# HEAT PULSES IN QUARTZ AND SAPPHIRE AT LOW TEMPERATURES

R. J. von Gutfeld* and A. H. Nethercot, Jr.
IBM Watson Research Center, Yorktown Heights, New York
(Received 3 April 1964)

Experiments have been performed on the propagation of heat pulses in single-crystal dielectric materials at temperatures sufficiently low that only boundary and "defect" scattering should be effective in deflecting the phonons from direct rectilinear flow. Such heat-pulse experiments can give more direct and unambiguous information then the usual thermal conductivity measurements on how the thermal phonons travel across the crystal since their trajectories can be resolved both in time and in space. The technique is somewhat similar to pulse measurements of the attenuation of microwave phonons except that the phonons have a much higher frequency, are incoherent, and are not monochromatic. Also, the thermal detector is sensitive to the arrival of scattered phonons arriving at various times. Heat-pulse techniques do not appear to have been previously applied to solid materials, although somewhat similar methods have been used extensively on liquid helium (at very much slower speeds).

The major findings to be reported here for the temperature range 3.8-8.5°K are that (1) approximately 1/15 of the heat flux for quartz and ~$\frac{1}{4}$ for sapphire reaches the detector in essentially uninterrupted direct rectilinear line-of-sight propagation; (2) the remainder of the heat flux is scattered, the angular and temperature dependences being those characteristic of a small-angle scattering process; (3) the velocities of the unscattered heat pulses are not given by the conventional longitudinal and transverse sound velocities, but by suitably defined "wave" (energy) velocities; (4) related to this, more than two unscattered transverse heat pulses are observed in quartz.

Both $X$-cut and $Z$-cut samples of natural quartz and synthetic sapphire obtained from the Valpey Crystal Co. were investigated. They were cylindrical in shape ($D = \frac{5}{8}$ in.) with polished end faces on which were evaporated thin metallic films to generate and detect the heat pulses. The generator was of constantan, ~500 Å thick, and 0.020 in. square. The resistance was about 15 Ω, and current pulses of up to 1 A and of duration as short as 0.1 μsec were used. The detector was a thin alloyed superconducting film

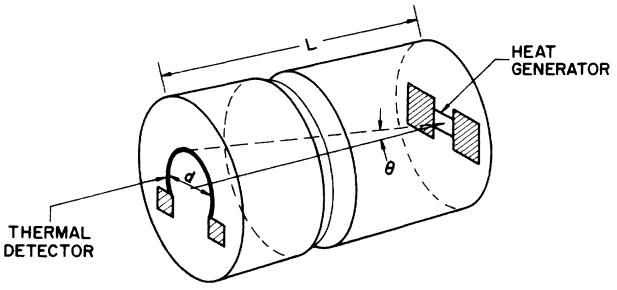


FIG. 1. Schematic diagram of the sample (length $L$) showing the circular detector (diameter $d$), the square heat pulse generator, and the peripheral cut made to control the scattered phonons. The annular detector width is 0.004 in. The shaded areas are evaporated silver "lands." The phonon trajectories lie along and near the cone of angle $\theta$.

of thickness ~1500 Å, whose resistance was sensitive to temperature changes. A 6% Sn-94% In alloy was used at 3.8°K and a 35% Bi-65% Pb alloy at 8.5°K. Because of the circular shape of the detector (Fig. 1), the important phonons were those whose net motion lay near a cone centered on the axis of the sample, the cone angle ($\theta$) being determined by the length ($L$) and diameter ($d$), where $\sin\theta = d/2L$.

The thermal time constant of the 3.8°K detector was measured to be less than 0.04 μsec by the use of an attenuated giant pulse ruby laser to directly heat the detector (rise and fall times of the light <0.04 μsec). For films of this thickness, a theoretical limit of 0.008 μsec is set by blackbody phonon radiation.[1,2] A somewhat longer time constant of ~0.04 μsec is predicted from experimentally measured dc interfacial thermal conductances.[1]

The shapes of the received heat pulses are shown in the upper trace of Fig. 2(a) for a typical phonon propagation experiment on a $Z$-cut quartz rod at 3.8°K with $L = 1$ cm and $\theta = 14.5°$. The pulse duration was 0.1 μsec. The phonons involved corresponded to a broad band of frequencies which extended from approximately 40 to 400 Gc/sec. The integrated heat flux which arrived at the detector was consistent with the input power so that the energy transport mechanism was verified as a thermal one. One longitudinal and then two transverse pulses are

