (1967).