mentally, we found that the two peaks were different in height, but their difference was within the 20% experimental accuracy.

The third-harmonic output was found to be elliptically polarized with the ratio of the two circularly polarized components being 5 ± 1. The theoretical ratio, given by[3] $|[(\lambda'-\epsilon^{1/2})f_+^{(3\omega)}-m_+^{(3\omega)}]/[(\lambda'+\epsilon^{1/2})f_+^{(3\omega)}-m_+^{(3\omega)}]|^2$, is 4.8. Comparison of the phase-matched third-harmonic signals from the liquid crystal and from the fuchsin basic dye solution yields $|\chi_{++++}^{\mathrm{NL}}|/|\chi_{\mathrm{Dye}}^{\mathrm{NL}}| \approx 0.1$. We also measured the phase-matched third-harmonic generation from samples with different thickness. The third-harmonic intensities were indeed roughly proportional to the square of the sample thickness. Investigation of phase-matching conditions $\Delta m_{jkln}=0$ with other combinations of $jkln$ is presently in progress.

In summary, we have shown that the third-harmonic generation in a cholesteric liquid crystal is phase matchable. This effect should be common for nearly all cholesteric liquid crystals. That our experimental results agree well with the theory is another triumph of de Vries's model[3] for cholesteric liquid crystals.

We would like to thank Dr. N. M. Amer for helpful discussions. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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# SECOND SOUND IN NaF[†]

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Propagation of heat pulses in NaF has been studied to higher temperatures in a purer crystal than studied by McNelly *et al*. At the highest temperautres the second-sound velocity fails to level off at the theoretically predicted limiting value.

In a recent paper McNelly et al.[1] reported the observation of the onset of second sound in solid sodium fluoride, and indicated that purer crystals would perhaps demonstrate the phenomena more clearly. The purpose of the present paper is to corroborate the existence and extend the range of observation of second-sound propagation in a very pure crystal of NaF grown independently at Northwestern University.

Our purest crystal was grown by an extended multiple-growth technique starting with ultrapure NaF powder. The temperature variation of the thermal conductivity for this crystal is shown in Fig. 1; an insulator's peak value of thermal

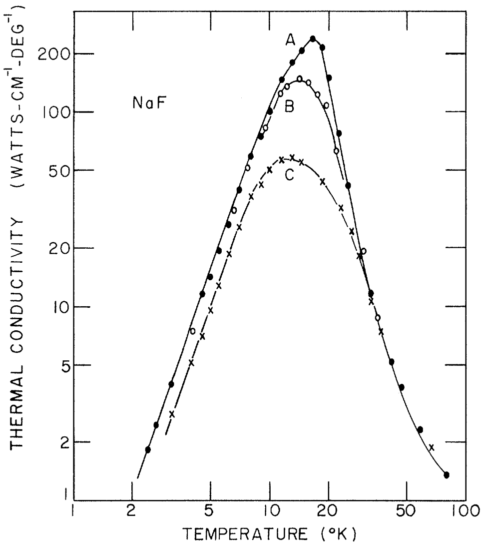

FIG. 1. Thermal conductivity versus temperature for pure NaF crystals. Curve $A$, NaF sample, this paper; curve $B$, NaF sample, Ref. 1; curve $C$, typical singly grown NaF (smaller cross section).

conductivity $K_{\mathrm{peak}}$ is a sensitive indicator of its purity, and the conductivity of 240 W/cm deg (at 16.5°K) for our purest sample may well be the highest value ever measured for an insulator. A complete analysis, based on the Callaway[2] model for lattice thermal conductivity, allows one to deduce relative strengths of impurity and intrinsic-process phonon-phonon scattering rates. Such an analysis has been done for our purest crystal but a discussion of the subtleties of such an analysis is too lengthy for the present paper and will be published elsewhere.[3] It is enough now to indicate that our purest crystal (curve $A$, Fig. 1) had between a factor of 2 and a factor of 5 less impurities than the best crystal[4] in Ref. 1 (curve $B$, Fig. 1).

Heat pulses were propagated through our samples using the techniques described in Ref. 1. Figure 2 shows heat pulses in the $K_{\mathrm{peak}}=240$ W/cm deg crystal for several different temperatures. The behavior seen here is similar to Ref. 1, but more dramatic. The topmost trace (9.6°K) shows well-defined longitudinal and transverse first-sound pulses. By 12.5°K, the "transverse" pulse is seen to behave in an unusual fashion; it has broadened considerably and its peak has shifted to later times. At 15°K a new pulse, which we identify as second sound, is seen. It arrives later than the transverse pulse and has much greater amplitude. The transverse peak is marked by an arrow. By 17.3°K, the second-sound pulse has slowed enough to allow one to see the transverse ballistic pulse clearly. A comparison with Fig. 1(b) of Ref. 1 is instructive. At 15°K the signal in our crystal is seen to return to the base line after the second-sound pulse. In contrast, at about the same temperature the second-sound peak in their crystal is superimposed on a broad diffusive ramp.

