tion-metal surface-state energies self-consistently.[11] The Simons-Bloch radii can be used to reduce greatly the number of adjustable parameters in nonlocal pseudopotentials.[12]

The mathematical interpretation of the elemental coordinates $r_\sigma{}^\alpha$ and $r_\pi{}^\alpha$ is that they correspond to $(s+p)$-hybridized orbitals and $(2p-s-p)$-hybridized orbitals, respectively. (Note that $r_\pi{}^\alpha$ measures the residual strength of π interactions after subtraction of the more stable σ interactions.) A physical interpretation of the bonding coordinates r_σ and r_π can be given in terms of bond charges,[13] which have been shown to play a decisive role in the tetrahedral-octahedral transition of octet compounds.

The fact that r_σ and r_π are powerful structural coordinates suggests that the (lumped) bond charge may be decomposed into σ and π components. Then the signs in Eq. (3) suggest that the π charge is shared (+ sign) while the σ bond charges are transferred. This could correspond in real space to an effective bond potential between atoms A and B which has a triple camelback structure. The π-bond charge would be associated with the central well, while the two wells near the effective σ turning points $r_\sigma{}^{A,B}$ competed for the σ charge. All of these effects are small and are superimposed on the nonbonding charge density which, to lowest order, is simply a superposition of atomic charge densities. However, it would appear that these small effects are the ones responsible for structural phase transitions.

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Measurement of Kapitza Resistance by Use of Transient Temperature Response

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We show that the transient temperature response of a freely suspended sample to heat impulses and to heat pulses of varying duration may be interpreted to yield values of the thermal-boundary (Kapitza) resistance to heat flow into He I and He II. Our results show that in He II the thermal flux is carried by first and second sound, each of which has a characteristic Kapitza resistance.

We have developed a new heat-pulse technique for investigation of thermal-boundary (Kapitza) resistance in both He I and He II, which yields evidence for the contributions of first and second sound to the thermal flux in He II.[1,2] Accurate measurements can be made in He I since the data do not require the large corrections which limit the usefulness of conventional steady-state cell measurements.[3]

The injection of a heat pulse into a test body immersed in liquid helium produces a transient temperature response at a point on the surface of the test body. Analysis of this transient provides a direct measurement of the thermal radiative, or Kapitza, relaxation time, $\tau_K = R_K C_A$, where C_A is the sample heat capacity per unit area and

R_K is the Kapitza resistance.

Experiments were carried out in both He I and He II at saturated vapor pressure over the temperature range 1.0 to 3.8 K, using single-crystal samples of white sapphire (Al_2O_3) and sodium chloride in the form of thin disks nominally 2 cm in diameter and 2 mm thick, and with varying degrees of surface polish. A thin-film, superconducting bolometer of tin or aluminum, and a thin-film resistive heater were vapor deposited in the center of opposing sample disk faces. Electrical current pulses applied to the heater caused an injection of some thermal energy into the crystal which was sufficient to elevate its temperature 5 to 20 mK above that of the surrounding liquid-helium bath. The time development and eventual relaxation of the sample surface temperature was monitored with the bolometer. The thermal-boundary resistances of the sample-bath, bolometer-sample, and bolometer-bath interfaces formed a flux-dividing network such that the bolometer output signal was proportional to the sample temperature elevation. Distortion of the signal due to the finite bolometer relaxation time, typically 10 ns, was insignificant since this time is much shorter than the effective signal time constant in the region of measurement, ~2 μs.[4]

