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Infrared Absorptance of Single-Crystal Antimony and Bismuth*†

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The absorptance of single-crystal antimony has been measured in the region of 1 to 20 μ at liquid-helium temperatures. There are two independent absorptance maxima depending on crystal orientation and radiation polarization. One maximum is located at 10.6 ± 0.1 μ for the case of the sample binary axis normal to the surface and the radiation electric vector parallel to the bisectrix axis. The other maximum is found at 5.7 ± 0.1 μ for the same crystal orientation, and the electric vector parallel to the trigonal axis. The infrared data are interpreted on the basis of the effective-mass approximation of free carriers. The carrier-independent part of the dielectric constant is found to be $\epsilon_0=80\pm5$. The infrared data are consistent with a three-band model as proposed by Datars. A very light mass, $m^*\approx0.005m_0$, along the trigonal axis is of particular interest. The bismuth data agree with the previous results of Boyle and Brailsford.

I. INTRODUCTION

ANTIMONY, bismuth, and arsenic are semimetals which occupy the Group V column of the periodic table. It is generally believed that the electronic properties of these elements arise from a slight overlap between the otherwise full valence band and the conduction band. This overlap results in a small, but equal number of mobile holes and electrons.

The electronic structure of antimony was first studied in detail by Shoenberg[1] by means of the de Haas–van Alphen oscillations in the magnetic susceptibility. Shoenberg was able to fit these data to a model of three tilted ellipsoids very similar to the electron ellipsoids in bismuth.[2] The Fermi energy of these carriers was determined to be 18×10^{-14} erg. The total number of carriers in this particular set of ellipsoids was found to be 3.6×10^{19} per cm^3, assuming a three-ellipsoid model. This carrier concentration agrees well with that determined by Freedman and Juretschke[3] from galvanomagnetic measurements on antimony. They arrived at a value of 3.7×10^{19} per cm^3 for the electron concentration using a two-band model. The number of holes was assumed equal to the number of electrons. Assuming an isotropic relaxation time, they concluded Shoenberg's carriers were holes.

Recently, Dexter and Datars[4] expressed the opinion that Shoenberg's carriers are electrons on the basis of cyclotron resonance measurements using circularly polarized microwaves. Subsequently, Datars[5] reported observing three sets of carriers in antimony, which he identified tentatively as one electron and two hole bands.

Optical studies of conducting materials have long been interpreted on the basis of the Drude theory of free carriers, modified with the advent of quantum mechanics by the effective mass approximation. Spitzer and Fan[6] have used infrared studies of semiconductors to determine the carrier-independent part of the dielectric constant as well as the effective mass of the carriers. The determination of the effective mass by the infrared studies was in good agreement with the values found by other techniques for determining the effective mass. More recently infrared studies by Boyle and Brailsford[7] have been applied to the semimetal bismuth to provide information concerning the electronic band structure as well as the carrier-independent part of the dielectric constant. Consequently, it was expected that infrared studies of antimony would contribute toward unraveling its band structure.

II. THEORY

Crystals possessing rhombohedral structure, such as antimony, may be classified optically as uniaxial crystals. The optical axis of antimony is the threefold symmetry axis. The other independent axis is perpendicular to the trigonal axis and lies in the binary-bisectrix plane.

The "dielectric anomaly" model[7] of an isotropic metallic crystal presumes it to possess N Drude-type carriers per unit volume, each having an effective mass $m^*=m_0/\alpha'$ and a relaxation time τ. In addition, the metal is presumed to have a dielectric constant ϵ_0 which is assumed independent of frequency over the wavelength range of interest. Such a metal may be formally characterized by a complex dielectric constant which is a function of ϵ_0, m^*, N, and τ. The real and imaginary parts of the dielectric constant are, of course, related to the real and imaginary parts (n and k) of the complex index of refraction. The optical constants are related to the real and imaginary parts of the dielectric constant

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[1] D. Shoenberg, Phil. Trans. Roy. Soc. (London) **A245**, 1 (1952).

[2] D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

[3] S. J. Freedman and H. J. Juretschke, Phys. Rev. **124**, 1379 (1961).

[4] W. R. Datars and R. N. Dexter, Phys. Rev. **124**, 75 (1961).

[5] W. R. Datars, Can. J. Phys. **39**, 1922 (1961).

[6] W. G. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957).

