

ent one, but modified to take into account the effects of other bands, would provide a better model for the quantitative treatment of the data. The effective Hamiltonian given in Eq. (2) can be readily extended to the case of a band interacting with a number of other bands, but the location and character of other bands near the zone edge in bismuth are not at present known.

This experiment indicates the power of the method of interband magnetoreflexion measurements in exploring the energy band structure of metals. Masses and  $g$  values for both conduction and valence bands can be studied. In addition, bands can be studied not only at the Fermi surface (as with de Haas-van Alphen effect and cyclotron resonance) but at energies above the Fermi energy; and information about lower lying bands can be obtained. Furthermore, the temperature dependence of the band parameters can be studied up to room temperature and possibly higher. It is interesting that the detection of transitions due to a mass as large as  $\sim 0.2m_0$  is possible at room temperature and with transient pulse techniques. This lends encouragement to experiments in other metals with high carrier masses at low temperatures, with steady magnetic fields. By using magnetic fields of the order of 100 kilogauss and higher, this method could be applicable to the investigation of a number of metals.

The pulse experiments logically suggested the possibility that this phenomenon could be observed at lower fields and at low temperatures with photon energies well above those used in the pulse exper-

iments, thereby permitting the observation of interband transitions to higher quantum numbers. Such experiments were indeed successfully realized and are discussed in the following Letter.

We wish to thank Dr. L. M. Roth and Professor G. F. Koster for valuable discussion in connection with the theory for two interacting bands in a magnetic field.

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\*Operated with support from the U. S. Army, Navy, and Air Force.

<sup>1</sup>R. J. Keyes, S. Zwerdling, S. Foner, H. H. Kolm, and B. Lax, *Phys. Rev.* **104**, 1804 (1956). In this experiment damped oscillatory magnetic fields up to 150 kgauss, with a half period of approximately 150 microseconds, were used.

<sup>2</sup>B. Lax, K. J. Button, H. J. Zeiger, and L. M. Roth, *Phys. Rev.* **102**, 715 (1956).

<sup>3</sup>J. K. Galt, W. A. Yager, F. R. Merritt, B. B. Cetlin, and A. D. Brailsford, *Phys. Rev.* **114**, 1396 (1959).

<sup>4</sup>E. O. Kane, *J. Phys. Chem. Solids* **1**, 249 (1957).

<sup>5</sup>M. H. Cohen and E. I. Blount, *Phil. Mag.* **5**, 115 (1960).

<sup>6</sup>B. Lax, *Bull. Am. Phys. Soc.* **5**, 167 (1960); B. Lax and J. G. Mavroides, *Advances in Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1960), Vol. 9. Recently P. A. Wolff has also obtained the above result (private communication).

<sup>7</sup>B. Abeles and S. Meiboom, *Phys. Rev.* **101**, 544 (1956).

<sup>8</sup>W. C. Dash and R. Newman, *Phys. Rev.* **99**, 1151 (1955).

<sup>9</sup>G. Dresselhaus (private communication).

<sup>10</sup>P. W. Anderson, *Phys. Rev.* **100**, 749 (1955).

<sup>11</sup>B. Lax, *Phys. Rev. Letters* **4**, 511 (1960).

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## INTERBAND MAGNETOREFLECTION IN BISMUTH. II. LOW FIELDS

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Magnetoreflexion measurements in bismuth have been carried out at liquid air temperatures and below with static magnetic fields up to 38 kilogauss. The measurements were made using a magnetospectrometer similar to that of Zwerdling et al.,<sup>1</sup> except that infrared reflection techniques were used. Best results were obtained by sweeping the magnetic field at a fixed wavelength. This was done at wavelengths between 6 and 14  $\mu$ , using an NaCl prism.

