Heat Transport in Bismuth at Liquid-Helium Temperatures*

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The temperature dependence of the thermal conductivity κ of bismuth has been investigated between 1.3 and 2°K. In zero magnetic field, this dependence is found to be anisotropic; κ is roughly proportional to T^3 for heat flow along the bisectrix, but increases significantly faster than T^3 for heat flowing along the trigonal. Application of a small transverse magnetic field (~50 Oe) causes the thermal conductivity to drop by several percent at 1.3°K. This, combined with low-field transverse-magnetoresistance measurements, is cited as evidence for an electronic contribution to the heat current. At higher fields, quantum oscillations in the thermal conductivity are observed, their peak-to-peak amplitude amounting to 7 to 8% of the zero-field conductivity at 1.3°K. It is suggested that the anisotropic temperature dependence of the thermal conductivity can be understood qualitatively in terms of the electron-phonon interaction for a system which has a very small and highly anisotropic Fermi surface. The electrical resistivity is also measured and found to be proportional to T^2 between 1 and 4°K for both directions of current flow; this temperature dependence is unexplained.

INTRODUCTION

EARLY measurements[1] of the thermal conductivity of bismuth suggested that, at temperatures lower than about 3°K, the heat current is carried almost entirely by the phonons. Furthermore, the conductivity κ was found to be closely proportional to T^3, and this was cited as evidence that the mean free path (mfp) of the carriers was limited by the size of the specimen. Although the early investigators found no magnetic field dependence, Steele and Babiskin[2] reported de Haas–van Alphen type oscillations in the thermal conductivity up to fields of about 13 kOe. If, indeed, phonons carried the heat, and their mean free path was size limited, what was the cause of the thermal conductivity oscillations? Clearly, there must be a contribution by electrons, but to our knowledge the existence of this has never been clearly demonstrated in the zero-field measurements.

The present work was undertaken to resolve this problem.

Preliminary accounts of these measurements have already been published.[3–5]

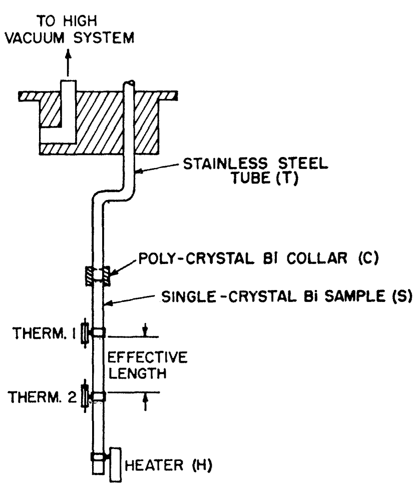

FIG. 1. Details of sample mounting.

METHOD

The measurements were made in a conventional low-temperature double-Dewar system. One distinguishing feature was the inclusion of a nitrogen can in the machine, so that the sample could be cooled very slowly. The details of sample mounting inside the vacuum chamber are shown in Fig. 1. T was a $\frac{1}{8}$-in.-o.d. stainless-steel tube which passed through the top plate of the vacuum case and was soldered into a bismuth collar C which, in turn, was soldered to the specimen S with Cd-Bi solder. This method minimized both the effects of strain due to differential expansion and the thermal resistance between sample and bath. The thermometers Th1 and Th2 and the heater H were attached to the sample with 4-mm-wide phosphor-bronze clips to keep strains at a minimum. The width of these clips was somewhat of an encumbrance because it did not allow one to measure the absolute value of the thermal conductivity. However, as we were mostly interested in the temperature and field dependence, this was not considered a very serious drawback. Several checks were made to ensure good thermal contact. Firstly, it was made certain that the thermal conductivity was independent of the heat input. Secondly, thermometer calibrations were made both with and without exchange gas in the vacuum chamber, and runs in which these differed by more than a fraction of a millidegree were

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[1] S. Shalyt, J. Phys. U.S.S.R. 8, 315 (1944); G. K. White and S. B. Woods, Phil. Mag. 3, 342 (1958).
[2] M. C. Steele and J. Babiskin, Phys. Rev. 98, 359 (1955).
[3] D. D. Manchon, Jr., and S. M. Bhagat, Bull. Am. Phys. Soc. 12, 99 (1967).
[4] S. M. Bhagat and D. D. Manchon, Jr., Phys. Letters 24A, 147 (1967).
[5] S. M. Bhagat and D. D. Manchon, Jr., Bull. Am. Phys. Soc. 12, 355 (1967).