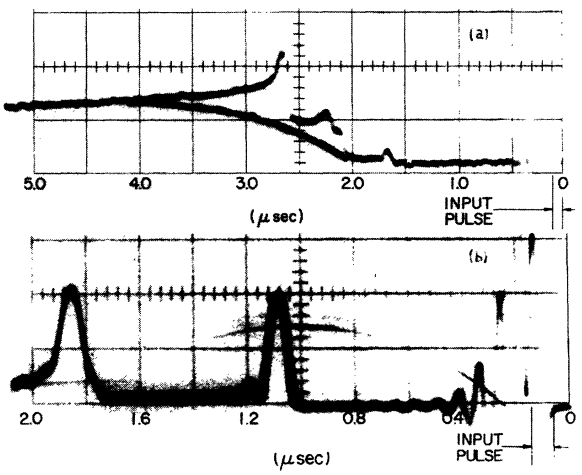


FIG. 2. The received heat pulses at the detector for $\theta = 14.5°$ and $L = 1$ cm. The upper trace in Fig. 2(a) is a typical curve for quartz and the lower trace shows the results obtained with the direct phonons removed from the beam. Figure 2(b) shows typical results obtained for sapphire. Some ringing in the pulse circuit is evident.

evident, the middle one being split into two. Similar curves have also been taken for other lengths and temperatures, for a number of propagation angles, and for a number of different samples. A similar curve for $Z$-cut sapphire shown in Fig. 2(b) shows only the longitudinal pulse and then a broadened pulse due to the two (unresolved) transverse modes.

The appearance of "extra" pulses in quartz is related to the complicated acoustic refraction properties of anisotropic media.[3] Calculation of the acoustic Poynting vector shows that, in general, the direction of energy propagation does not coincide with the direction of the phase velocity. In fact, for a given transverse mode there can be, for certain given directions of energy propagation, up to three widely different directions and magnitudes of the phase velocity; this, in turn, can give rise to as many as three energy velocities and hence to three heat pulses in this one direction (an effect which has not previously been observed). Since the present experiment uses a small incoherent source of phonons, it is clear that the phase velocity of the disturbance has no significance and that only the "wave" (energy) velocity is important. These wave velocities can be found for quartz with the help of calculations given by Farnell[4] and are shown plotted against $\theta$ by the solid lines in Fig. 3 for the particular azimuthal angles, $\varphi = \pm 30°$. It is seen that five pulses are predicted for $\varphi = +30°$ for $4° < \theta < 18°$ (since the middle transverse mode folds back on itself twice) and three for $\varphi = -30°$. Actually, the detector encompasses all angles $\varphi$, not just $\varphi = \pm 30°$. However, the velocity is stationary with respect to $\varphi$ at $\varphi = \pm 30°$, and thus many more phonons arrive simultaneously at the detector at or near these angles than at other angles; of course, some residual smearing between those pulses corresponding to $\varphi = \pm 30°$ is expected. For comparison, the predicted phase velocities are also given in Fig. 3 by the dashed curves. It is clear that the experimentally observed velocities agree quite well with the energy-velocity curves and not at all well with the phase-velocity curves. Only four pulses were well resolved, but the presence of the others can be inferred from the relative broadenings of these four. Similar effects, including the presence of an "extra" pulse, were observed for $X$-cut quartz. The observed lack of such "extra" pulses is expected for sapphire [Fig. 2(b)] because of its much higher degree of isotropy; also, the measured heat-pulse velocities in sapphire again agree better with the calculated energy velocities than with the phase velocities.

The shapes of the heat pulses due to scattering

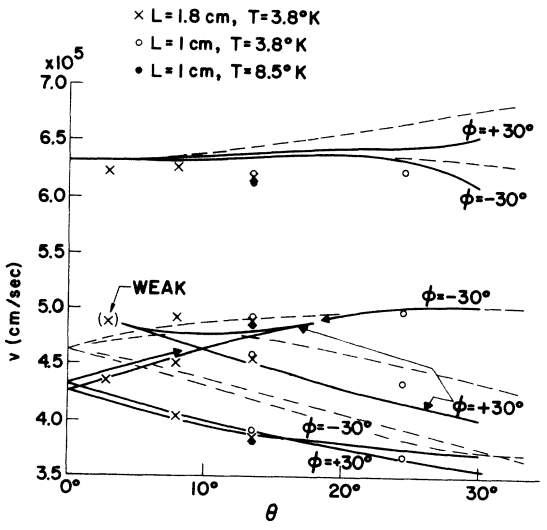


FIG. 3. The observed and predicted velocities for quartz as a function of the cone angle $\theta$. The solid curves are those predicted for the energy velocities and the dashed curves those for the phase velocities. Both sets of curves have been adjusted by 1% to allow roughly for the change of elastic constants with temperature. (Note that one curve, $\varphi = -30°$, is interrupted as shown by the arrow heads so that the multivalued nature of the $\varphi = +30°$ mode having the "extra" peaks is emphasized.)

