Ortho-para conversion of solid hydrogen as a function of density

A. Driessen* and E. van der Poll

Natuurkundig Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Isaac F. Silvera

Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 23 April 1984)

The ortho-para conversion in solid H_2 as a function of density has been studied experimentally by isochoric measurements and Raman scattering. We do not find the double peak observed earlier by Pedroni *et al.*, which was attributed to structure in the phonon density of states. Conversion in lattices with nonrandom distributions of ortho molecules is probably responsible for the scatter of the experimental data in the literature. A theoretical model by Berlinsky for conversion involving the one-phonon density of states is used to determine the phonon density of states. This is in good agreement with direct experimental results.

I. INTRODUCTION

One of the most fascinating and explicit quantummechanical properties of molecular hydrogen is the orthopara classification. Isolated molecules are classified in terms of the total nuclear spin I and the rotational states J as para- (I = 0, even J) and ortho- (I = 1, odd J) hydrogen. Although conversion from ortho states to para states is absolutely forbidden for an isolated molecule, in the condensed phases conversion takes place at a slow but measurable rate. Because of this, ortho- and para-H₂ can be treated as two different molecular species. In the solid state the ground state and many thermodynamic properties are strongly influenced by the ortho concentration, C_1 .¹ It is thus important to be able to modify and measure C_1 . Not only is the conversion mechanism itself interesting, but a number of physical properties of the solid can be determined by a careful study of conversion.

In recent studies of the equation of state (EOS) of H_2 ,² we made several long-time studies of the isochores of H₂ and observed conversion rates which were in disagreement with published rates in the literature. Although these differences were small, they were significant. In particular we were unable to reproduce the double peak in the decay rate at densities ρ/ρ_0 between 1.2 and 1.4 (ρ_0 is the zero-pressure density) observed by Pedroni et al.³ The dominant factor controlling the density dependence of the conversion rate is the density of one- (and two-) phonon final states required to conserve energy due to the change of rotational quantum number in a conversion. The double peak has been interpreted by Berlinsky⁴ as reflecting structure in the one-phonon density of states. We have also supplemented isochoric EOS measurements with Raman scattering measurements in a high-pressure optical cell. These data fail to reveal a double peak. We have analyzed conversion data to generate the one-phonon density of states. This is in agreement with results from neutron scattering and infrared absorption. Finally, we suggest some sources of the scatter of conversion rates in earlier work. An important possibility may be due to nonrandom distribution of ortho molecules in the solid state.

The paper is structured as follows: In Sec. II we present the theoretical background; experimental results are presented and discussed in Secs. III and IV. The phonon density of states is determined in Sec. V.

II. THEORETICAL BACKGROUND

Although most of the ideas concerning conversion of hydrogen in solids were developed by Motizuki and Nagamiya,⁵ we shall follow the formulation of Berklinsky and Hardy,⁶ who have given the most recent theoretical treatment.

The thermodynamic equilibrium ortho-para concentration of H_2 and D_2 is shown in Fig. 1 (after Ref. 1). In order to attain equilibrium, a suitable external perturbation is required which can cause a simultaneous change in the rotational and nuclear spin states. The conversion or transition ratio W can be calculated from the golden rule:

$$W = \frac{2\pi}{\hbar} \sum_{i,f} P_i |\langle f | H_{\text{int}} | i \rangle |^2 \delta(E_i - E_f) , \qquad (1)$$



FIG. 1. Equilibrium ortho-para concentration of H_2 and D_2 as a function of temperature.



