

Phonon density of states of solid parahydrogen at pressures up to 150 MPa, determined by the neutron scattering method

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The phonon density of states (PDS) of a parahydrogen quantum crystal at liquid-helium temperature and pressures of 0, 80, and 150 MPa was determined from data for incoherent inelastic neutron scattering. Anharmonic phonon damping strongly affects the form of the real PDS in this pressure range. © 1995 American Institute of Physics.

1. The properties of solid hydrogen, which is the simplest molecular quantum cryogenic crystal, are of definite interest from the standpoint of fundamental science. To obtain information at the microscopic level, which is especially important for the theory of crystals, it is necessary to study the dynamical lattice properties, primarily, by the method of neutron scattering. In the case of solid hydrogen the large zero-point vibrations¹ make it more difficult to obtain experimental information and to use the standard methods for calculating the dynamical properties of the lattice. The large amplitude of the zero-point vibrations $\langle u_z^2 \rangle$ ($\approx 18\%$ of the distance d between nearest neighbors in the crystal lattice) should produce appreciable anharmonic effects in the dynamics of the crystal lattice of solid hydrogen, including at the level of the phonon density of states (PDS) $g(\epsilon)$. A high-frequency tail, which is of an anharmonic nature,² was observed, for example, in $g(\epsilon)$ of vanadium, where the amplitude of the lattice vibrations is less than $0.02d$ at $T=300$ K.

In the beginning of the 1970s a number of attempts were undertaken to obtain by different methods — calorimetric,^{3,4} optical,⁵ and neutron^{6–8} — data for the dynamics of the crystal lattice of hydrogen. Neutron spectroscopy was applied both in the time-of-flight variant^{6,7} and as a three-axis spectrometer variant (Ref. 9). The data obtained for the PDS of solid hydrogen differ substantially, especially at high frequencies; theoretical calculations⁹ also do not describe the experimental results (see Fig. 1). It is important that the form of the PDS in these works is of a pseudoharmonic character (only the anharmonic renormalization of the phonon energies is taken into account); specifically, there is no high-frequency anharmonic tail.² The real PDS should include fully the effects of anharmonicity, reflecting the existence of a finite phonon lifetime τ . Moreover, in Refs. 6 and 7 samples with a high concentration of the orthomolecules (spin $I=1$, angular momentum $J=1$), which have a large incoherent neutron scattering cross section ($\sigma_{in}=79.9$

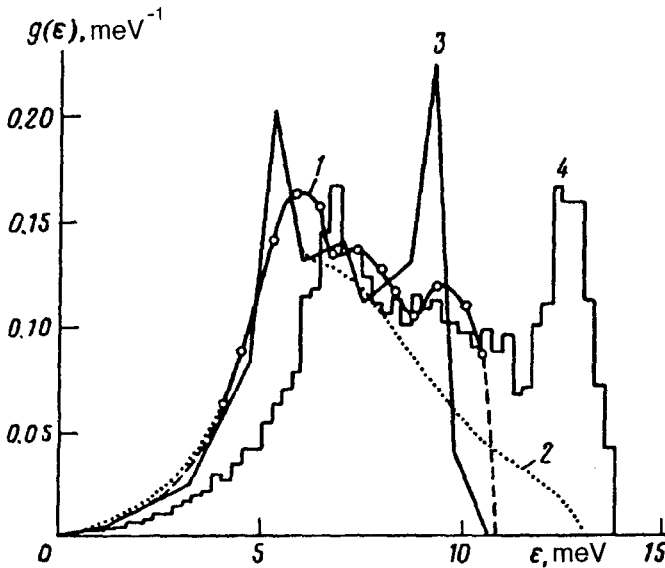


FIG. 1. Phonon density of states $g(\epsilon)$ of a hcp lattice of solid parahydrogen with zero external pressure. 1—Experiment of Ref. 6; 2—experiment of Ref. 7; 3—calculation from the dispersion curves,⁸ histogram; 4—theoretical calculation with the Lennard-Jones pair potential.⁹

b/molecule) were used. This resulted in a widely distributed background from multiple scattering, reaching $\sim 50\text{--}100\%$ of the recorded neutron intensity.⁹