As further discussed below, the Kapitza relaxation-time constant τ_K was obtained in He I from the exponentially decreasing initial portion of the free relaxation signal, well before the appearance of the characteristic $t^{-1/2}$ diffusion response of bulk helium. In He II, the free-sample temperature decay was observed to be nearly exponential for all time, but with a time constant which increased with the length of the input heat pulse. This dependence was weak for temperatures between 2.15 K and T_λ, requiring a thousandfold increase in pulse length to produce a significant change in the observed relaxation-time constant. This He-II time constant, $\tau_<$, nearly pulse-length independent, was found to be significantly less than $\tau_>$, the time constant observed in He I at 2.21 K, just above T_λ. In both sodium chloride and sapphire samples, the ratio $\tau_</\tau_>$ was approximately 0.4; this large change in time constant over a 50-mK range through T_λ is in contrast to a change of less than 5% over a 500-mK range on either side of T_λ. For temperatures below 2.15 K, the time constant in He II was found to be increasingly sensitive to the input-heat-pulse length, with decreasing system temperature, down to 1.0 K. The pulse-length dependence of the time constant was found to be independent of sample-temperature excursion over a thirtyfold range. The possibility of critical heat-flux effects was ruled out for the experimental flux values. Also sample surface condition was considered irrelevant since this phenomenon was observed with similar magnitude for a number of specimens with widely differing surface finish. Finally, there is no known intrinsic property of a surface which could produce a change in heat flux with a time delay, ~10 μs, which we observe, since this delay implies an appreciable storage of thermal energy by the surface.

We first derive the sample thermal impulse response in a diffusive medium (He I) in the isothermal, one-dimensional approximation. A dielectric single crystal has much higher thermal conductivity (~4 W/cm K) than He I (~2×10^{-4} W/cm K) and hence we take the sample temperature T_s to be uniform throughout its volume; the surface in contact with the bath thus defines an isothermal contour. The diffusivity of He I is sufficiently low (~7×10^{-4} cm²/s) so that, during the time span of the experimental transient, the thermal flux penetration into the helium is effectively confined to a thin diffusion skin depth of the order of 10^{-3} times any typical sample dimension. Thus $T_0(t)$, the increase of interface temperature of the bath in contact with the crystal, is not sensitive to details of the sample geometry and, for the one-dimensional case of uniform flux penetration of the semi-infinite slab, is given by

$$T_0(t) = (\pi G_0 C_0)^{-1/2} \int_0^t \Phi(t-t')(t')^{-1/2}\,dt', \qquad (1)$$

where G_0 and C_0 are, respectively, the conductivity and specific heat of the helium.[5] The flux, Φ, is given self-consistently by the Kapitza law as $\Phi = R_K^{-1}[T_s(t) - T_0(t)]$. If $P(t)$ represents the power dissipated uniformly throughout the volume of the crystal of total heat capacity C_s (as from the thermalization of a heat pulse), then the equation of energy balance with the bath surface temperature given self-consistently by Eq. (1) may be solved by using Laplace transforms. The solution for impulse-power per unit heat capacity, $P(t)/C_s = h_0\delta(t)$, we call the diffusive impulse response $\mathcal{T}_s(t)$ and is given by

$$\mathrm{Re}[(1 + i\cot\theta)e^{\beta^2 t}\,\mathrm{erfc}(\beta t^{1/2})],$$

where

$$\beta = \tau_K^{-1/2} e^{i\theta}, \quad \theta = -\cos^{-1}[(C_A^2/4\tau_K G_0 C_0)^{1/2}].$$

The internal equilibration of the injected heat-pulse energy within the sample volume may be adequately described by a heat function, $h(t)$, which gives the effective uniform power per unit heat capacity produced by the thermalization process within the high-conductivity crystal. Of particular interest is t_e, the total time required for the equilibration process; for $t > te$, $h(t)$ remains zero and the sample temperature is freely relaxing via flux loss to the bath. We may thus express the sample temperature, using Duhamel's theorem, as[5]

$$T_s(t) = \int_0^{te} h(t')\, \mathcal{T}_s(t-t')dt'. \tag{2}$$

For $t/\tau_K < 1.5$, $\mathcal{T}_s(t)$ has an exponential dependence, being proportional to $\exp[-(t/\tau_K)|\cos 2\theta|]$. For the data analysis to be tractable, it is necessary that the regime of the free relaxation, $t > t_e$, occur during a period when $\mathcal{T}_s(t)$ has this simple exponential behavior. This results in the imposition of a window condition for the observation of a temperature relaxation dominated by the Kapitza, or radiative, decay: $t_e < t < 1.5\tau_K$. Depending upon sample geometry, the sample equilibration time, t_e, may be either greater or less than the Kapitza time constant, τ_K, making the choice of sample configuration crucial to the practical success of the experiment. When the window condition is satisfied, the exponential form of $\mathcal{T}_s(t)$ results in an exponentially decreasing sample temperature during this interval, with an effective time constant $\tau_{\rm eff} = \tau_K/|\cos 2\theta|$. The experimentally observed relaxation, fitted to a simple exponential over this interval, gives $\tau_{\rm eff}$ and hence τ_K since the phase, θ, is determined self-consistently from $|\theta| = \cos^{-1}[\frac{1}{2}C_A(G_0C_0\tau_{\rm eff}|\cos 2\theta|)^{-1/2}]$. For the samples used in our work, the phase was found to lie in the range $84° < |\theta| < 90°$, and the resulting phase correction to $\tau_{\rm eff}$ was small, of the order of 2% or less.