FIG. 2. The two-phonon density of states of H_2 .

where P_i is the probability that the system is initially in one of the g_i states *i*, and *f* is the final state; E_i and E_f are the initial and final energies of the system. H_{int} is the interaction Hamiltonian and has three additive parts which can change the nuclear spin states: H_{SS} , the nuclear spin-spin interaction; H_{RS} , the rotation-spin interaction; and H_{EQ} , the electric quadruple interaction. H_{EQ} is only important for D₂ as spin- $\frac{1}{2}$ H has no electric quadrupole moment. H_{SS} is the dominant term with H_{RS} yielding a 2-3% correction to H_{SS} .⁵

The δ function in Eq. (1) requires conservation of energy. The rotational energy change in a conversion is

$$BJ_{i}(J_{i}+1) - BJ_{f}(J_{f}+1)$$

At low temperature the ortho and para molecules are in states J=1 and 0, respectively, so that $\Delta E/k_B = 2B/k_B$ = 171 K. For energy conservation the final state involves the creation of one or more phonons. The theoretical density dependence for two-phonon creation is

$$W \sim \rho^{12/3} g_{2 \text{ ph}}$$
, (2)

where $g_{2 ph}$ is the two-phonon density-of-states function. From the zero-pressure two-phonon density of states shown in Fig. 2 (from Ref. 6), it is clear that this is an open channel for conversion, with the conversion energy 2*B* lying approximately at the maximum.

With rising density, the phonon energy shifts upward (see, e.g., Berkhout and Silvera⁷) rapidly, reducing the two-phonon density at 2*B*. Figure 3 (from Ref. 6) shows the result more quantitatively. Already at a moderate pressure of 1 kbar, corresponding to $18 \text{ cm}^3/\text{mol}$, the two-phonon conversion is practically zero.

For the one-phonon conversion Berlinsky⁴ finds the fol-



FIG. 3. The two-phonon conversion rate in solid H_2 as a function of molar volume.

lowing result:

$$W(\rho/\rho_0) = \text{const} \times (\rho/\rho_0)^{10/3} g(E_{10}; \rho/\rho_0) , \qquad (3)$$

where $g(E_{10};\rho/\rho_0)$ is the one-phonon density of states at $E_1 - E_0 \equiv E_{10} = 2B$, and density ρ .

We would like to relate $g(E_{10};\rho/\rho_0)$ to the one-phonon density at $\rho = \rho_0$ at the energy corresponding to E_{10} . To a fairly good approximation we can assume that all parts of the phonon spectrum scale uniformly with density,⁸ i.e.,

$$\omega_{\rm ph}(\rho/\rho_0)/\omega_{\rm ph}(\rho=\rho_0) = F(\rho/\rho_0) , \qquad (4)$$

for all phonon frequencies $\omega_{\rm ph}(\rho/\rho_0)$. Here $F(\rho/\rho_0)$ is a function depending only on density, which can be determined from the Debye temperature Θ_D :⁹

$$F(\rho/\rho_0) = \Theta_D(\rho/\rho_0) / \Theta_D(\rho = \rho_0) .$$
(5)

The phonon density-of-states function scales as the inverse of the square of the energy because, following Berlinsky,

$$g(E) \sim U_{\delta}^{2}(E)\delta(E_{10}-E)$$
, (6)

where U_{δ} is the displacement of a molecule due to the lattice vibration with energy E. U_{δ} scales as $E^{-1/2}$ and $\delta(E_{10}-E)$ as E^{-1} . We therefore can write for the phonon density of states,

$$g(E;\rho/\rho_0) = g\left[\frac{\Theta_D(\rho=\rho_0)}{\Theta_D(\rho/\rho_0)}E,\rho=\rho_0\right] \left[\frac{\Theta_D(\rho=\rho_0)}{\Theta_D(\rho/\rho_0)}\right]^2.$$
(7)

Together with Eq. (3) we get for the one-phonon conversion,

$$W(\rho/\rho_0) \sim (\rho/\rho_0)^{10/3} g \left[\frac{\Theta_D(\rho = \rho_0)}{\Theta_D(\rho/\rho_0)} E_{10}, \rho = \rho_0 \right] \left[\frac{\Theta_D(\rho = \rho_0)}{\Theta_D(\rho/\rho_0)} \right]^2$$

(8)



FIG. 4. Conversion as a function of time for k = 4%/h: solid line, random distribution of J = 1 pairs; dashed line, totally frozen distribution of J = 1 pairs.

In Sec. V we will use this relation to construct the onephonon density of states from experimental values for the conversion rate.