[7] W. S. Boyle and A. D. Brailsford, Phys. Rev. **120**, 1943 (1960).

in the following manner:

$$\mathrm{Re}\,\epsilon=n^2-k^2=\epsilon_0-\frac{N\alpha' e^2\lambda^2}{\pi m_0 c^2}\left[1+\left(\frac{\lambda}{\lambda_\tau}\right)^2\right]^{-1}, \tag{1}$$

$$\mathrm{Im}\,\epsilon=2nk=\frac{N\alpha' e^2\lambda^3}{\pi m_0 c^2\lambda_\tau}\left[1+\left(\frac{\lambda}{\lambda_\tau}\right)^2\right]^{-1}, \tag{2}$$

where λ is the wavelength of the radiation and $\lambda_\tau=2\pi c\tau$. The other constants have their usual significance. Since there are two optically independent directions in single-crystal antimony, the quantities ϵ_0, α', τ may be anisotropic. Furthermore, due to the fact that antimony has at least two sets of carriers, and quite likely more, the product $N\alpha'$ can be very complex. In particular, for the case of the crystallographic binary axis normal to the surface, and the electric vector parallel to the bisectrix axis, the product $N\alpha'$ may be expressed generally as

$$(N\alpha')_{1,2}=\tfrac{1}{2}n_\alpha(\alpha_1+\alpha_2)+\tfrac{1}{2}n_\beta(\beta_1+\beta_2)+\tfrac{1}{2}n_\gamma(\gamma_1+\gamma_2)+\cdots, \tag{3}$$

where n_α is the number of carriers in the band which has as its reciprocal mass components α_1 and α_2 along the binary and bisectrix crystallographic axis, respectively. Similar definitions hold for the β, γ, $\cdots$ bands.

Correspondingly, for the binary axis normal and the electric vector parallel to the trigonal axis, $N\alpha'$ may be written as

$$(N\alpha')_{1,3}=n_\alpha\alpha_3+n_\beta\beta_3+n_\gamma\gamma_3+\cdots. \tag{4}$$

This one crystal orientation with the two polarizations provides all of the relevant optical information. A convenient check may be obtained by using the trigonal axis normal to the surface, in which case the optical properties are independent of polarization and $N\alpha'$ should be identical with that given by Eq. (3).

The absorptance A of an infinitely thick crystal is defined as $A=1-R$, where R is the reflectance. The absorptance may be expressed in terms of the optical constants by the well-known expression

$$A=4n/[(n+1)^2+k^2]. \tag{5}$$

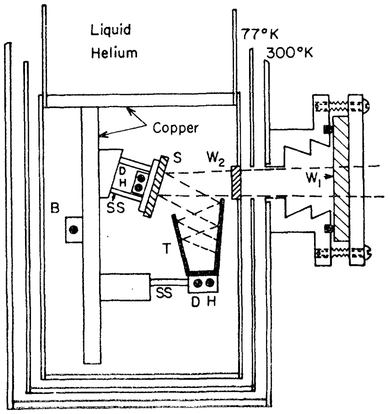

FIG. 1. Schematic diagram of the sample holder and detection apparatus for the measurement of absolute absorptance.

The behavior of A as a function of wavelength may be obtained theoretically from Eqs. (1) and (2). In the limit $\lambda\to 0$, the carrier contribution to the real part of the dielectric constant vanishes and the absorptance is governed almost entirely by the dielectric constant ϵ_0. In this region the reflectance should be that of a dielectric crystal possessing an index of refraction $n=\epsilon_0^{1/2}$. Consequently, the dielectric constant may be determined in principle by an extrapolation of A as $\lambda\to 0$. Furthermore, in the limit $\lambda/\lambda_\tau\ll 1$, the absorptance exhibits a sharp maximum at a wavelength such that $n^2-k^2=1$. At longer wavelengths the absorptance decreases rapidly to the point where the crystal behaves almost as a perfect reflector. Thus, from a determination of ϵ_0, and the wavelength of maximum absorptance, the value of $N\alpha'$ may be determined. In addition the shape of the absorptance curve should indicate the degree to which a dielectric anomaly model of antimony is applicable.

III. EXPERIMENTAL DETAILS

In the near infrared, the radiation was monochromated by means of a single beam, double-pass, prism spectrometer of our own design. A calcium fluoride prism was used in the region of 1 to 8μ, and for the region 8 to 20μ a potassium bromide prism was substituted. The resolution was 0.5 to 2% depending on the wavelength range. The polarizer utilized a single reflection from selenium at its Brewster angle and achieved a polarization of about 99%. The polarizer was similar in design to that described by Takahashi.[8]

For the studies on bismuth in the region 30 to 300μ, an echellete grating monochromator was designed and built in this laboratory. The gratings were blazed at 20 deg. The resolution of the grating instrument was approximately 2 to 5%, which was adequate to obtain a good water-vapor spectrum in the far infrared. A globar was used as a source in the region 30 to 120μ, and a high-pressure mercury arc was used for longer wavelengths.