are more difficult to explain, especially for the quartz, since it is seen in Fig. 2 that the effects of scattering in $Z$-cut sapphire are dramatically less. (Thermal conductivity data on a particular sapphire crystal[5] indicated that the mean free path for "defect" scattering was of the order of several millimeters; thus the extreme sharpness of the pulses observed here was not expected.) For the quartz there are perhaps three distinct regions for each individual detection pulse—the pulse itself, the rapid partial recovery, and the longer tail (or background, later to be called the "ramp"). In order to further investigate this behavior, a peripheral cut was made into the side of the crystal to limit the angular spread of the scattered phonons. As the cut was made successively deeper and as scattered phonons were thereby blocked from the detector, there was a gradual, but accelerating, decrease in the intensity of the whole pattern, the long tails (or "ramp") decreasing most rapidly. This decrease was roughly similar to that predicted[6] for dislocation scattering; however, other small-angle scattering mechanisms could behave similarly. The last cut, which blocked off by a few degrees the line-of-sight path between generator and detector, abruptly removed the pulses themselves and the short tails, leaving only the weaker "ramp." This "ramp" is shown by the lower curve in Fig. 2(a), but, in order to include both the phonons scattered by roughly +5° and -5° or more with respect to the detector line-of-sight direction, the ordinates are increased by a factor of two.

Because of the short time constant of the detector, its response should be proportional to the rate of arrival of energy. Thus, from the integrated areas under the two curves shown in Fig. 2(a) and other similar curves, it can be estimated that, for a given amount of energy that arrives (unscattered) within the expected pulse interval (0.1 $\mu$sec), on the order of 10 times that energy is scattered by roughly 5° or more and arrives in the "ramp" outside the expected pulse interval. About five times that same energy is scattered by less than 5° and gives the short and roughly exponential tails with decay times of about $\frac{1}{2}$ $\mu$sec. (Boundary scattering becomes important after about 4 $\mu$sec and these phonons are not considered.) Thus on the order of 1/15 of the energy arrives unscattered within the expected pulse interval, while the remainder arrives at times altered by 5% or more. This finding is roughly consistent with the average thermal conductivity mean free path at this temperature, $l = 3K/C_V\bar{v}$, which has been estimated[7] to be 1 or 2 cm: Even though most of the phonons have been scattered, the small-angle scattering does not decrease the forward velocity and hence the heat flux very much. Since the scattering appears to be predominantly a small-angle process, it may arise from dislocation lines or small-angle grain boundaries.[8] This interpretation would be consistent with the experimental observation that the received pulse shapes for quartz (and sapphire) do not change much with temperature between 3.8 and 8.5°K. Thus, the scattering is certainly not proportional to $\omega^4$ (as is expected for Rayleigh scattering), but is more like $\omega^1$ or $\omega^0$.

The possibility of observing "second sound" in crystalline solids has been frequently discussed since the original treatment of the effect some time ago.[9] It does not appear that any of the broadening observed in quartz and sapphire up to $T = 8.5$°K can be attributed to such a phenomenon (even if it were only incipient and involved only the higher frequency fraction of the phonons) since the observed broadening does not increase rapidly enough with temperature. It is also apparent that quartz is not a good subject for such studies since the "defect" scattering is not particularly small and the anisotropy is large.

The authors would like to thank Dr. J. A. Armstrong for the use of the giant-pulse ruby laser and Mr. W. K. Schug for his help with the thin film evaporations. We would also like to acknowledge helpful conversations with Dr. H. H. Nickle and Dr. N. S. Shiren and the encouragement of Dr. Ben Josephson. The possible importance of such heat pulse measurements first occurred to one of the authors (A. H. N.) during a conversation with Dr. M. P. Sarachik and Dr. G. K. Gaulé.

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*Also a doctoral candidate at Department of Physics, New York University, New York, New York.

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## ELECTRON-NUCLEAR DOUBLE RESONANCE STUDY AND EXCHANGE POLARIZATION OF THE SELF-TRAPPED HOLE IN LiF†*

Ramayana Gazzinelli‡ and Robert Mieher§
Columbia Radiation Laboratory, Columbia University, New York, New York
(Received 11 May 1964)

This Letter discusses the results of a detailed electron nuclear double resonance (ENDOR) study of the self-trapped hole in LiF. In addition to a verification of the accepted model of the self-trapped hole, the experimental hyperfine constants of the lattice nuclei provide a measure of the large exchange polarization of closed electron shells at points distant from the nuclei of a simple molecule.