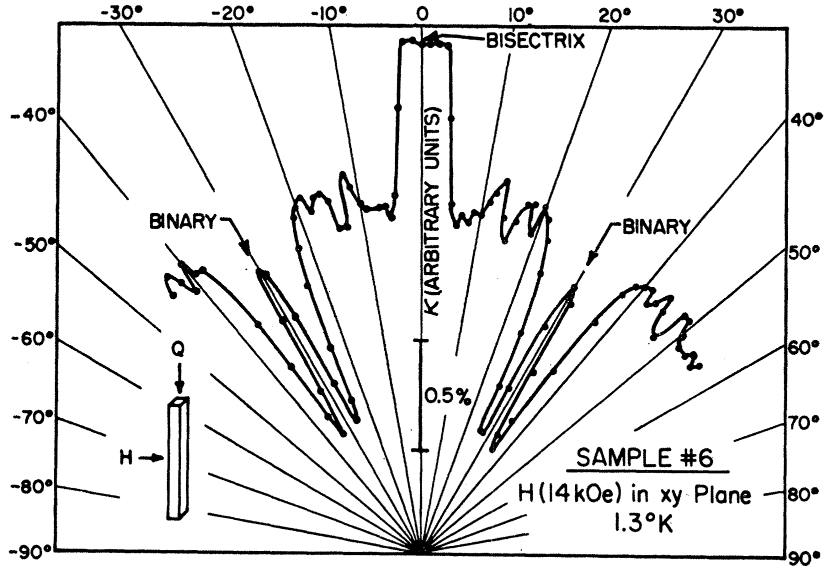

FIG. 2. Polar plot of the thermal conductivity along the trigonal direction κ_z in a transverse magnetic field.

rejected. We used carbon resistance thermometers calibrated against the 1958 helium vapor pressure scale[6] both at zero field and in a field of 500 Oe, and fitted by computer to an expression of the form suggested by Clement and Quinnell.[7] Typical deviations from the least-squares fit were a fraction of a millidegree. For high-field measurements, essentially a linear interpolation scheme was used (Ref. 9). The temperature of the bath could be held constant to within 20 μdeg during a conductivity measurement using circuitry similar to that described by Sommers.[8] It is estimated that the field variation over the effective length of the sample ($\sim$1 in.) amounted to about 0.5% of the field at the center. The high-field de Haas–van Alphen oscillations were studied on a point-by-point basis as well as by continuous recording.[9]

Electrical resistivity measurements were made using a standard four-terminal network. For zero-field measurements of electrical resistivity, a pair of Helmholtz coils (suitably oriented) was used to cancel out the earth's magnetic field to about 0.05 Oe.

As far as the temperature dependence is concerned, the relative error in the thermal conductivity is about 1%. For field dependence at a given temperature, the precision is probably better by a factor of 5 or so. However, because of uncertainty in effective length and cross section, the error in the absolute value may be quite large ($\sim$15%). Electrical resistivities were measured with a relative error of about 2%.

[6] H. Van Dijk *et al.*, Natl. Bur. Std. Monograph **10**, (1960).

[7] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

[8] H. S. Sommers, Jr., Rev. Sci. Instr. **25**, 793 (1954).

[9] Further details can be found in D. D. Manchon, Jr. and S. M. Bhagat, University of Maryland Technical Report No. 710 (unpublished).

SAMPLE PREPARATION

The samples were grown from a starting material quoted to have a purity of 99.9999%.[10] The single crystals were grown in open graphite boats in a vacuum of about 10^{-5} Torr, and cut to size on an Agietron sparkcutter. Sample axes were determined using a combination of light-figure and x-ray back reflection techniques. It is estimated that the sample axes are known to within 2°. After mounting, the angular dependence of the thermal conductivity, in the presence of a transverse magnetic field, was monitored in order to confirm the orientation and alignment from symmetry plots. Figure 2 shows a typical symmetry plot for a trigonal crystal, the magnetic field being rotated in the x-y plane. It should be noted that, because of odd powers in the field dependence, $K(H)$ is not necessarily equal to $K(-H)^2$ (Ref. 11).