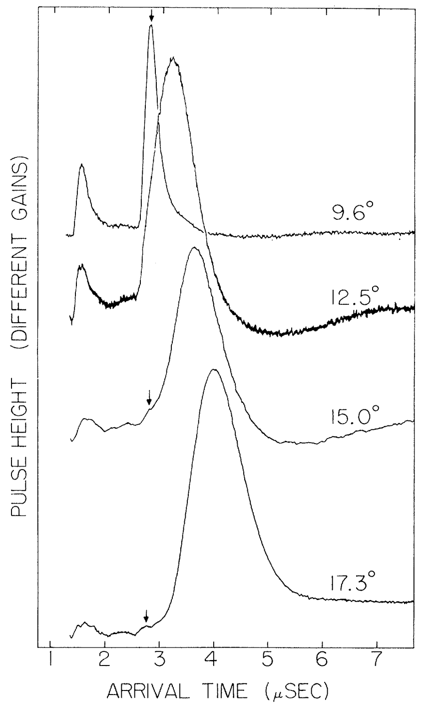

FIG. 2. Heat pulses in the purest NaF sample ($l=8.3$ mm) in the ⟨100⟩ direction for several different temperatures. The arrows mark the peak of the transverse ballistic pulse. Note the movement of the second-sound peak to later times for higher temperatures.

Our ability to follow second sound out to higher temperatures is reflected in the temperature dependence given in Fig. 3. It is seen that the pulse moves linearly to later arrival times and broadens as the temperature is increased. The sharp rise at the highest temperatures is due to the arrival of the diffusive scattering signal which dominates when the rate of momentum-destroying phonon collisions ($\tau_R^{-1}$) becomes sufficiently high. We observe that the linear shift seen in Ref. 1 continues to yet higher temperatures and that no leveling off towards the expected fully developed second-sound velocity occurs before diffusion forces the curve upward. In particular, at 18°K the arrival time for the peak of the second-sound pulse is essentially at the value expected from existing theory, but has yet to

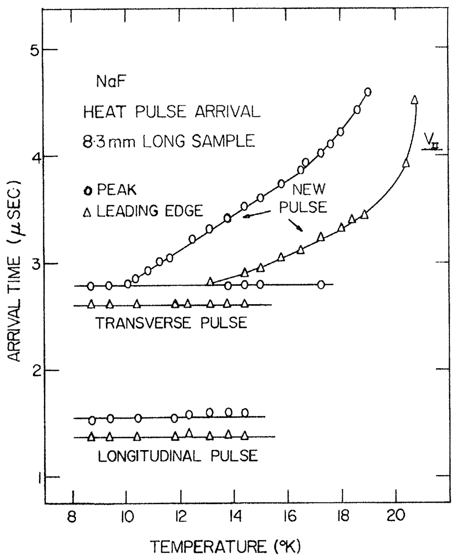

FIG. 3. Arrival times versus temperature for leading edges and peaks of longitudinal ballistic pulse, the transverse ballistic pulse, and the second pulse. $V_{\rm II}$ is the expected arrival time for fully developed second sound.

level off.

Thus, in spite of the fact that we have investigated second sound in a crystal of substantially higher purity, the behavior found in Ref. 1 is seen to continue to higher temperatures. This behavior is not predicted by current theories and is distinct from that seen so far in solid helium. Ackerman and Guyer[5] observed a gradual approach to a constant second-sound velocity with increasing temperature. If a leveling off is to be seen in NaF, it must occur much more abruptly since at 18°K the second-sound velocity is so close to the predicted value.[6] This difference between solid helium and NaF could be understood if the ratio of momentum-conserving to momentum-destroying processes $(\tau_N^{-1}/\tau_R^{-1})$ for NaF were significantly lower than that for solid helium. Alternatively, the behavior seen here and in Ref. 1 could be intrinsic to NaF.

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[6] $V_{\rm II}$ was calculated using Eq. (12) of Ref. 5 with the effect of sound-velocity anisotropy included by use of Houston's approximation.

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# ELECTRONIC PHASE SHIFTS AT THE FERMI SURFACE OF COPPER*

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The results of a phase-shift analysis of the Fermi surface of copper using the Korringa-Kohn-Rostoker method are reported. The values of the first four phase shifts and the Fermi energy differ from those obtained recently by Lee from an augmented-plane-wave calculation.

The augmented-plane-wave[1] (APW) and Korringa[2]-Kohn-Rostoker[3] (KKR) methods for band calculations have the feature that the single-particle potential does not enter explicitly into the computation of the dispersion curves when the muffin-tin approximation is used. The only relevant quantities are the partial-wave phase shifts $\eta_l$ of the angular momentum components for scattering, at a particular energy, from the effective potential. Thus, as discussed in some detail by Segall and Ham,[4] it should be possible to treat the $\eta_l$'s as parameters to be adjusted to obtain agreement between measured and computed Fermi-surface data. Since experience with alkali, noble, and transition metals has shown that only the first three or four phase shifts are important for the convergence of the KKR method, this approach appears to be both an attractive