Single-crystal specimens were grown from Bi of "99.999" % purity. Surfaces were obtained by

cleaving at nitrogen temperature along a trigonal plane. A diamond saw was used to cut two samples 2 mm  $\times$  3 mm  $\times$  25 mm from the crystal. The cuts were made so that the magnetic field parallel to the exposed trigonal surface was in one case along the bisectrix axis  $[10\bar{1}0]$ , and in the other case along the binary axis  $[11\bar{2}0]$ . The surface was then polished with Buehler No. 3 grit to obtain a good reflecting surface. The surface strains were removed by electropolishing.<sup>2</sup> Back-reflection Laue patterns gave the crystal orientation and revealed minor strains. The samples

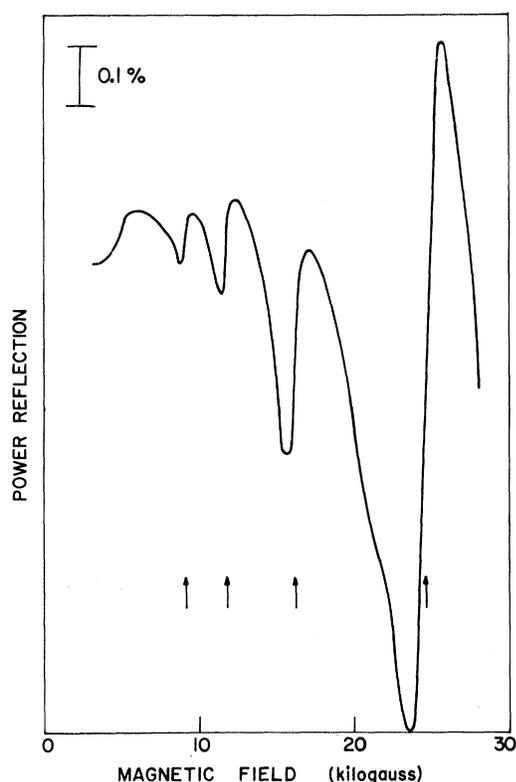


FIG. 1. Variation of power reflection with magnetic field on bismuth for photon energy  $\Delta\epsilon = 0.1041$  eV. The arrows indicate the field for which interband transitions of this photon energy occur. The magnetic field is along  $[11\bar{2}0]$  and the inner Dewar is at  $4.2^\circ\text{K}$ .

were freely mounted with Teflon tape in a copper sample holder attached by a copper rod to the bottom of the inner Dewar which contained either liquid helium or liquid air.<sup>3</sup>

A typical trace of the variation of power reflection with magnetic field at constant photon energy is shown in Fig. 1. The line shape is characteristic of dispersion curves. The center of the straight portions of trace, indicated by arrows, is taken as the value of the magnetic field for which the infrared photon induces an interband transition between a magnetic level of the valence band to one of the conduction band. The resolution was sufficient to identify lines with peak to peak intensities from 3% to 0.05%. The intensity of a given line was found to increase with increasing magnetic field and to decrease with increasing quantum number.

Each interband transition appearing in the magnetic field trace (as in Fig. 1) was identified, and the results plotted in terms of photon energy  $\Delta\epsilon$  vs magnetic field  $H$ , as in Fig. 2  $[11\bar{2}0]$  and Fig. 3  $[10\bar{1}0]$ . These measurements were obtained near liquid helium temperature. Quantitatively, the results at liquid air temperature were essentially the same except that the lines sharpened and increased in intensity as the temperature was lowered. For  $H$  along  $[11\bar{2}0]$ , only the light-mass ( $\sim 0.01m_0$ ) transitions are seen. For  $H$  along  $[10\bar{1}0]$ , both light ( $\sim 0.01m_0$ ) and heavy ( $\sim 0.02m_0$ )