We have determined that the appropriate sample configuration is a circular thin disk, with a diameter-to-thickness ratio ~ 10. Thermalization of the input heat pulse, injected near the center of the disk face, occurs mainly by collisions of the ballistically propagating phonons with the sample surfaces. In the thin disk, the frequency of these collisions is high and the impulse equilibration time was found to be $\tau_e < 0.7\tau_K$ so that a window of $0.8\tau_K$ was available in which to determine $\tau_{\rm eff}$ (see Fig. 1). That the time constant obtained by an exponential fit to the He I data was the true Kapitza time constant was confirmed experimentally by a simple test. If $t_e < 1.5\tau_K$, a slight increase of t_e produced by increasing the input pulse length results in an exponential relaxation with the same time constant because of the additive property of the exponential form of $\mathcal{T}_s(t)$ for $t/\tau_K < 1.5$. If $t_e > 1.5\tau_K$, $\mathcal{T}_s(t)$ is not a simple exponential, and the observed sample temperature, $T_s(t)$, although it may be fitted with an exponential, has an apparent time constant which depends strongly on the input pulse length. Insensitivity of the observed time constant to a slight increase in heat-pulse duration assured that the window condition was satisfied. This fact was confirmed by direct derivation of the time dependence of the impulse heat function through deconvolution of the transient relaxation signal for $2.15\ {\rm K} < T < T_\lambda$ in He II, where the sample response function was observed to be purely exponential.[6]

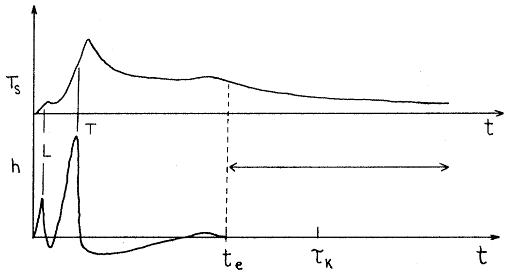

FIG. 1. Schematic illustration of an observed bolometer signal (upper curve) and the derived heat function (lower curve) in arbitrary units, as a function of time. Features arising from longitudinal- and degenerate transverse-acoustic modes are labeled L and T. The observation-time window $t_e < t < 1.5\tau_K$ is indicated by the double-headed arrow. The rms voltage signal-to-noise ratio was about 10 with sufficient system bandwidth to provide ten or more statistically independent points in the fitting interval; this leads to an overall accuracy of fit of 3% in computing the time constants.

As is well known, He II in the temperature range 1.0 K to T_λ supports two nearly commuting degrees of freedom: first and second sound.[7,8] These are associated, respectively, with the propagation of pressure and temperature waves. Khalatnikov-type theories of Kapitza resistance impose only continuity of stress and strain boundary conditions on the thermal phonon flux, hence they entertain only coupling to first sound. However, the second-sound mode may be excited by thermal fluctuations at a He II boundary and so we also include this mode of coupling the crystal thermal flux into He II in order to explain the results of our experiments.[8,9] The coupling to first sound we associate with a boundary, or Kapitza, resistance, $R_{\rm KI}$. The coupling to second sound we associate with a parallel Kapitza resistance, $R_{\rm KII}$, in series with the familiar second-sound-wave impedance, $R_{\rm II} = (C_{\rm II}v_{\rm II})^{-1}$, where $C_{\rm II}$ is the He II specific heat and v_{II} is the speed of second sound. Except for singular behavior within 10 mK of T_λ, a region we do not discuss here, the properties of energy transport by first sound are known to be continuous through the λ transition. The time necessary for the establishment of diffusive flow is given by $G_0/C_0 v_{\mathrm{I}}^2 \sim 10^{-10}$ s or less for $T > 1.0$ K; v_{I} is the velocity of first sound.[10] This time is much less than the times of interest, so that the propagation of first-sound thermal energy is described by the diffusion equation; hence the He II interface temperature associated with this mode is given as for He I by Eq. (1), where now G_{I} replaces G_0 and C_{I} replaces C_0. Such a relation results in an effective, time-dependent, bath impedance $R_{\mathrm{I}}(t)$ to the first-sound flux which is seen in series with R_{KI}. The total impedance, $R_{\mathrm{KII}} + R_{\mathrm{II}}$, to second sound, on the other hand, is constant in time. As a result, the splitting of the total heat flux between the two modes depends on pulse length.