The dominant conversion mechanism is the interaction between the nuclear spins of two H₂ molecules. As para-H₂ has nuclear spin zero, this interaction takes place only between ortho-H₂ molecules. The conversion rate therefore should be proportional to the number of J=1 pairs, i.e.,

$$\frac{dC_1}{dt} = -kC_1^2 , \qquad (9)$$

where k is the conversion rate constant given in %/h, t is time in units of h, and C_1 the concentration of J = 1 molecules. Equation (9) has the following solution:

$$C_1^{-1} = kt + C_1^{-1}(t=0) . (10)$$

This equation can be conveniently displayed as a straight line in a $1/C_1$ against t plot; k will then be the slope of this line (see, e.g., Fig. 4).

Equation (9) is valid only as long as the number of J=1 pairs is proportional to C_1^2 , which is the case for a random distribution. Schmidt¹⁰ has made an analysis of nonrandom distributions. He starts with

$$\frac{dC_1}{dt} = -k\frac{M}{12}C_1 , \qquad (11)$$

where M is the mean number of nearest ortho-H₂ (o-H₂) molecules surrounding each o-H₂ molecule. For H₂ in equilibrium with 12 nearest neighbors $M_{eq}/12=C_1$.

There are different effects, which can establish nonrandom distributions.

A. Conversion itself

Conversion reduces the number of nearest $o-H_2$ neighbors and tends to create isolated $o-H_2$ molecules, which will have a strongly reduced conversion rate. The deviation in M is, following Schmidt,¹⁰

$$\frac{dM}{dt} = \frac{k}{12} \left[M^2 - 2\sum_n n^2 W_n \right], \qquad (12)$$

where n is the number of nearest $o-H_2$ neighbors, and

$$W_n = C_1^2 (1 - C_1)^{12 - n} \begin{bmatrix} 12 \\ n \end{bmatrix}$$
(13)

is a binomial distribution for the $o-H_2$ pairs. Combining Eq. (12) with Eq. (13), one gets conversion, when the lattice is totally frozen, with no possibility of randomizing the $o-H_2$ distribution.

We have calculated conversion for k = 4%/h and different starting concentrations (Fig. 4) using Eq. (9) (solid line) and with a frozen distribution Eqs. (12) and (13) (dashed line). It can be seen that after more than 10–15 h the concentrations are measurably different for the two conditions.

In order to avoid nonrandom conversion, one has to be sure that the diffusion rate is sufficiently high to maintain a random pair distribution. The diffusion rate obeys Fick's law

$$J_n = -D \operatorname{grad} N , \qquad (14)$$

where J_n is the number of molecules crossing unit area in unit time, D is the diffusion coefficient, and N is the number of molecules per unit volume. For classical

TABLE I. The thermal diffusion coefficient D of H_2 at different volumes and temperatures. E is the activation energy.

V (cm ³ /mol)					
	E/k_B (K)	T = 4.2 K	$T = 10 { m K}$	T = 20 K	T = 37 K
23	180ª	5×10 ⁻²²	3×10 ⁻¹¹		
20	420 ^a	5×10 ⁻⁴⁶	3×10^{-21}	1×10^{-21}	
17.5	1500 ^b	$< 1 \times 10^{-100}$	3×10 ⁻⁶⁸	5×10 ⁻³⁶	5×10 ⁻²¹

^aExperimental results from Ref. 27.



FIG. 5. Experimental results of Schmidt¹⁰ for the ortho-para conversion in solid H_2 at 12, 4.2, and 1.57 K.

thermal diffusion D is related to the activation energy E for self-diffusion by

$$D = D_0 e^{-E/k_B T} . (15)$$

For H₂, Ebner and Sung¹¹ find in the high-temperature limit $D_0 = 2 \times 10^{-3}$ cm²/sec. Table I gives D calculated from Eq. (15) as a function of volume and temperature.

Schmidt¹⁰ found the following limits for the diffusion rate with respect to ortho species: $D > 10^{-19}$ cm²/sec, random distribution; $D < 10^{-23}$ cm²/sec, the lattice is totally frozen. He also measured the zero-pressure conversion at different temperatures with the result that at 4.2 K conversion can be accurately represented by the random distribution (see Fig. 5).