The method of measuring the absolute absorptance is somewhat similar to that employed by Biondi.[9] The most significant difference is that the technique is extended to much greater wavelengths in the present experiment than used by Biondi, who worked in the very near infrared, where the power available is several orders of magnitude greater than in the far infrared. In addition, Biondi's technique employed a light pipe, whereas the present arrangement achieved very good geometry by bringing the radiation directly through the side of the Dewar.

The apparatus used in this experiment is illustrated schematically in Fig. 1. The sample S and radiation trap T are connected thermally through the stainless steel supports SS to the liquid-helium bath. The system is aligned by visible light so that the radiation passing

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[8] S. Takahashi, J. Opt. Soc. Am. **51**, 441 (1961).

[9] M. A. Biondi, Phys. Rev. **102**, 964 (1956).

through the window W_2 falls on the sample and so that all radiation reflected from the sample is collected by the trap T which is coated with an acetylene black absorber. Window W_1 is a 6-mm-thick optical window of potassium bromide which is transparent to about 25μ. For longer wavelengths, 0.8 mm of polyethylene is used in place of the potassium bromide. Window W_2, in general, is sodium chloride for the near infrared and crystal quartz for the far infrared. In order to achieve maximum sensitivity in the far infrared it is necessary to prevent room temperature radiation from entering the experimental chamber; otherwise, the temperature of the sample and trap would be raised excessively, since the thermal resistance of the supports SS may be as large as 10^5 deg per W. Quartz is an extremely effective filter of room-temperature radiation and is also very transparent in the far infrared. The thermometer detectors, D, are $\frac{1}{4}$-W carbon resistors. The resistor insulating material is ground off to assure good thermal contact with the sample and trap.

The sample and trap thermometers are calibrated absolutely by passing a known amount of power through the carbon resistor heaters H. Consequently, the radiation absorbed by the sample and trap can be measured. The absorptance is then given by the power absorbed by the sample, divided by the sum of the power absorbed by the sample and trap combined.

The detection system could be operated in a dc manner using a potentiometer and a sensitive galvanometer. Slow drifts in the bath temperature could be canceled out by using two arms of a bridge circuit connected to the helium bath. One arm is the thermometer D and the other arm B is a dummy resistor connected thermally to the bath. Short-period noise and temperature changes (e.g., due to vacuum pumps pumping on the helium bath) were not seen because the galvanometer time constant was sufficiently long so as not to respond to this type of noise. By reducing the thermal time constants of the detectors, the system could be operated in an ac fashion by chopping the beam at 5 cps. The amplifier system of the latter technique utilized standard low-noise and narrow-band amplifiers. The dc technique proved more amenable for making precise (about 0.5 to 2%, depending on the radiation intensity) absorptance measurements, and the ac for making rapid scans or looking for fine structure. A minimum detectable power of about 3×10^{-11} W was achieved.

The samples were thin slabs (1 cm×1 cm×1 mm) of single-crystal antimony and bismuth cut from ingots which were zone refined here, or from ingots of high-purity antimony supplied by Ohio Semiconductor Company. Four different antimony samples gave identical results, within experimental error. The samples were aligned by standard x-ray diffraction techniques. A brightly polished surface, which was flat to within 1 to 2 deg was obtained by means of an etch solution which consisted of five parts fuming red nitric acid, two parts hydrofluoric acid, and six parts glacial acetic acid. The etch solution is presumed to have removed any cold working which existed on the surface, since the x-ray diffraction pattern showed no indication of cold working after etching. The bismuth samples were electropolished.

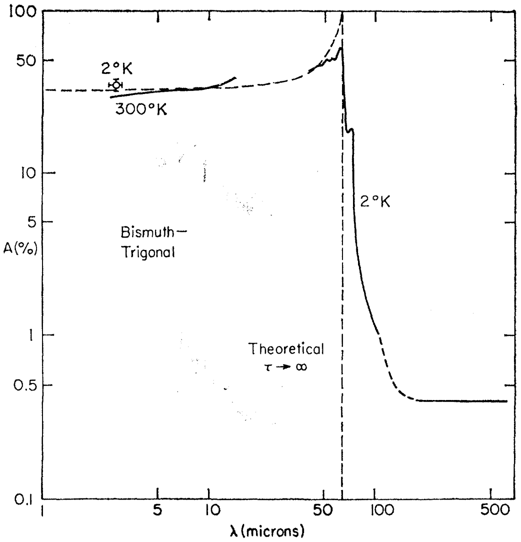

FIG. 2. The infrared absorptance of a bismuth sample with the trigonal axis normal to the surface. The dashed section of the solid curve at $\sim 120\ \mu$ indicates the absence of experimental data for this portion of the curve. The dashed curve is a theoretical absorptance curve based on the dielectric anomaly model assuming Boyle's parameters (see reference 7) and an infinite relaxation time.