CRYSTAL STRUCTURE AND BAND STRUCTURE

Bismuth has a rhombohedral structure only slightly distorted from a cube, giving a single trigonal (z) axis, and three binary axes (x) perpendicular to it. At right angles to the binary axes are the bisectrix (y) directions. The Fermi surface consists of a single hole ellipsoid of revolution about the z axis, and three electron ellipsoids lying along the binary axes, but tipped out of the basal plane by about 6°. The Fermi temperature is 180°K and the dimensions of the hole and electron ellipsoids are (14:14:45) and (5.4:7.9:79) respectively, in units

[10] Cominco 69 grade.

[11] This was also observed by Steele and Babiskin, Ref. 2.

of 10^{-22} g cm sec^{-1}.[12–15] It should be noted that the momentum of a 1°K phonon is 10.6×10^{-22} g cm sec^{-1}.

RESULTS

The significant parameters for the samples used in this investigation are given in Table I. It should be noted that the resistivity ratios were measured at the end of a series of thermal conductivity runs, and therefore it is likely that the samples were actually somewhat better than is indicated by the numbers in column 3. The samples seem to deteriorate on repeated coolings from room temperature, and therefore several thermal conductivity runs were made while the sample was being maintained at 4.2°K.

A. Thermal Conductivity

(i) *Temperature Dependence*

Figure 3 shows the observed temperature dependence of κ_y/T^3 and κ_z/T^3 at zero field and in a transverse field of 500 Oe. Clearly, in zero field κ_y varies roughly as T^3 while the variation in κ_z is somewhat faster. Two further points should be noted: (a) the value of κ seemed to scale roughly with the resistivity ratio, (b) even allowing for sample size and resistivity ratio (or what we believe to be strain) effects, κ_z was significantly smaller than κ_y. This is probably the reason why the early measurements all gave a nearly T^3 dependence.

(ii) *Field Dependence*

As shown in Fig. 4, application of a transverse magnetic field causes the thermal conductivity to drop very rapidly within the first 50 Oe, and very slowly thereafter.[16] The initial fall is almost certainly due to the reduction in the electronic component of $\kappa(\kappa_{el})$, in approximate agreement with the low-field electrical magnetoresistance (Fig. 6), assuming the Wiedemann-Franz law. The variation in the magnitude of $\kappa(0)-\kappa(500)$ might be expected to yield the temperature dependence of κ_{el}. However, in the present investigation we did not have sufficient precision to explore this.

For magnetic fields larger than about 2 kOe, de Haas–van Alphen type oscillations became clearly evident (Fig. 5). The measured periods were $(1.60\pm0.02)\times10^{-5}$ Oe^{-1} for $\mathbf{H}\|z$ and $(7.10\pm0.05)\times10^{-5}$ Oe^{-1} for $\mathbf{H}\|x$, which compare favorably with those obtained by other investigators.[17] At 1.3°K and 30 kOe, the peak-to-peak amplitude of the oscillation was about 7% of $\kappa(0)$. It is an extremely tedious job to obtain the temperature dependence of the amplitude when the quantum oscillations are being studied on a point-by-point basis, so a continuous recording scheme was tried. Unfortunately, the results were not very conclusive.

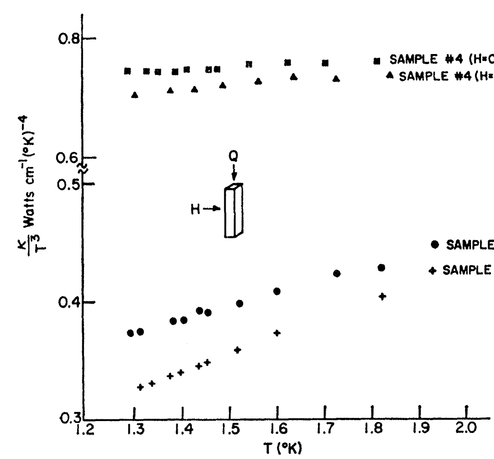

FIG. 3. Observed temperature variation κ_y/T^3 (sample No. 4) and κ_z (sample No. 7) in zero field and in a transverse field of 500 Oe.