B. Clustering of J = 1 molecules at low temperature

At sufficiently low temperature quantum diffusion becomes important. The J=1 rotational excitations can hop from one lattice site to another.¹² The attractive electric quadrupole-quadrupole (EQQ) interaction between J=1 pairs is responsible for clustering of J=1 molecules which increases the conversion rate. Figure 5 shows the result of conversion measurements at 1.57 K by Schmidt.¹⁰ The enhanced conversion at this temperature, in comparison with conversion at 4.2 K, can be seen very clearly.

C. Solidification of an ortho-para mixture followed by quenching

White and Gaines¹³ report an experiment where they were able to detect a phase separation in a H_2 - D_2 mixture by calorimetric and visual observation. When they slowly cooled down a liquid mixture and solidification already had started, the remaining liquid had an enriched H_2 content. Consequently after complete solidification the solid contained H_2 -rich and D_2 -rich phases. Warming up again, the H_2 -rich phase melted first, which was detected by a significantly lower melting temperature than could be expected from the freezing temperature. White and Gaines only did experiments on H_2 - D_2 mixtures, but there is experimental evidence that $o-H_2$ and $p-H_2$ have a similar behavior. This will be discussed when we compare the conversion rates of several authors with ours.

We propose the following picture for the solidification of a liquid $o-H_2$ and $p-H_2$ mixture: Because of the higher melting temperature,^{14,15} ortho-H₂ will tend to solidify first, which means that the remaining liquid will be enriched with $p-H_2$. After complete solidification and sufficient time, diffusion will tend to establish a random distribution. However, if the sample is cooled down immediately below the temperature where diffusion is efficient, the partial phase separation will be conserved.

This separation is also favored by pressure. In a previous paper² we determined the contribution of o-H₂ molecules to the pressure, which came out to be negative and nonlinear in concentration. With Table I of this reference one can calculate that a n-H₂ solid at 18 cm³/mol and T = 8 K with a perfectly separated ortho and para phase will have a pressure 6 bars lower than the same solid



FIG. 6. The isochore cell mounted in the cryogenic environment.

Run	V (cm ³ /mol)	$C_1(t=0)$ (%)	$\begin{array}{c} C_1(t=t_{\rm fin}) \\ (\%) \end{array}$	t _{fin} (h)	k (%/h)	Δk (%/h)		
I	20.4	75^{+0}_{-5}	17.4±0.5	172.25	2.56	0.09		
II	17.7	75^{+0}_{-5}	17.6±0.5	106	4.10	0.14		
III	17.65	75^{+0}_{-5}	18.5±0.5	97.3	4.18	0.16		

TABLE II. Summary of the results of runs I, II, and III.

without separation.

Also the resulting ortho-para conversion rate is quite different if phase separation occurs because the rate is proportional to the number of J = 1 pairs. In a completely random distribution the number of pairs is proportional to C_1^2 [see Eq. (10)], whereas in a solid with perfect separation of phases there is linear proportionality to C_1 . For a normal-H₂ sample with $C_1 = \frac{3}{4}$, the average conversion rate for the entire sample in the case of perfect separation will be $\frac{4}{3}$ of that with a random distribution.

We conclude this section by noting that Krause and Swenson¹⁶ have observed an ortho-para conversion anom-

aly in solid hydrogen under pressure at elevated temperatures. Unfortunately, we have made no long-time studies of the conversion rate at these temperatures and are unable to shed any light on their unexplained observations.

III. EXPERIMENTAL RESULTS

The conversion constant k as a function of molar volume has been determined by two types of experiments. As pointed out in the preceding section, it is of great importance to measure this conversion in a sample with a random distribution of the J=1 molecules. Therefore,



FIG. 7. The high-pressure Raman scattering cell.



FIG. 8. The experimental Raman scattering setup.

the thermal treatment of the sample should be chosen so that at least in the beginning and every 10-20 h (depending on the conversion rate) thermal diffusion is effective.