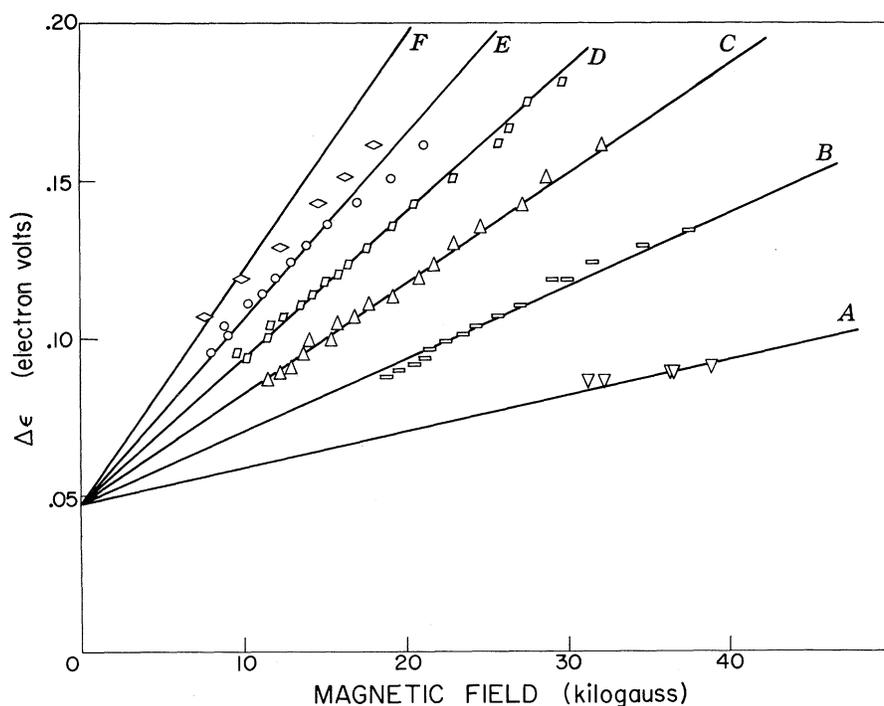
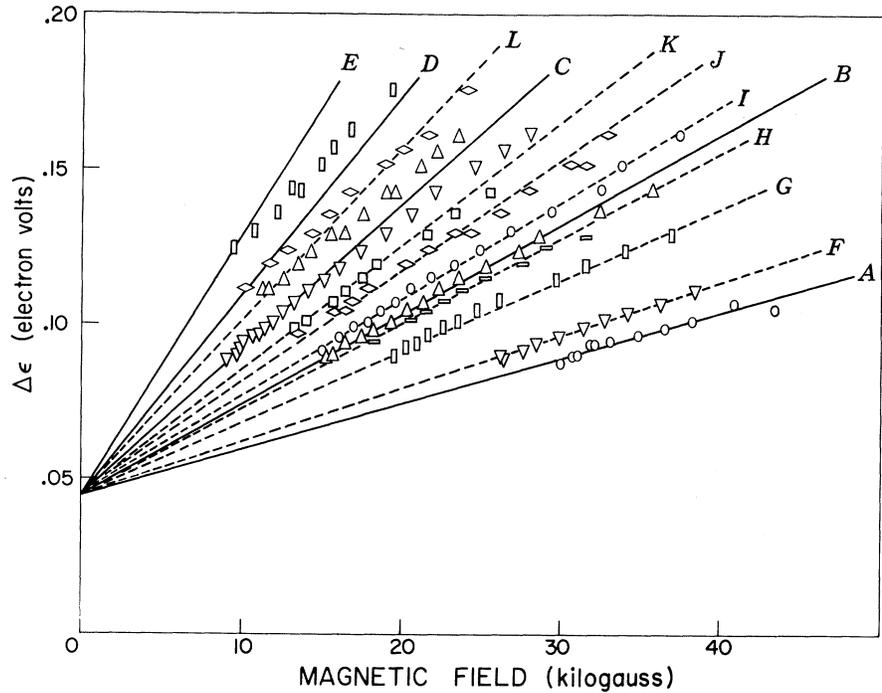


FIG. 2. Photon energy for interband transition vs magnetic field on bismuth. The magnetic field is along  $[11\bar{2}0]$  and the inner Dewar is at  $4.2^\circ\text{K}$ . The various transitions are identified by A,  $(0\uparrow 0\uparrow)$ ; B,  $(0\uparrow 0\uparrow)$  and  $(1\uparrow 1\uparrow)$ ; C,  $(1\uparrow 1\uparrow)$  and  $(1\uparrow 1\uparrow)$ ; D,  $(1\uparrow 1\uparrow)$  and  $(2\uparrow 2\uparrow)$ ; E,  $(2\uparrow 2\uparrow)$  and  $(2\uparrow 2\uparrow)$ ; and F,  $(2\uparrow 2\uparrow)$  and  $(3\uparrow 3\uparrow)$ . (See Fig. 2 of preceding Letter.)