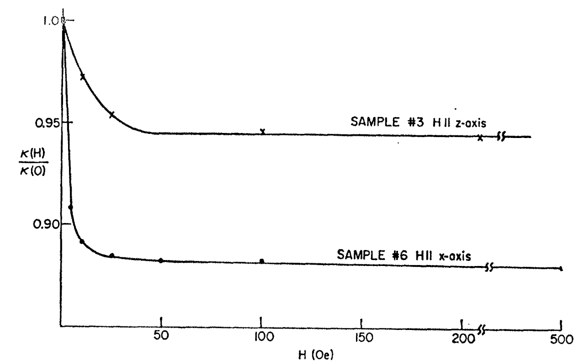

FIG. 4. Observed dependence of the thermal conductivity on magnetic field in small fields at 1.3°K.

B. Electrical Resistivity

The electrical resistivity of the samples was studied both as a function of temperature at zero field, and as a function of small transverse fields at 1.3°K. As shown in Fig. 6 both R_y (#4) and R_z (#7) are proportional to T^2 between 1.3 and 4.2°K, in agreement with the recent data of Friedman.[18] The low-field transverse magnetoresistance, Fig. 7, was measured in order to elucidate the rapid fall observed in κ as already explained above. Next, de Haas–Shubnikov oscillations were studied and their phase compared to that of the thermal conductivity oscillations. The two were found to be in phase, which indicates that the thermal conductivity oscillations cannot be attributed to κ_{el}.[2] It is needless to add that the enormous magnetoresistance of bismuth precludes the

[12] M. S. Khaikin and V. S. Edelman, JETP Pis'ma i Redaktsiyu **49**, 107 (1965) [Soviet Phys.—JETP Letters **22**, 77 (1965)].
[13] A. P. Korolyuk, JETP Pis'ma i Redaktsiyu **49**, 1009 (1965) [Soviet Phys.—JETP Letters **22**, 701 (1966)].
[14] M. S. Khaikin and V. S. Edelman, JETP Pis'ma i Redaktsiyu **47**, 878 (1964) [Soviet Phys.—JETP Letters **20**, 587 (1965)].
[15] W. S. Boyle and G. E. Smith, Progr. Semicond. **7**, 1 (1963).
[16] This slow reduction region is not completely understood at present. Further work is in progress to clarify this point.
[17] See R. N. Bhargava, Phys. Rev. **156**, 785 (1967).
[18] A. N. Friedman, Phys. Rev. **159**, 553 (1967).

TABLE I.

Sample No.	Axis	Resistivity ratio $\rho_{300°K}/\rho_{4.2°K}$	Cross section (mm×mm)	λ_{ph} at 1.3°K (mm)
2	Bis.	85	2.41×3.15	0.8
3	Bis.	140	1.57×3.10	1.2
4	Bis.	320	3.30×2.95	3.1
5	Trig.	···	3.80×3.85	1.3
6	Trig.	104	3.80×3.85	1.1
7	Trig.	370	3.30×3.60	1.6

possibility of finding any electronic conductivity at 30 kOe.

DISCUSSION

A. Thermal Conductivity

Since $\kappa_{el}(0)$ amounts to only a few percent of the $\kappa(0)$ even at the lowest temperature, from now on we will pretend that κ is essentially equal to κ_{ph}. The nearly T^3 temperature dependence of κ_{ph} suggests that the resistance comes mainly from boundary scattering. The effective mean free path of the phonons was evaluated, using the measured values of the speed of sound and the heat capacity at 1.3°K (column 5 of Table I), and found to be of the order of the specimen size. To allow for a possible additional scattering mechanism, we put

$$1/\kappa_{ph}=W_b+W_?=a/T^3+bT^n$$

even though Mathiessen's rule is probably not valid. Least-squares analyses of the data, with the assumption that the "boundary" term be left unaltered by the magnetic field, showed that $n=-5$ or -6 fit quite well. The values of a and b from the least-squares analyses are listed in Table II, and the fits are shown in Fig. 8 for $n=6$. It may be noted that both a and b vary with the resistivity ratio. Variation in a is to be expected if the lower values of $\rho_{300°K}/\rho_{4.2°K}$ imply strains in the sample. The phonon and electron wavelengths are comparable in bismuth, and strains should scatter them equally. On the other hand, variation in b is just symptomatic of the failure of Mathiessen's rule. Again, $b(500)$ is much larger than $b(0)$. Some of this change can be accounted for by recalling that $\kappa_{el}(500)$ is essentially zero.