The first type of measurement, runs I, II, and III, which were done in the isochore cell (Fig. 6), gives the average result for conversion over a typical period of 100 h. Virgin samples of the $n-H_2$, from a Mattheson ultrahigh purity cylinder with pressure 200 bars, were introduced in the high-pressure system and pressurized to the final pressure within 30 mins. Thereafter the pressure of the solid sample was measured as a function of temperature. In this way, the sample was periodically warmed up to about 5 K below the melting temperature. Immediately after the last pressure measurement, the sample was melted and three different gas samples were taken to determine the C_1 concentration spectroscopically. The molar volume was determined by measuring the melting temperature and the use of the tables given in Ref. 9. The results of these three runs are summarized in Table II, where the errors are also given due to uncertainty in the initial concentration [which could differ from normal concentration ($C_1 = 0.75$) due to catalytic conversion], and the error due to uncertainty in the final concentration measurement.

The second type of experiment, runs IV to VIII, is the



FIG. 9. Result of the spectroscopic concentration measurements. Arrows indicate the warming up of the sample: run IV.



FIG. 10. Result of the spectroscopic concentration measurements. Arrows indicate the warming up of the sample: run V.

best experimental manner to directly measure the concentration C_1 as a function of time. One measures the Raman intensities of the $J=0\rightarrow 2$ and $J=1\rightarrow 3$ transitions, which are proportional to the concentration of J=0 and J=1 molecules. There is no need for any absolute calibration, unlike other measurements, e.g., NMR,¹⁰ because only the relative intensities enter into the formula, Eq. (16), for the calculation of the concentration.

We used the Raman scattering cell shown in Fig. 7 and measured C_1 as a function of time at the same molar volume as our isochore measurements. Figure 8 gives a view of the optical Raman scattering system. Light from an argon-ion laser (Spectra Physics 165, output typically 1 W at 514.5 nm) enters the top window of the Raman scattering cell via several dielectric reflectors. The light scattered under 90° is collected and focused on the entrance slit of a double monochromator (Spex 1401). Finally the light intensity is measured by means of a cooled photomultiplier tube (RCA 31034), which is connected to an SSR photon-counting system via a pre-amplifierdiscriminator. The output is recorded on a dual-pen recorder.

The concentration C_1 can be determined from the relative intensities of the rotational Raman lines, I_{02} and I_{13} . (I_{ik} is the Raman intensity of the $J=i\rightarrow k$ transition.) The following relation between these intensities and the concentration can be derived:¹



FIG. 11. Result of the spectroscopic concentration measurements. Arrows indicate the warming up of the sample: run VI.



FIG. 12. Result of the spectroscopic concentration measurements: run VII.

$$C_0 = 1 - C_1$$

$$= \frac{I_{02}/I_{13}}{I_{02}/I_{03} + (5\tau/3)/[(\omega - \omega_{02})/(\omega - \omega_{13})]^3}, \quad (16)$$

where ω is the laser angular frequency, ω_{02} and ω_{13} are the rotational transition angular frequencies, and $\tau=0.597$ at T=293 K and $\tau=1$ for $T\ll 6B/k_B$, $B/k_B=85.4$ K.

Figures 9 to 13 show the results of the Raman scattering measurements. Arrows indicate the time of warming up to a few degrees below the melting temperature. The straight lines are a weighted computer fit through the measured points. The weight was determined assuming that the relative intensities I_{02}/I_{13} could be measured with equal relative precision at the concentrations we have chosen. To give some impression for the weight in Fig. 9, we have drawn some error bars at different concentrations, which correspond to a constant relative error of 1% in the relative intensities.

Table III summarizes the results of runs IV to VIII and also gives the resulting error for the conversion constant. The volumes are determined by measuring the melting temperature and the use of the tables given in Ref. 9.



FIG. 13. Result of the spectroscopic concentration measurements. Arrows indicate the warming up of the sample: run VIII.

