Lattice Dynamics of Solid Deuterium by Inelastic Neutron Scattering

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The dispersion relations for phonons in solid ortho-deuterium have been measured at 5 °K by inelastic neutron scattering. The results are in good agreement with recent calculations in which quantum effects are taken into account. The data have been fitted to a third-neighbor general force model. The effective force constants which are obtained show that the bond stretching forces between nearest-neighbor molecules are dominant and this bond stretching constant is 174 dyn cm^{-1}. The elastic constants are deduced and the isothermal compressibility is calculated to be $B^{-1}=2.19\times10^{-10}$ cm^2 dyn^{-1}. The density of states and the heat capacity is calculated and the Debye temperature is found to be $\theta_0=114$ °K.

Among molecular crystals, solid hydrogen is of particular interest, both because of the molecular and structural simplicity which make it a suitable candidate for *a priori* calculations, and because the molecules are sufficiently light for quantum effects to be of importance in understanding the lattice dynamics.[1] Using the technique of inelastic neutron scattering, we have studied in detail the phonon dispersion relations for hcp ortho-deuterium at 5 °K. The results agree rather well with recent calculations[2] and with Raman Scattering experiment[3] and illustrate both the simplicity of the intermolecular forces and the importance of quantum effects. A preliminary description of these measurements has been presented earlier.[4]

Solid ortho-deuterium crystallizes in a nearly ideal hcp structure with an intermolecular separation of 3.607 Å. At low temperatures the rotational quantum number is zero, so that the molecule is spherically symmetric and may be considered as a single particle with a neutron scattering length $2a_c j_0(\frac{1}{2}\kappa a)$, where a_c is the coherent scattering length of the deuteron.[5] j_0 is a spherical Bessel function, $\vec{\kappa}$ is the scattering vector of the neutron, and a the separation between the deutetrons in the molecule ($a=0.742$ Å). The form of this scattering length and the large Debye-Waller factor, which is a consequence of the zero-point oscillations, results in a rapid decrease with κ of the neutron-scattering cross section. The measurements, which were performed on a triple-axis spectrometer at the DR3 reactor, were therefore restricted to the first few Brillouin zones.

The crystal was prepared in the following manner: A 1-cm-diam tube, coated on the inside with a thin layer of teflon, was filled with liquid ortho-deuterium and slowly cooled through the melting point, resulting in a polycrystalline sample. This was annealed at a temperature close to the melting point for several days, and then cooled to 5 °K over a period of a few hours. The resulting sample contained single crystals as large as 1 cm^3, and measurements were made on these by carefully shielding the rest of the sample with cadmium. The resulting neutron groups were generally intense and well defined and had a width consistent with the resolution of the apparatus, indicating that the excitations have a long lifetime.

The measured phonon energies are shown in Fig. 1, together with a Born-von Karman fit to the results, using a third-nearest-neighbor tensor force model. The parameters of this model, which is identical to that described by Houmann and Nicklow,[6] are given in Table I. From these, the predominance of nearest-neighbor bond-stretching forces is clear, since β_2, γ_1, α_1 approximately have the ratio 3:2:1 and all other force constants are small.

Self-consistent phonon calculations have recently been carried out for D_2 by Klein and Koehler[2] and Biem and Mertens.[2] They used an effective intermolecular potential $V(R)$ which is related to the true potential $\phi(R)$ by

$$V(R)=f^2(R)[\phi(R)-\hbar^2/2M\nabla^2\ln f(R)]\ ,$$

where $f(R)$ is a short-range Jastrow correlation function which minimizes the ground-state energy. $\phi(R)$ was taken as a Lennard-Jones potential with parameters determined from studies of the gas phase. As shown in Fig. 1, the results of Klein and Koehler[2] agree very well with our measurements. The results of Biem and Mertens[2] also have the same form as the experimental dispersion relations, but the theoretical energies are consistently about 15% too high. It should be emphasized that, if the true potential $\phi(R)$ is used in a Born–von Karman calculation of the phonon energies, the results are widely at variance with the experiments, and the quantum corrections are therefore an essential part of the theory.

From the third-nearest-neighbor force-constant model, the density of phonon states has been cal-

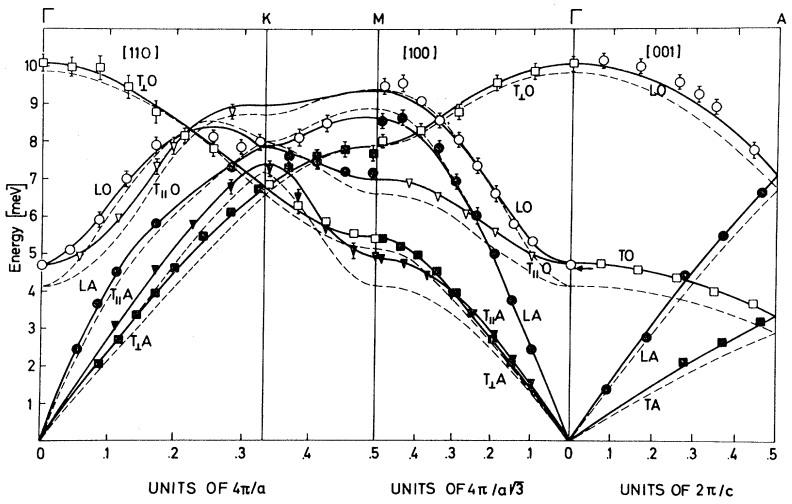

FIG. 1. Phonon dispersion relations for ortho-deuterium at 5 °K. The full lines are the results of the Born-von Karman fit and the dashed lines the calculations of Klein and Koehler (Ref. 2). The arrow at Γ shows the frequency of the TO mode as derived from Raman spectroscopy (Ref. 3).

culated and the elastic constants shown in Table I have been deduced.[6] From the density-of-states function, the heat capacity and the Debye temperature have been determined. The heat capacity may be compared with the experimental results of Hill and Lounasmaa.[7] The calculated heat capacity lies about 8% below their measured curve. For the Debye temperature at $T = 0$ °K we find $\Theta_0 = 114$ °K. This may be compared with the value of Θ_0 which can be calculated using the elastic constants.[8] If the elastic constant C_{13} is estimated by applying the simplified central-force model[9] and the values in Table I are used, we find $\Theta_0 = 111$ °K. The heat-capacity measurements of Hill and Lounasmaa[7] give $\Theta_0 = 106.5$ °K.