It is important to note that in the studies listed above the PDS was measured only in the absence of external pressure ($p=0$). Solid molecular hydrogen is interesting in that, in addition to the simplicity of the hcp crystal structure and the character of the intermolecular interaction, it has an anomalously high compressibility. For example, according to the equation of state,¹⁰ the density of solid molecular hydrogen is 1.9 times higher at pressure $p=1060$ MPa.¹⁰ As a result, the intermolecular interaction is substantially stronger: The energy ϵ_m of the maximum of the PDS increases to $\epsilon_m^3 \approx 3.6\epsilon_m(p=0)$. For comparison, the initial maximum energy of the PDS, $\epsilon_b=13$ meV, for the very plastic indium lattice is only $\approx 7\%$ higher at $p=1000$ MPa.¹¹ In this situation it is important to obtain direct experimental information about the real PDS of solid parahydrogen as a function of the pressure.

2. We performed measurements of the inelastic neutron scattering by polycrystalline parahydrogen ($I=0, J=0$) at liquid-helium temperature and pressures $p=0, 80,$ and 150 MPa. The sample consisted of a $50 \times 15 \times 3$ -mm plate and was placed in a pressure chamber made of the aluminum alloy V-96T. At the highest measured pressure the molar volume V of the molecular crystal was $\approx 35\%$ lower than the initial volume. The measurements were performed on a high-pressure stand using a pulsed neutron source of the Fakel electron accelerator.¹² In this work inelastic and elastic neutron scattering spectrometers were used simultaneously, and the measurements of the transmission spectra in

the direct beam were also performed. This made it possible to monitor the density (pressure) and the para-ortho composition of the sample at each stage of the experiment and to determine the energy dependence of the double-differential inelastic incoherent neutron scattering cross sections (DDS).¹³

The experimental DDS were measured with a 16-detector backward-geometry spectrometer using the time-of-flight technique. In this procedure the sample is bombarded by neutron pulses with a "white" spectrum and the monochromator-separated neutrons with energy near $E_f=3.6$ meV are recorded. The inelastic scattering spectra measured in this manner were analyzed as a function of the variable initial neutron energy E .^{1,12} To refine the energy E scale of the measured spectra, measurements of the diffraction spectra were specially performed on a reference sample — a germanium crystal — for each scattering angle.

For the chosen experimental conditions the recorded phonon production occurs during a para-ortho transition ($0 \rightarrow 1$), $\Delta E(0 \rightarrow 1)=14.6$ meV induced by inelastic scattering of a neutron with energy $E \geq \Delta E(0 \rightarrow 1)+E_f=18.2$ meV. The scattering spectrum has a specifically threshold nature: Single scattering with phonon production is "switched on" at neutron energy $E=18.2$ meV, double scattering is switched on at $E=32.8$ meV, triple scattering is activated at $E=47.4$ meV, and so on. In addition, some neutron energy $\epsilon=E-18.2$ meV is expended on the excitation of a phonon in one scattering event; in the second scattering event $\epsilon'=E-(18.2+14.6+\epsilon)$ meV. This factor must be taken into account when separating the contribution of single scattering of neutrons in order to determine the spectrum $g(\epsilon)$.

In the incoherent approximation the DDS of single neutron scattering by polycrystalline parahydrogen, in application to the experimental procedure employed here, has the form¹⁴

$$S_1 = \frac{3\sigma_{in}}{\pi} (E_f/E)^{1/2} j_1^{1/2}(x) \exp(-2W) \left\{ \delta(\epsilon) + \sum_{n=1}^{\infty} (h^{-2}\kappa^2/2m)^n F_n(\epsilon)/n! \right\}, \quad (1)$$

where $j_1(x)$ is the molecular form factor (spherical Bessel function), $x=0.37\kappa$, κ is the momentum transferred by a neutron to the crystal lattice, $2W=\kappa^2\langle u^2 \rangle/3$, $\langle u^2 \rangle$ is the mean-squared displacement (for $p=0$ we have $\langle u^2 \rangle=0.45 \text{ \AA}^2$), m is the mass of a H_2 molecule, $F_n(\epsilon)$ represents the series of functions

$$F_1 = g(\epsilon)/[\epsilon(1 - \exp(-\epsilon/T))], \quad F_n = \int F_1(\epsilon-z) F_{n-1}(z) dz. \quad (2)$$