TA	BLE	III.	Summary	of	the	results	of	runs	IV	to	VIII	
----	-----	------	---------	----	-----	---------	----	------	----	----	------	--

	V	k	
Run	(cm ³ /mol)	(%/h)	Remarks
IV	18.7	4.30±0.44	k different
		3.39±0.04	because of real physical effect
V	17.6	4.48 ± 0.2	k different due to
		4.04 ± 0.11	statistical error
		4.52 ± 0.28	
		4.18 ± 0.13	Average
VI	20.9	2.30 ± 0.03	
VII	18	3.78 ± 0.12	
VIII	14.5	5.30±0.49	

IV. COMPARISON OF THE RESULTS AND DISCUSSION

With the experimental results from the preceding section we are able to display the conversion rate as a function of density (Fig. 14). In this plot we also include the experimental determinations of other authors.

(a) The most extensive measurements at zero pressure were made by Schmidt¹⁰ by NMR. He gets a conversion rate of $k = 1.90 \pm 0.03\%$ /h, which is determined at three temperatures over a time range of circa 900 h. He is in agreement with most of the previous experiments (see references in his paper).

(b) Ahlers¹⁷ determined the conversion rate at three densities by measurement of the heat conduction of a gaseous sample before and after solidification. We have made a small correction to his molar volumes, in order to get the correct volume for $n-H_2$ at zero pressure: $V=22.91 \text{ cm}^3/\text{mol.}^{18}$

(c) Pedroni *et al.*³ have made measurements by means of NMR and a piston-pressure technique. The most remarkable feature in their result is a double peak in the plot of the conversion rate against density. The calculation of Berlinsky⁴ shows qualitative agreement with these results, but there remain some unexplained differences.

(d) Silvera *et al.*¹⁹ have measured the conversion rate by means of Raman scattering in the same experimental set-



FIG. 14. The H_2 conversion rate as a function of density.

up as we have used. In the first 25 hours they found irregularities in the measurement of the concentration, probably due to a periodic warming up of the sample to just below the melting temperature. We could observe the same effect in our run V (see Fig. 10). From 25 to 200 h they found a constant value, $k = 3.56 \pm 0.06\%$ /h. We have redetermined their density by comparing their phonon frequency with the most recent calibration by Lassche et al.²⁰ and get V = 18.9 cm³/mol.

(e) Jochemsen²¹ has done conversion measurements at four densities. He determined the concentration of his samples before and after solidification by means of Raman scattering of gas samples.

(f) Buzerak and Meyer²² have made conversion measurements from 0 to 1300 bars.

There is qualitative agreement over the whole pressure range. When comparing this set of data, it should be pointed out that the determination of the conversion rate by means of Raman scattering is the most reliable one, because all parameters can be controlled and measured in situ. Raman scattering gives a continuous measurement of the concentration C_1 with very low scatter in the results, typically in the order of 0.5% (see Figs. 9–12). The problem of catalytic conversion in the liquid sample in the short time of preparing the solid does not affect the results, because no assumptions about the initial concentration are made. All systematic errors can be avoided or at least detected by proper thermal treatment. The density can be determined by measuring the melting temperature and using the volumes along the melting line as given in Ref. 9 with an error smaller than 1%. The error bars in our results as given in Table III are therefore mainly a consequence of the number of measured Raman spectra in each run. These are small and do not suffer from systematic errors possible in other methods of determining the concentration.

Although at least qualitative agreement is found among all data, the results of Pedroni *et al.*³ show, in the density region for ρ/ρ_0 from 1.2 to 1.4, a deviation well outside their stated error bars. In this context our run IV, Fig. 9, is remarkable. Here we measured two different conversion rates in the same sample. In the first few hours the conversion rate agrees with the results of Pedroni *et al.*³ whereas thereafter conversion is reduced by more than 20% for the rest of the experiment, now agreeing with our other experimental conversion rates.

We think that this higher conversion rate is due to a nonrandom distribution of the J = 1 pairs as discussed in Sec. II. In fact, the samples of Pedroni *et al.*³ were solidified at zero pressure and thereafter compressed to higher densities.²³ It may have been possible that the justsolidified sample had a concentration gradient and that there was not sufficient time for thermal diffusion at low densities. Once at higher densities, the sample temperature of 4.2 K does not allow diffusion.