The self-trapped hole in alkali halide crystals was discovered by Känzig[1] in an electron spin resonance (ESR) investigation of KCl x rayed at liquid nitrogen temperature. This defect was called the $V_K$ center, and detailed ESR studies were made in different materials by Känzig and co-workers.[2,3] Also, optical studies were made by Delbecq and co-workers.[4] Both the ESR and optical data were analyzed in terms of a negatively charged diatomic molecule, e.g., $F_2^-$, oriented along a [110] axis of the crystal (i.e., the hole is shared by two halide ion lattice sites).

The ESR of the $V_K$ center is characterized by a large, anisotropic hyperfine interaction between the unpaired electron and the two nuclei of the molecule. Since the fluorine nucleus has a spin of $\frac{1}{2}$, the ESR of $F_2^-$ consists of three hyperfine lines ($m_I[\mathrm{F}]=\pm1,0$) with a separation between the $m_I[\mathrm{F}]=\pm1$ lines of about 1800 gauss when the magnetic field is parallel to the molecular axis and a separation of about 150 gauss when the field is perpendicular to the axis. The single resonance lines in LiF are about 12 gauss wide due to unresolved hyperfine interactions with the surrounding nuclei of the lattice.

The detailed ENDOR results for the $V_K$ center are shown in Fig. 1. Because of the low symmetry at most of the neighboring nuclear sites, it was necessary to determine the angular dependence of the ENDOR lines for rotations about the three principal axes of the defect. Identification

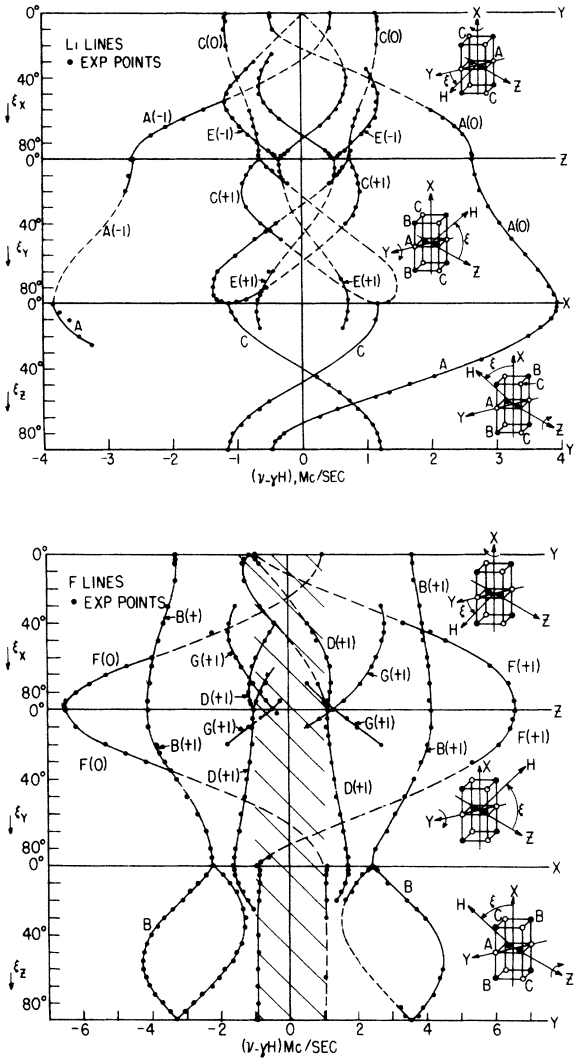
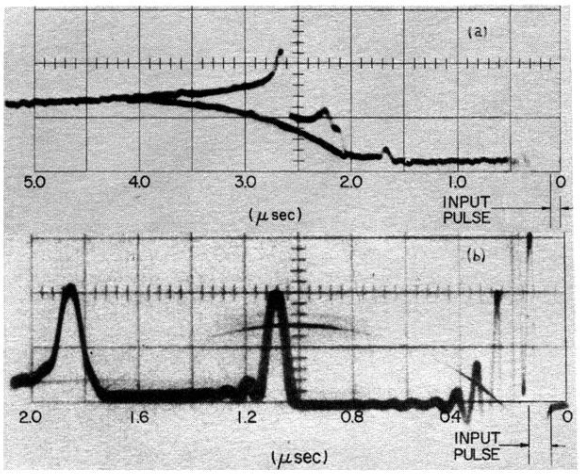



FIG. 1. Angular dependence of ENDOR lines for $V_K$ center. Letters indicate the nuclear group and (±1), (0) indicate the single resonance line ($m[\mathrm{F}]=\pm1,0$) for which the data were taken. Because the magnetic field is a function of crystal orientation for the $m[\mathrm{F}]=\pm1$, the ENDOR data are plotted as $\nu-\gamma H$.

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