The isothermal compressibility constant may also be calculated from the elastic constants and we find $B^{-1} = 2.19 \times 10^{-10}$ cm^2 dyn^{-1}. The compressibility of solid deuterium has been measured directly at 4.2 °K by Stewart[10] who finds $B^{-1} = (3.0 \pm 0.15) \times 10^{-10}$ cm^2 dyn^{-1}. Bezuglyi[11] has deduced the compressibility from sound-velocity measurements and finds $B^{-1} = 2.1 \times 10^{-10}$ cm^2 dyn^{-1}.

The Debye-Waller factor has been determined experimentally by measuring Bragg reflection intensities at reciprocal lattice points out to (114). When these intensities are corrected for the variation of $j_0(\frac{1}{2}\kappa a)$ in the cross section, the results, shown in Fig. 2, are in good agreement with a calculation based on the force-constant model, which gives a root-mean-square displacement $\langle u_j^2 \rangle^{1/2}$ of 0.50 Å. The slope of the drawn curve in Fig. 2 corresponds to this value.

TABLE I. Third-nearest-neighbor force model for solid ortho-deuterium at 5 °K. In the simplified central-force model $C_{13} = 25 \times 10^8$ dyn cm^{-2}.

Force constants dyn cm^{-1}		Elastic constants 10^8 dyn cm^{-2}	
α_1	63	C_{11}	82
β_1	−9	C_{12}	29
γ_1	127	C_{33}	102
α_2	6	C_{44}	23
β_2	174	C_{13}	···
γ_2	−9	B	46
α_3	−2		
β_3	4		
γ_3	1		

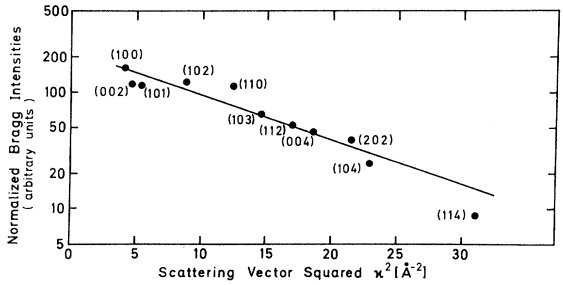

FIG. 2. The intensities of the elastic scattered neutrons in ortho-deuterium at 5 °K. The intensities are normalized by the factor $Q^{-1}\,[j_0(\frac{1}{2}\kappa a)]^{-2}$, where Q is the crystallographic Q value and j_0 is the Bessel function referred to in the text. The full curve is calculated from the density-of-phonon-states function and the slope of the curve corresponds to a root-mean-square displacement of the deuterium molecules of 0.50 Å.

Our results have therefore shown that solid ortho-deuterium may be considered as a close-packed array of spherical molecules in which nearest-neighbor bond-stretching forces are dominant. There is good agreement between the measured phonon energies and those calculated using a potential derived from gas-phase studies, provided that quantum effects are taken into account. We intend to extend these measurements to higher temperatures and pressures, and to attempt to measure the phonon lifetimes near the melting point.

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This paper is respectfully dedicated to the memory of the late Professor Lothar Meyer who introduced us to this field, participated fully in the early stages of the experiment and, through his advice and inspiring personal example, contributed greatly to its satisfactory conclusion.

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Velocity of Second Sound in NaF

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The velocity of drifting second sound and the heat capacity per unit volume are calculated for NaF for temperatures from 0 to 40 °K. The velocity of second sound decreases by 24% as the temperature is increased from 10 to 30 °K, because of the dispersion of the phonon frequency spectrum.

INTRODUCTION

In recent articles,[1] Jackson, Walker, and McNelly and McNelly *et al.* have reported on observations of the development of heat pulses in very-pure NaF crystals. Pulses were observed which had some of the properties expected of second-sound pulses. However, they found that the velocity of the observed pulses did not approach the expected theoretical value for the velocity of second sound. It appears that the theoretical value they used was the value for absolute zero, not the value for the temperature at which the experiments were performed. However, because of the dispersion in the phonon frequency spectrum, the theoretical value for the velocity of second sound (v_{II}) is not constant, but decreases with increasing temperature.

To facilitate the interpretation of such experiments, we have carried out a detailed calculation of v_{II} for NaF with both the dispersion and the anisotropy of the phonon frequency spectrum included. It is found that the value of v_{II} is significantly less (0.4–11%) at the temperatures at which the second-sound experiments were performed (9–21 °K) than it is at absolute zero.

We describe our calculation below, present our results, and compare them with the experimental results of Jackson *et al.*[1] For completeness, the heat capacity per unit volume is also given. We conclude by suggesting a reason for the differences between the velocities of the pulses observed by Jackson *et al.* and our calculated values for v_{II}.

THEORY

According to theory, when second sound exists, variations in the local temperature $T(\vec{x}, t)$ are described by the damped wave equation[2]