FIG. 3. Photon energy for interband transition vs magnetic field on bismuth. The magnetic field is along  $[10\bar{1}0]$  and the inner Dewar is at 4.2°K. The light-carrier transitions follow the solid lines and the heavy-carrier transitions follow the dashed lines. The identification for the light mass is A,  $(0\uparrow 0\downarrow)$ ; B,  $(0\uparrow 0\downarrow)$  and  $(1\uparrow 1\downarrow)$ ; C,  $(1\uparrow 1\downarrow)$  and  $(1\uparrow 1\downarrow)$ ; D,  $(1\uparrow 1\downarrow)$  and  $(2\uparrow 2\downarrow)$ ; E,  $(2\uparrow 2\downarrow)$  and  $(2\uparrow 2\downarrow)$ . The identification for the heavy mass is F,  $(0\uparrow 0\downarrow)$  and  $(1\uparrow 1\downarrow)$ ; G,  $(1\uparrow 1\downarrow)$  and  $(1\uparrow 1\downarrow)$ ; H,  $(1\uparrow 1\downarrow)$  and  $(2\uparrow 2\downarrow)$ ; I,  $(2\uparrow 2\downarrow)$  and  $(2\uparrow 2\downarrow)$ ; J,  $(2\uparrow 2\downarrow)$  and  $(3\uparrow 3\downarrow)$ ; K,  $(3\uparrow 3\downarrow)$  and  $(3\uparrow 3\downarrow)$ ; L,  $(3\uparrow 3\downarrow)$  and  $(4\uparrow 4\downarrow)$ . (See Fig. 2 of preceding Letter.)



masses are observed. Experimentally, the light masses are distinguished from the heavy masses by their relatively greater intensity and by the disappearance of some of the light-mass transitions when polarized radiation is used.

For both orientations, the points identified with a given transition follow straight lines, particularly for transitions with low quantum number. As in the pulsed-field experiments,<sup>4</sup> the results of Figs. 2 and 3 show a convergence of the straight lines for different transitions to an energy gap  $\epsilon_g = 0.047 \pm 0.003$  ev.<sup>5</sup> The value for  $\epsilon_g$  was determined in each case by drawing the best straight line through the experimental points associated with low quantum number. The lines drawn through the experimental points for high quantum number were joined to this value of the gap. The deviation from linearity for the higher transitions may be an indication of nonquadratic energy surfaces at these high energies.

In order to interpret the interband transitions, the model illustrated by Fig. 2, of the preceding paper was adopted. The energy of an interband transition is written as

$$\Delta\epsilon = \epsilon_g + (n_c + \frac{1}{2})\hbar\omega_c^c \pm \frac{1}{2}\beta g_{\text{eff}}^c H + (n_v + \frac{1}{2})\hbar\omega_c^v \pm \frac{1}{2}\beta g_{\text{eff}}^v H, \quad (1)$$

in which  $c$  and  $v$  refer to the conduction and valence bands, respectively,  $g_{\text{eff}}$  is the spectroscopic splitting factor, and  $\beta$  is the Bohr magneton. Using this expression, one can in principle determine from the four lowest transitions the masses and  $g$  values for both the valence and conduction bands. From Eq. (1), we find that the experimental results are consistent with approximately equal masses for the two bands and  $g$  factors approximately as given by Cohen and Blount,<sup>6</sup>

$$g_{\text{eff}} \approx 2m_0/m^*. \quad (2)$$

For  $H$  in the  $[11\bar{2}0]$  direction, the value  $m_c^*/m_0 = 0.010$  is obtained for the mass of the conduction band. The effective mass of the valence band  $m_v^*/m_0$  differs from  $m_c^*/m_0$  by less than 10%. For  $H$  in the  $[10\bar{1}0]$  direction, we find the effective mass of the light electron to be  $m_c^*/m_0 = 0.0080 \pm 0.0002$  with  $|(m_c^* - m_v^*)/m_0| < 0.0003$ . For the heavy electrons in this orientation there are two possibilities. Either the valence and conduction masses are approximately equal, with  $m_c^*/m_0 = 0.019$  and  $|(m_c^* - m_v^*)/m_0| < 0.002$ ; or,  $m_c^*/m_0$  and  $m_v^*/m_0$  are quite different,  $m_c^*/m_0 = 0.019$  and  $m_v^*/m_0 = 0.011$ . This ambiguity can be resolved by using higher fields to look for the lowest observable transition  $(0\uparrow 0\downarrow)$ . The conduction band masses are in agreement with those

deduced from Shoenberg's<sup>7</sup> de Haas-van Alphen data and Galt et al.<sup>8</sup> (cyclotron resonance).