Since quantum oscillations *are* observed in the thermal resistivity, it is suggested that the b/T^6 is due to electron-phonon scattering. Although the number of electrons is small, ultrasonic attenuation measurements show a surprisingly large deformation potential of around 1 eV,[13] giving a mean free path (mfp) of about 1 cm for 1°K phonons. The problem is to explain the extremely rapid temperature dependence.

TABLE II. Least-squares fits to $T^3/\kappa=a+b/T^3$.

Sample number	$H=0$[b] a	$H=0$[b] b	$H=500$ Oe a	$H=500$ Oe b
2	5.53	−0.32		
3	3.53	−0.29		
4	1.28	0.11	1.29	0.22
5	2.74	0.94	2.57	2.01
6a[a]	3.30	0.46	3.11	1.56
6b	3.18	0.70	3.04	1.64
7	1.93	1.30	1.97	1.93

[a] (6a and 6b refer to different set of runs on the same sample.)
[b] Units of a: $(\text{watts})^{-1}$ cm $(°k)^4$, b: $(\text{watts})^{-1}$ cm $(°k)^7$.

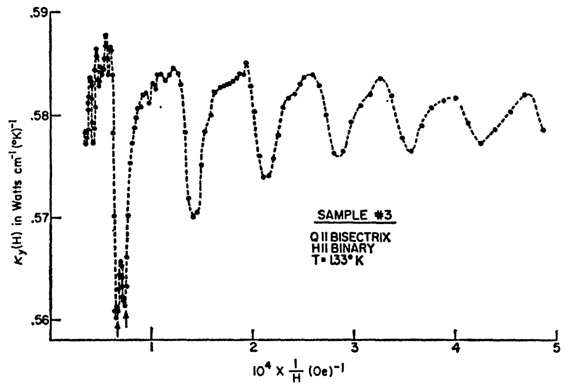

FIG. 5. Quantum oscillations in κ_y with magnetic field along the x axis. The period of these oscillations corresponds to that expected from de Haas–van Alphen measurements on two of the electron ellipsoids (Ref. 13). Note the spin-splitting (arrows) and the appearance of higher-frequency oscillations arising from the other electron ellipsoid.

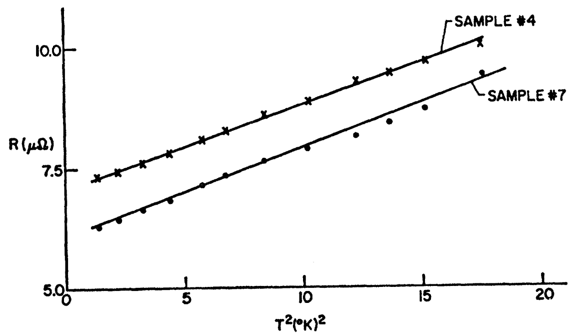

FIG. 6. Temperature variation of the electrical resistivity of Bi in zero (∼0.05 Oe) magnetic field.

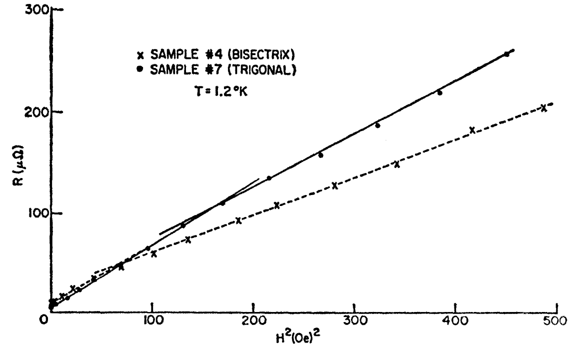

FIG. 7. Transverse magnetoresistance in bismuth in small applied fields at 1.3°K. The full curve is for current along the z axis and magnetic field along y axis, while the dashed curve is for $j\|y$, $H\|z$.