Our run IV can be explained by similar arguments. The sample was quickly frozen and cooled down to nearly 4.2 K. At a certain moment, because of slight warming up of the sample, the distribution of the J = 1 pairs probably changed to random with a resulting reduction of the conversion rate.

The presence of inhomogeneities in concentration C_1 has been seen directly several times in our experiments. In our high-pressure cell (see Fig. 7) we measure the concentration of our sample only in a small region formed by the focused laser beam, a cylinder of about 50 μ m length. Our total sample, however, has a length of a few cm. Inhomogeneities of a sample in the beginning of an experiment could be detected by measuring the concentration before and after warming up. In this way the concentration in the region of the laser focus changed several percent in a short time. This can be seen in Figs. 9, 10, and 13.

The results of Jochemsen²¹ show a fairly large deviation from other results. This can be explained by the fact that he had no control on the distribution of J = 1 pairs in his experiments. His samples were in the ordered fcc phase at low temperature for long periods, where thermal diffusion is practically zero, but where quantum diffusion could be important. The influence of the structural change from hcp to fcc ordered on the conversion rate is also unknown.

As a conclusion we suggest the solid line in Fig. 14 as the most realistic one for random conversion. Especially our three data points at about $\rho/\rho_0=1.30$, measured with two different methods over a time range of days and which are in essential agreement, give experimental evidence for the reliability of our data.

Above $\rho/\rho_0=1.4$ we have only one data point with fairly large error bars, which is in agreement with the data of Pedroni *et al.*³ Their data points seem to be a correct extension of low-density measurements, and are also in agreement with those of Ahlers¹⁷ and at least qualitatively with those of Jochemsen.²¹ We therefore suggest in this region the dashed line as an average of all data. We can not give an explanation why some of the data points of Pedroni *et al.* seem to deviate from this line. Detailed information (which is not given in Ref. 3 and 23) about the experimental procedure and the thermal history of the different samples is required. However, we have suggested some possible sources of difficulty.

V. THE PHONON DENSITY OF STATES

In a previous work, Berlinsky,⁴ showed that the dip in the conversion rate observed by Pedroni *et al.* could be explained by a dip in the theoretical density of onephonon states (see Fig. 16). here we show that the absence of such a dip as presented in Fig. 14 is in agreement with the experimental phonon density of states. Berlinsky calculated the conversion rate from the phonon density of states. We prefer the inverse procedure. The phonon density of states then can be compared with experimental^{24,25} and theoretical²⁶ results.

For this calculation we use Eq. (9), which relates the conversion rate and the phonon density of states. As this equation includes only one-phonon processes, we subtract the two-phonon contribution to the conversion rate, which is significant only in the low-density region (see Sec. II). The results are plotted in Figs. 15 and 16, which show the one-phonon density of states as a function of energy. Two



FIG. 15. The one-phonon density of states: solid line, our result; dashed line, Stein *et al.* (Ref. 24); dashed-dotted line, Bickerman *et al.* (Ref. 24); dotted line, Balasubramanian *et al.* (Ref. 25).

different experimental densities of states are shown in Fig. 15, measured by neutron scattering²⁴ and infrared absorption²⁵ and a theoretical²⁶ density, Fig. 16, together with our calculated density of states. The g(E) is given in arbitrary units, but for all curves, the area under the curve (the total density of states) is nearly the same. Our result—solid line—which is a transformation of the smooth line in Fig. 14, compares well with the other experimental densities of states. The rather significant high-energy tail, which is attributed to anharmonic effects, is remarkable. Also plotted are the transformed data points by different authors with the same symbols as in Fig. 14. The peak of Pedroni *et al.*¹³ at about 70 cm⁻¹ seems to be less probable in comparison with the other



FIG. 16. The one-phonon density of states: solid line, our result; dashed line, theoretical result from Klump *et al.* (Ref. 26).

densities of states.

As a conclusion we find that Berlinsky's model applied to our experimental results gives a realistic phonon density of states, in agreement with other experimental results. We take this as a confirmation of our experimental results, and the theoretical model proposed by Berlinsky.

