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]

$$\frac{\partial^2 T(\vec{x},t)}{\partial t^2}+\frac{1}{\tau_{ss}}\frac{\partial T(\vec{x},t)}{\partial t}-v_{II}^2\nabla^2 T(\vec{x},t)=0\ , \qquad (1)$$

where τ_{ss} and v_{II} are, respectively, the relaxation time and propagation velocity of second sound. τ_{ss} is also referred to as the relaxation time for resistive processes. For drifting second sound, the only type likely to be observed, this equation is valid provided that $\omega\tau_N \ll 1$, where ω characterizes the rate of change of the temperature and τ_N is a relaxation time descriptive of phonon scattering by normal processes. For second-sound pulses to be observed, it is required that $\omega\tau_{ss} \gtrsim 1$. Nevertheless, Eq. (1) is still valid when $\omega\tau_{ss} \ll 1$. For such slowly varying processes the first term in (1) becomes relatively unimportant, so that the solution of (1) becomes indistinguishable from the solution of a diffusion equation. Because of this, Eq. (1) can be used to study the behavior of heat pulses in the region of temperatures between where well-developed pulses of second sound are possible and where only pure diffusive behavior results.

To use (1) to study heat pulses in the region of temperature mentioned above, one needs reliable values for τ_{ss}, as well as for v_{II}. Since τ_{ss} depends in a complicated way on the anharmonic forces and the imperfections in the crystal, it is not easily calculated. However, if the thermal conductivity K of the sample being studied is measured, τ_{ss} can be calculated from[3]

$$\tau_{ss}=K/(C_0 v_{II}^2)\ , \qquad (2)$$

provided, of course, that v_{II} and C_0, the heat capacity per unit volume, are known. It is because of this that we have calculated both v_{II} and C_0. Note that the validity of (2) follows from the fact that the damped wave equation is valid for slowly varying processes ($\omega\tau_{ss} \ll 1$) for which the ordinary diffusion equation $C_0(\partial T/\partial t)=K\nabla^2 T$ is also valid.[3]

TABLE I. Computed heat capacity per unit volume and velocity of second sound as functions of temperature.

Temperature T(°K)	Heat Capacity per unit volume $C_0(10^5$ ergs/cm$^3)$	Velocity of second sound $v_{II}(10^5$ cm/sec)
0	0.0000	2.0209
9	0.164 47	2.0133
12	0.395 69	1.9914
15	0.790 50	1.9531
18	1.413 4	1.8912
21	2.343 4	1.8067
24	3.665 7	1.7090
27	5.459 2	1.6101
30	7.780 3	1.5177
33	10.657	1.4344
36	14.084	1.3614
39	18.067	1.2944

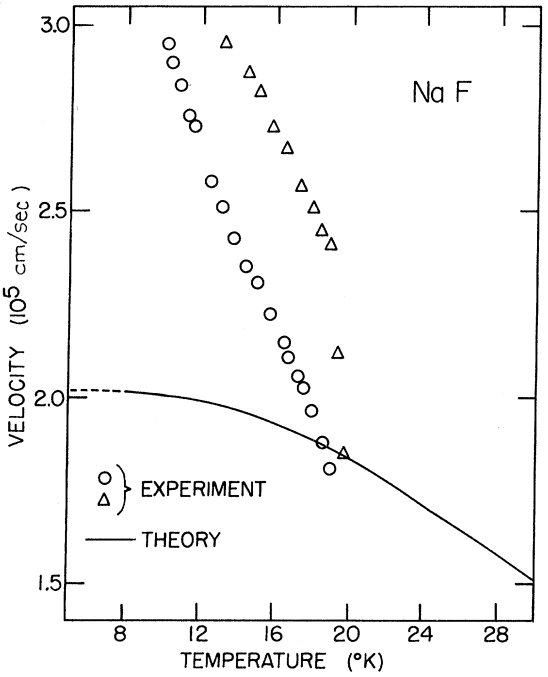

FIG. 1. Computed velocity of second sound vs temperature. Experimental velocities from Ref. 1: triangles refer to the leading edge of the pulse; circles refer to the pulse peak. For comparison, first-sound velocities in the ⟨100⟩ direction in NaF are 6.17×10^5 and 3.19×10^5 cm/sec.

By neglecting the first term in (1) and associating the coefficients in (1) with those in the diffusion equation, one obtains (2).