In expression (1) the separated term $\delta(\epsilon)$ describes the cross section of the transition ($0 \rightarrow 1$) with no phonon production. The term of the sum with $n=1$ gives the relation between the one-phonon cross section $P_1(\epsilon)$ and the desired function $g(\epsilon)$ and for $n>1$ the sum determines the cross section of multiphonon processes $M_1(\epsilon)$. Taking into account M_1 according to expression (1) is not always justified because of the difficulty of this procedure. For estimates the analytical representation of F_n is therefore in the form of a Gaussian.¹⁴

The high intensity of multiphonon processes $M_1(\epsilon)$ and of one-phonon double scattering makes it impossible to represent their contributions as small corrections to $P_1(\epsilon)$.

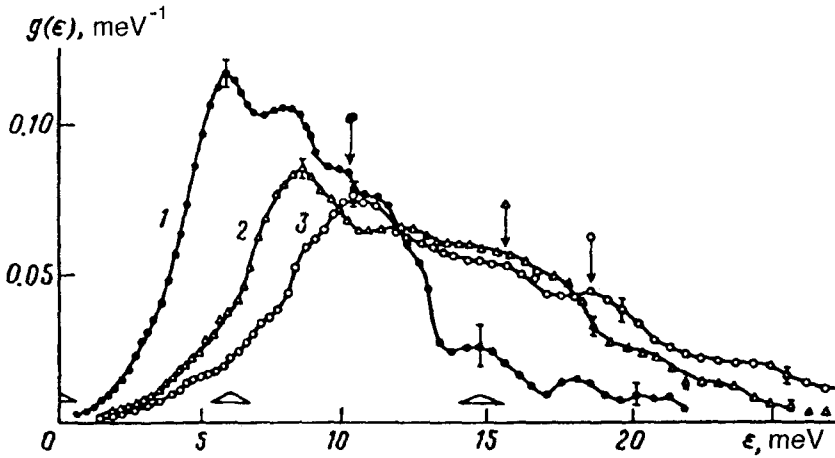


FIG. 2. Phonon density of states $g(\epsilon)$ for three pressures: 1 — $p=0$, 2 — $p=80$ MPa, 3 — $p=150$ MPa.

In the present work the experimental DDS $S_{\text{exp}}(\epsilon)$ are separated into components by an iteration procedure on the basis of the inverse spectral problem¹⁵ and the PDS is reconstructed. The calculation is performed independently for each of 16 angular scattering spectra with averaging of the results. It is important that, according to the point of an improperly posed problem, the separation algorithm must take into account the correlation between the contributions of the multiphonon scattering M_1 and double scattering. We have therefore used the relation of Ref. 15 which relates the integral cross section of a $R(0 \rightarrow 1)$ transition to the one-phonon double scattering with $\epsilon' = 0$: $P_2(0)/R = \hbar^2 \kappa^2 Q T / 2M$, where $Q = 3(k\theta_D)^{-3}$ is the coefficient of ϵ^2 in the Debye part of the reconstructed PDS, and θ_D is the Debye temperature.

When the double multiphonon contribution is small, the function $P_1(\epsilon)$ is determined as follows:

$$P_1(\epsilon) = [S_{\text{exp}}(\epsilon) - M_1(\epsilon)] / (1 + C_M), \quad (3)$$

where C_M is the computed ratio of the intensities of one-phonon processes in multiple and single scattering. In addition to C_M , we took into account the decay of the neutron flux as the flux passes through a flat sample. Ignoring the geometric damping factor with double scattering distorts the final result by more than 10% even in the case $p=0$.