From the dynamics of parallel heat transport by the diffusive (first-sound) and the nondiffusive (second-sound) modes, the sample-temperature impulse response in He II, $\mathcal{T}_s^{\mathrm{II}}(t)$, has been obtained as the Laplace transform of

$$\mathcal{T}_s^{\mathrm{II}}(p) = [\tau_{\mathrm{K0}} + \tau_{\mathrm{KII}}(p\tau_{\mathrm{I}})^{-1/2}] \times [1 + p\tau_{\mathrm{K0}} + (p\tau_{\mathrm{I}})^{-1/2}(1 + p\tau_{\mathrm{KII}})]^{-1},$$

where

$$\tau_{\mathrm{KI}} = R_{\mathrm{KI}} C_A, \quad \tau_{\mathrm{KII}} = (R_{\mathrm{KII}} + R_{\mathrm{II}}) C_A,$$

$$\tau_{\mathrm{K0}}^{-1} = \tau_{\mathrm{KI}}^{-1} + \tau_{\mathrm{KII}}^{-1}, \quad \tau_{\mathrm{I}} = (R_{\mathrm{KI}} + R_{\mathrm{KII}} + R_{\mathrm{II}})^2 G_{\mathrm{I}} C_{\mathrm{I}}.$$

While the transform may be obtained by partial-fraction decomposition it is not conveniently useful. Simple asymptotic forms appropriate for short and long heat pulses, $p\tau_{\mathrm{I}} \gg 1$ and $p\tau_{\mathrm{I}} \ll 1$, are easily found. The transient temperature relaxation in both cases is found to be approximately exponential with $T_s(t) \propto \exp(-t/\tau_{\mathrm{K0}})$ or $T_s(t) \propto \exp(-t/\tau_{\mathrm{KII}})$ for short and long pulses, respectively. This result is easily understood: For very short heat pulses, the surface-temperature increase of the first-sound mode is small, so the flux is split by the parallel combination of R_{KI} and $R_{\mathrm{KII}} + R_{\mathrm{II}} \simeq R_{\mathrm{KII}}$. The time constant is thus $\tau_{\mathrm{K0}} = (\tau_{\mathrm{KI}}^{-1} + \tau_{\mathrm{KII}}^{-1})^{-1}$. Following a long heat pulse, the diffusive first-sound heat transport is very small, because of the large increase in diffusive surface temperature, and essentially all the flux loss by the sample is carried by the second-sound mode, with a resulting time constant, τ_{KII}. Thus, from the relaxation of the sample temperature following long and short pulses, the first- and second-sound Kapitza resistances, R_{KI} and R_{KII}, may be obtained. Near the λ point, this information is derived from the ratio $\tau_>/\tau_<$ which is obtained with short pulses, since $\tau_> = R_{\mathrm{KI}} C_A$, $\tau_< = [R_{\mathrm{KI}}^{-1} + (R_{\mathrm{KII}} + R_{\mathrm{II}})^{-1}]^{-1} C_A$. Typical results of our measurements on sodium chloride are shown in Fig. 2. Since both He I and He II support the first-sound mode, R_{KI} is continuous through T_λ.