ACKNOWLEDGMENTS

We would like to thank V. V. Goldman for stimulating discussions. The Stichting Fundamental Onderzoek der Materie (FOM) is acknowledged for partial financial support. One of us (I.F.S.) also acknowledges the National Science Foundation (Contract No. DMR-82-13662) for support.

- *Present address: Natuurkundig Laboratorium, Vrije Universiteit, Amsterdam, The Netherlands.
- ¹See, for example, the review by I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980), and references therein.
- ²A. Driessen, J. A. de Waal, and I. F. Silvera, J. Low Temp. Phys. **34**, 255 (1979); A. Driessen, Ph.D. thesis, University of Amsterdam, 1982.
- ³P. Pedroni, H. Meyer, F. Weinhaus, and D. Haase, Solid State Commun. 14, 279 (1974).
- ⁴A. J. Berlinsky, Phys. Rev. B 12, 1482 (1975).
- ⁵K. Motizuki and T. Nagamiya, J. Phys. Soc. Jpn. 11, 93 (1956).
- ⁶A. J. Berlinsky and W. N. Hardy, Phys. Rev. B 8, 5013 (1973).
- ⁷P. J. Berkhout and I. F. Silvera, J. Low Temp. Phys. 36, 231

(1979).

- ⁸F. G. Mertens and W. Biem, Z. Phys. 250, 273 (1972).
- ⁹A. Driessen and I. F. Silvera, J. Low Temp. Phys. 54, 361 (1984); A. Driessen, Ph.D. thesis, University of Amsterdam, 1982.
- ¹⁰F. Schmidt, Phys. Rev. B 10, 4480 (1974).
- ¹¹C. Ebner and C. C. Sung, Phys. Rev. A 5, 2625 (1972).
- ¹²J. van Kranendonk, J. Low Temp. Phys. 39, 689 (1980).
- ¹³D. White and J. R. Gaines, Proceedings of the 9th International Conference on Low Temperature Physics (Plenum, New York, 1965), p. 1104.
- ¹⁴R. D. Goodwin and H. M. Roder, Cryogenics 3, 12 (1963).
- ¹⁵N. G. Bereznyak and A. A. Sheinina, Fiz. Nizk. Temp. 6,

1255 (1980) [Sov. J. Low Temp. Phys. 6, 608 (1980)].

- ¹⁶J. K. Krause and C. A. Swenson, Solid State Commun. 31, 833 (1979).
- ¹⁷G. Ahlers, J. Chem. Phys. **40**, 3123 (1964).
- ¹⁸O. Bostanjoglo and R. Kleinschmidt, J. Chem. Phys. 46, 2004 (1967).
- ¹⁹I. F. Silvera, P. J. Berkhout, and L. M. van Aernsbergen, J. Low Temp. Phys. 35, 611 (1979).
- ²⁰L. Lassche, P. Zandveld, and A. Driessen (unpublished results).
- ²¹R. Jochemsen, Ph.D. thesis, University of Amsterdam, 1978.
- ²²R. F. Buzerak and H. Meyer (unpublished results); R. F. Buzerak, Ph.D. thesis, Duke University, 1975.

- ²³S. Dickson and H. Meyer, Phys. Rev. 138A, 1293 (1965).
- ²⁴H. Stein, H. Stiller, and R. Stockmeyer, J. Chem. Phys. 57, 1726 (1972); A. Bickerman, H. Spitzer, H. Stiller, H. Meyer, R. E. Lechner, and F. Volino, Z. Phys. B 31, 345 (1978). The latter measurements should be considered to be more accurate as a more careful correction for multiple scattering has been made.
- ²⁵T. K. Balasubramanian, Chen-Hsin Lien, K. Narahari Rao, and J. R. Gaines, Phys. Rev. Lett. 47, 1277 (1981).
- ²⁶K. N. Klump, O. Schnepp, and L. H. Nosanow, Phys. Rev. B 1, 2496 (1970).
- ²⁷G. W. Smith and C. F. Squire, Phys. Rev. 111, 188 (1958).