3. Figure 2 shows the PDS functions obtained for parahydrogen with $M_1(\epsilon)$ calculated in the Gaussian approximation. Comparing the result obtained for $p=0$ with the result shown in Fig. 1, we can see how the anharmonic damping of the phonons changes the shape of the pseudoharmonic PDS:⁸ The high-frequency peak and the sharp boundary become smeared and a high-frequency (anharmonic) tail appears. The low-frequency part of the real PDS for $p=0$ agrees with the results of Refs. 6 and 7. This shows that the damping of the phonons in this region is quite weak. The estimates made in Ref. 16 show that the phonon lifetime decreases from 10^{-11} to 10^{-13} s on passing from the Debye part of the PDS into the region of the anharmonic tail.

As the pressure increases, the qualitative form of the PDS does not change and is characterized by appreciable manifestations of phonon damping. For all reconstructed PDS, the average level of the tail is equal to $\approx 6\%$ of the maximum value. This shows that the character of the anharmonic interaction of the phonons changes very little in this pressure range. The PDS functions found for different molar volumes $V(p)$ (pressures) are described well by a similarity law: uniform stretching of the ϵ scale of the phonon spectrum with the coefficient

$$K = [V(0)/V(p)]^\alpha, \quad \alpha = 2. \quad (4)$$

This fact justifies the approach of Ref. 6 in determining the fragment of a real PDS on the basis of data for the ortho-para conversion of solid hydrogen. In accordance with the theory concerning the conversion mechanism,¹⁷ the change in the PDS with pressure reduces here to rescaling of the ϵ -scale according to a quadratic function of the density.

In Ref. 1 the Grüneisen parameter $\gamma_z = 2 \pm 0.1$ was determined according to the volume dependence of the zero-point vibrations $\langle u_z^2 \rangle$. It can be concluded that in the case of a quantum crystal the exponent α in Eq. (4) is an effective Grüneisen parameter averaged for all phonons. Here its value is identical to γ_z . Expression (4) can then be written as $K = \langle u_z^2(0) \rangle / \langle u_z^2(p) \rangle$. At the same time, the integral cross section of a $(0 \rightarrow 1)$ transition R depends via the factor $2W$ on the total zero-point vibration $\langle u^2 \rangle$. The contribution of the component $\langle u_z^2 \rangle$ to $\langle u^2 \rangle$ can therefore be determined in a model-free manner from the spectrum of inelastic incoherent scattering of neutrons by parahydrogen. This gives, in principle, a possibility for estimating the pressure range where the anharmonicity of the zero-point vibrations is still appreciable.

The arrows in Fig. 2 indicate the maximum (in the corresponding pseudoharmonic PDS) energies ϵ_b , fixed by the factor K (4) according to the initial value $\epsilon_b(p=0) = 10.2$ meV determined in Ref. 8. In Ref. 8 the PDS was calculated from the phonon dispersion curves measured by the method of coherent inelastic neutron scattering. As a result of methodological difficulties, only phonons with energy $\epsilon \leq 8$ meV were recorded, and for other values of ϵ the dispersion curves were extrapolated from the lowest energies according to the Born-Karman model. As follows from our results, the value $\epsilon_b(p=0) = 12.0$ meV provides a more adequate description of the real situation; this corresponds to values of ϵ_b of 18.2 and 21.8 meV, respectively, at pressures of 80 and 150 MPa.

4. The results of the present work were obtained on the basis of the harmonic theory of crystal lattice dynamics. In particular, only the term quadratic in κ was taken into account in the calculation of the Debye-Waller factor $2W$. The agreement of the Debye temperatures $\theta_D = 115, 197,$ and 226 K, determined in the present work, and the heat capacity data,³ where the factor $2W$ is not important, shows that the harmonic approximation can be used to describe the interaction of neutrons with the lattice of a solid-hydrogen quantum crystal.

The real PDS functions which were obtained exhibit appreciable anharmonic effects and can be used to construct theoretical models. A detailed investigation of the behavior of the phonon damping $\Gamma(\epsilon) \sim \tau^{-1}$ for the experimental pressure range, given that the scaling law is valid, could make it possible to predict the PDS for higher pressures.

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