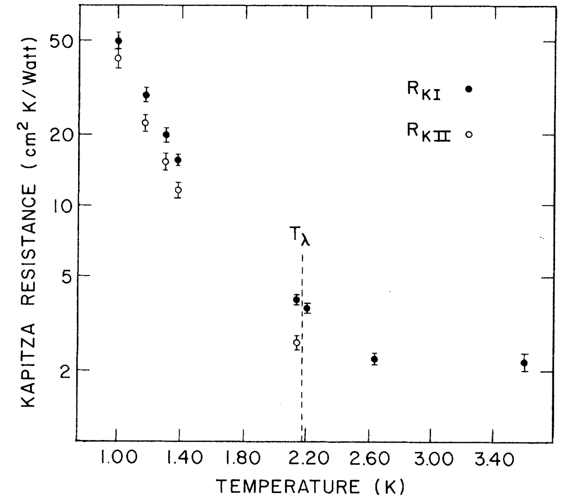

FIG. 2. First- and second-sound Kapitza resistances of sodium chloride as functions of temperature. Results for sapphire differ significantly only in magnitude (to the same degree of approximation, $90T^{-3}$ cm^2 K/W for $T < T_\lambda$) and in a more rapid decrease in R_{KI} for $T > 2.6$ K.

For 1.0 K $< T < T_\lambda$, both R_{KI} and R_{KII} may be fitted to within 10% by a law of the form $40T^{-3}$ cm^2 K/W, although the temperature dependence of each is not strictly T^{-3}. Steady-state measurements, which determine some combination of R_{KI} and R_{KII}, will thus have an implicit temperature dependence due to the variation of flux sharing with temperature. Above 2.6 K, the decrease in R_{KI} is slower, a result similar to that reported by Mate and Sawyer for the He I Kapitza resistance of copper.[3]

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Neutron-Scattering Study of the Ferroelectric Phase Transition in CsD_2PO_4[†]

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A neutron-scattering study of the ferroelectric transition in CsD_2PO_4 has yielded quasi-elastic diffuse distributions of intensity typical of a one-dimensional system with chainlike ordering parallel to the ferroelectric b axis of this monoclinic crystal. Therefore, despite such suggestive similarities as the large isotope shift in T_c, the transition is quite different from that of tetragonal KD_2PO_4 where the diffuse scattering clearly exhibits characteristics of three-dimensional dipolar interactions.

Although KD_2PO_4 has been the object for several neutron-scattering[1-3] studies, studies of structural phase transitions of hydrogen-bonded materials with neutrons are still relatively few. In addition to KD_2PO_4, $ND_4D_2PO_4$[4] and $H_2C_4O_4$ (squaric acid)[5] have also been studied, to mention only those materials in which considerable isotope effects are associated with the transition.

The crystal structure[6] of CsH_2PO_4 is quite different from that of KH_2PO_4, the well-known tetragonal prototype of the ferroelectric phosphates and arsenates. Nevertheless, as in the latter family, this material does undergo a phase transition to a ferroelectric state ($T_c = 153$ K),[6-8] and also there is a large isotope effect on T_c upon substitution of deuterium for hydrogen (T_c reported to be 267 K for CsD_2PO_4).[8] Clearly, there is a central role for strong hydrogen bonds in the transition mechanism. Despite these suggestive similarities the results of the present study demonstrate that the nature of the transition in the Cs compound has unique characteristics which set it apart from the KH_2PO_4 family.

CsH_2PO_4 crystallizes in the monoclinic space group $P2_1/m$ with two formula units per unit cell. Measurements in the present study show that CsD_2PO_4 is isostructural with CsH_2PO_4 since there are only small differences in the lattice parameters. At 265 K the following lattice parameters for CsD_2PO_4 were obtained: $a = 7.906$, $b = 6.364$, $c = 4.889$ Å, and $\beta = 107.7°$. Moreover, since no violation of the systematic extinction $(0k0)$ with $k = 2n+1$ was found in the low-temperature phase of either material, the ferroelectric space group in both cases is $P2_1$, with the polar axis being the unique b axis, as suggested by Uesu and Kobayashi.[6]

The neutron scattering experiments reported here were carried out on a single crystal of CsD_2PO_4. Sample crystals were prepared from CsH_2PO_4 by several recrystallizations from 99.8% D_2O. The crystal used in the experiments had well-developed $\{011\}$ and $\{100\}$ faces and a mass of about 1.5 g. For most measurements the crystal was aligned so that the scattering took place in the a-b plane. The crystal was of good quality, giving rocking curves with full width at half-maximum of 0.18°. Neutron-scattering ex-