These results definitely indicate that the theoretical expression, Eq. (4) of the preceding paper, does not give a good fit. The curvature for the theoretical curves of energy versus magnetic field is much sharper than that indicated in Figs. 2 and 3. Extension of these measurements to higher magnetic fields will permit the study of the departure from parabolicity and the added resolution will allow the independent determination of the masses for the valence and conduction bands together with the  $g$  values associated with them.

We are grateful of Dr. G. B. Wright for his generous loan of the apparatus for carrying out these experiments, Mr. E. Warekois for x-ray studies of the samples, Mr. D. F. Kolesar for his capable assistance with the experimental work, and Dr. G. Dresselhaus and Dr. H. J. Zeiger for many fruitful discussions.

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<sup>1</sup>S. Zwerdling, B. Lax, L. M. Roth, and K. J. Button, Phys. Rev. **114**, 80 (1959).

<sup>2</sup>G. E. Smith, Phys. Rev. **115**, 1561 (1959).

<sup>3</sup>Measurements on this apparatus indicate that the temperature of the sample holder differed by no more than 2°K from the bath temperature using the liquid air refrigerant. The temperature of the sample was not measured when liquid helium was used, but it is believed that the sample was somewhat above 4°K.

<sup>4</sup>B. Lax, J. G. Mavroides, H. J. Zeiger, and R. J. Keyes, preceding Letter [Phys. Rev. Letters **5**, 241 (1960)].

<sup>5</sup>A crude attempt to estimate this gap was made by W. S. Boyle and K. F. Rodgers, Phys. Rev. Letters **2**, 338 (1959). They stated that the "edge at 20 microns would set the lower lying states at about 0.05 ev below the Fermi surface." If  $\mathcal{E}_F$  ( $\approx 0.018$  ev) were subtracted this would give  $\mathcal{E}_g \approx 0.03$  ev, which is too small.

<sup>6</sup>M. H. Cohen and E. I. Blount, Phil. Mag. **5**, 115 (1960).

<sup>7</sup>D. Shoenberg, Physica **19**, 791 (1953); B. Lax, K. J. Button, H. J. Zeiger, and L. M. Roth, Phys. Rev. **102**, 715 (1956).

<sup>8</sup>J. K. Galt, W. A. Yager, F. R. Merritt, B. B. Cetlin, and A. D. Brailsford, Phys. Rev. **114**, 1396 (1959).

## DIFFERENCE IN LATTICE SPECIFIC HEATS IN THE NORMAL AND SUPERCONDUCTING PHASES\*

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A series of measurements of the heat capacity of annealed niobium in the normal and superconducting phases, carried out in this laboratory, was reported at the 1958 International Conference on the Electronic Properties of Metals at Low Temperatures.<sup>1</sup> One of the principal objectives of the investigation was the determination of the temperature dependence of the superconducting electronic specific heat  $C_{es}$ , and its comparison with the detailed predictions of the Bardeen, Cooper, Schrieffer<sup>2</sup> (BCS) theory. Although an exponential dependence of  $C_{es}$  with temperature was observed as required by the theory, it was not possible to make measurements below  $0.2T_c$  and hence the predicted change to the lower temperature exponential<sup>3</sup> could not be investigated. A new cryostat was therefore constructed for this and other investigations and the research on niobium was resumed.

According to current ideas, the determination

of  $C_{es}$  requires a measurement of  $C_n$ , the specific heat of the metal in the normal phase, and of  $C_s$ , the specific heat in the superconducting phase. Values of  $C_n$  were found to follow the relation:

$$C_n = \gamma T + A(T/\Theta)^3,$$

with  $\gamma = 7.62$  millijoules/mole deg<sup>2</sup> and  $\Theta = 231^\circ\text{K}$ . Values of the normal lattice term,  $A(T/\Theta)^3$ , were subtracted from  $C_s$  at the same temperature to yield values of  $C_{es}$  which, down to  $1.7^\circ\text{K}$ , were found to satisfy the following relation:

$$C_{es} = \gamma T_c [10 \exp(-1.63T_c/T)],$$

with  $T_c = 9.09^\circ\text{K}$ . It should be pointed out that this procedure assumes that the superconducting specific heat consists of independent lattice and electron contributions and that the lattice specific heat is identical in the normal and superconducting phases.