CALCULATIONS

When calculating v_{II}, it is important to consider the dispersion of the phonon frequency spectrum, since it leads to a value of v_{II} which decreases with increasing temperature. The formula for the velocity of drifting second sound, when no approximations concerning the dispersion or anisotropy of the frequency spectrum are made, is[4]

$$v_{II}=\left(V^{-1}\sum_{\vec{k}s} C_{\vec{k}s}\frac{\vec{k}}{\omega_{\vec{k}s}}\cdot\frac{\partial\omega_{\vec{k}s}}{\partial\vec{k}}\right)\times(3V^{-1}\sum_{\vec{k}s} C_{\vec{k}s})^{-1/2}\left(V^{-1}\sum_{\vec{k}s} C_{\vec{k}s}\frac{\vec{k}\cdot\vec{k}}{\omega_{\vec{k}s}^2}\right)^{-1/2}\ , \qquad (3)$$

where $\omega_{\vec{k}s}$ is the frequency of the normal mode with wave vector $\vec{k}$ and polarization index s (s goes from 1 to 6 for NaF). V is the volume of the sample, and

$$C_{\vec{k}s}=\frac{1}{4k_B T^2}\left(\frac{\hbar\omega_{\vec{k}s}}{\sinh(\hbar\omega_{\vec{k}s}/2k_B T)}\right)^2\ , \qquad (4)$$

where k_B is Boltzmann's constant. The heat capacity per unit volume is given by

$$C_0 = V^{-1} \sum_{\vec{k}s} C_{\vec{k}s} . \quad (5)$$

The deformation dipole model, which gives very good agreement with neutron scattering results,[5] has been used to determine the frequencies. The short-range forces include nearest-neighbor interactions, next-nearest-neighbor interactions between negative ions only, and angle bending forces.[6] The elastic constants ($C_{11} = 10.85$, $C_{12} = 2.290$, $C_{44} = 2.899$, in units of 10^{11} dyn/cm^2) and the density (2.851 g/cm^3) used in the model are the 4 °K values of Lewis, Lehoczky, and Briscoe.[7] These elastic constants lead to first sound velocities that are in good agreement with the arrival times of the leading edges of the ballistic pulses observed by Jackson *et al.*[1] The dielectric constants and restrahlen frequency used are the 2 °K values of Lowndes and Martin.[8] The calculations were performed with a sample of 64 000 points in the first Brillouin zone. The results are good down to 8 °K; below that temperature, the number of points in the Brillouin zone contributing to the sums in (3) and (5) becomes too small for the results to be reliable. The value of v_{II} at $T = 0$ °K was estimated with approximation J_8 of Betts, Bhatia, and Wyman.[9] The computed results for v_{II} and C_0 are given in Fig. 1 and Table I.

DISCUSSION

Jackson *et al.*[1] observed heat pulses with some of the properties expected of second sound. The velocities of propagation of these pulses can be determined by dividing the length of the sample used (8.3 mm) by the reported arrival times. The velocities obtained are plotted in Fig. 1. For all temperatures less than 18 °K, these velocities are greater than the calculated values for v_{II}.

If one considers second sound to refer to behavior which is within the realm of applicability of Eq. (1), the pulses observed at temperatures below 18 °K, strictly speaking, cannot be second-sound pulses, since v_{II} is the maximum propagation velocity for any effect describable by (1).[10] For Eq. (1) to be applicable, it is required that $\omega\tau_N \ll 1$, but it is not clear just how much smaller than one $\omega\tau_N$ must be. Since τ_N increases as the temperature is lowered, there must be some temperature below which (1) does not apply (assuming ω is not changed). A comparison of the velocities of the observed pulses with the calculated values for v_{II} suggests that $\omega\tau_N \ll 1$ ceased to be satisfied in the sample used at about 18 °K, and that below 18 °K the transition from the region where fully developed second-sound pulses are possible to the region where phonons propagate ballistically (i.e., without appreciable scattering) was being observed.

Jackson *et al.* did not report observing any well-developed heat pulses above 19 °K. This suggests that the relaxation time τ_{ss} had become so small at 19 °K that the transition to the higher-temperature region where only pure diffusion results had already begun. This interpretation could be checked by performing experiments at the temperatures where the transition to pure diffusion takes place and comparing the results obtained with the predictions of Eq. (1).

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