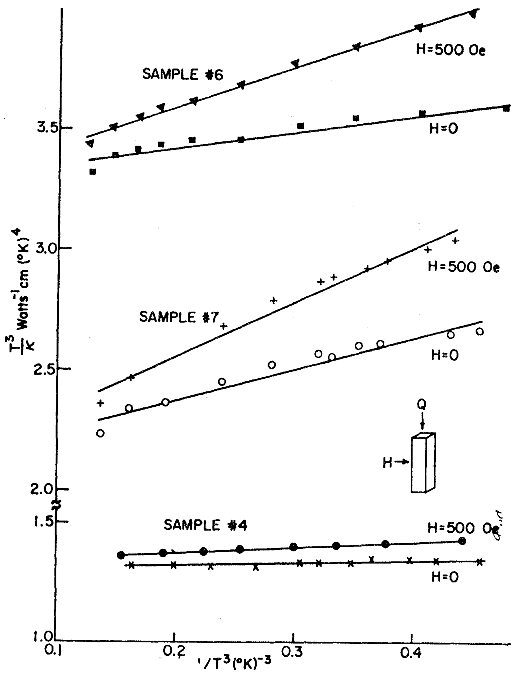

FIG. 8. T^3/κ as a function of $1/T^3$ in zero field and in applied field of 500 Oe. The straight lines show the least-squares fits to the data. The constants of the least-squares fits are given in Table II.

The electron-phonon interaction must satisfy the usual conservation conditions,

$$k+q=k',$$
$$E_k+cq=E_{k'},$$

where the k's refer to the electron momenta. Since the typical phonon q at 1°K is of the order of the size of the Fermi surface, there will, in general, be a number of phonons whose momenta are so large that, if absorbed by an electron (or hole), they would make it leave that piece of the Fermi surface. At the same time, the phonons do not have sufficient momentum to cause intervalley scattering. Thus, there will be a higher-momentum portion of the phonon spectrum for which the electron-phonon scattering becomes impossible. This "ineffectiveness" becomes even more pronounced as the temperature increases. This is probably the basic reason for the faster-than-$1/T^3$ term. In addition, since the ellipsoids are highly eccentric, the cutoff is different in different directions, accounting for the observed anisotropy in the temperature dependence. A very simple computation suggests that the temperature dependences of the resistivity from the differently oriented ellipsoids may vary from $1/T^2$ to $1/T^{4.5}$. Parts which vary as $1/T^3$ will be indistinguishable from the "boundary" term. The basic assumption underlying the present picture is that, although the conduction of heat is a diffusion process, those collisions in which a phonon loses its momentum along the direction of heat flow are most effective in limiting the heat current.

B. Electrical Resistivity

The T^2 dependence of the electrical resistivity is not at all easy to understand. On a very naive picture one could use Sondheimer's ideas,[19] combine them with the fact that $q\approx k$ and therefore the angle between k and k' is not small, and write for the resistivity an expression of the form[20]:

$$\rho\propto(T/\Theta')^3J_3(\Theta'/T),$$

where

$$\Theta'=\Theta_{\mathrm{Debye}}\cdot\frac{2k_{\max}}{q_{\mathrm{Debye}}}\simeq\Theta_{\mathrm{Debye}}\cdot\frac{2k_{\max}}{q_{\mathrm{Debye}}}$$

and

$$J_3(\Theta'/T)=\int_0^{\Theta'/T}\frac{z^3dz}{(e^z-1)(1-e^{-z})}.$$

This will, indeed, give roughly a T^2 temperature dependence at low temperatures (~4°K and below), since for a $\Theta_{\mathrm{Debye}}=120$°K, $\Theta'\sim9$°K. However, Friedman finds a T^2 dependence extending to much higher temperatures. In addition, it is not clear that (i) phonons are the only source of scattering, and (ii) $k_{y\,\max}$ is the appropriate cutoff, so it is safer to say that the temperature dependence of ρ is unexplained.

CONCLUSIONS

At 2°K and below, the thermal conductivity of bismuth is largely due to phonons; the electronic component being about 10% at 1.3°K in very pure unstrained samples. Although boundary scattering is the major limiting factor, it is suggested that scattering by electrons is important and manifests itself clearly in a term in the thermal resistivity varying faster than $1/T^3$. The electrical resistivity varies as T^2 between 1.3 and 4.2°K.

ACKNOWLEDGMENTS

We are very grateful to Dr. W. B. Willott for several useful discussions and to F. Pascoe for assistance in constructing the apparatus. We would also like to thank the Computer Science Center of the University of Maryland for making their facilities available to us.

[19] E. H. Sondheimer, Proc. Phys. Soc. (London) **A65**, 561 (1952).
[20] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England 1960), Chap. IX.