IV. RESULTS

Boyle and Brailsford's[7] infrared measurements in bismuth gave results concerning the carrier masses and concentrations, in addition to the dielectric constant in bismuth. Bismuth was used as a sample in the course of our experiments to check the absolute absorptance method (a different technique than used by Boyle) for obtaining information on the basis of the dielectric anomaly model. The absolute absorptance of a single-crystal bismuth sample is shown in Fig. 2. The trigonal axis is normal to the surface and the radiation is unpolarized. In the short-wavelength region the absorptance is found to be $A=(34\pm1)\%$, at 2°K, which agrees well with the absorptance of 33% expected for a crystal with a dielectric constant equal to 100 as previously found in bismuth.[7] A similar value for the absorptance is found at room temperature. The position of maximum absorptance is found to be $61.3\ \mu$ in good agreement with Boyle's[7] result of $62.7\ \mu$. The secondary structure at $72\ \mu$ in bismuth is thought perhaps to be due to an indirect transition mechanism. The work on bismuth indicates that the absolute absorptance measurements offer a satisfactory technique for the interpretation of the dielectric anomaly model, and in addition, confirms the previous infrared measurements.[7]

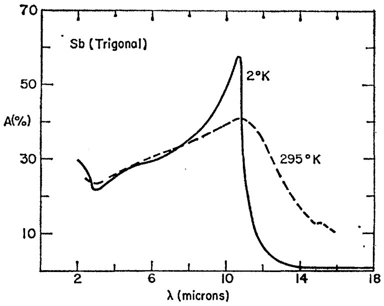

FIG. 3. The absorptance of an antimony sample with the trigonal axis normal to the surface. The dashed curve is measured at room temperature and the solid curve at helium temperatures. The radiation is unpolarized.

Figure 3 shows the absorptance of an antimony sample whose trigonal axis is normal to the surface. The radiation is unpolarized. In Fig. 3 the dashed curve was taken at room temperature using a reflection method incorporated into a Perkin–Elmer Model 21 recording infrared spectrometer. Lowering the temperature to 2°K results in a considerable sharpening of the peak. The solid curve in Fig. 3 was measured at 2°K. The position of the maximum absorptance was located at $10.7\pm0.1\ \mu$ for the room-temperature measurement, and at $10.6\pm0.1\ \mu$ for the low-temperature measurement.

Figure 4 shows the absorptance for a sample at 2°K with the binary crystallographic axis normal to the surface. As indicated in Fig. 4 the radiation electric vectors are parallel to the bisectrix and trigonal axes. For the case of the polarization along the bisectrix axis the observed maximum absorptance is at $10.5\pm0.1\ \mu$ which is in good agreement with the value of $10.6\ \mu$ expected from Fig. 3. If one takes into account that the polarization is only about 99% complete the $10.5\ \mu$ maximum should be corrected to $10.6\ \mu$ and the agreement between the two crystal orientations becomes exact.

The maximum absorptance for the electric vector parallel to the trigonal axis in Fig. 4 occurs at $5.7\pm0.1\ \mu$. It is important to note that the broadening of the curves in Figs. 3 and 4 cannot be accounted for in terms of the relaxation time associated with lattice and impurity scattering.[10] Indeed, if that were the only process contributing to the absorption, the ratio λ/λ_τ should be of the order of 10^{-4} at low temperatures, making the maxima very sharp. The width of the curves indicate that the ratio is about 10^{-1}. This means that some care must be exercised in the determination of ϵ_0 from the extrapolation of the absorptance to the short-wavelength region since the extinction coefficient k in Eq. (5) may not vanish as expected from Eqs. 1 and 2.

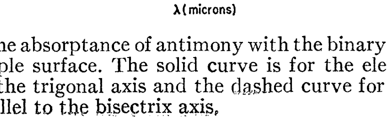

FIG. 4. The absorptance of antimony with the binary axis normal to the sample surface. The solid curve is for the electric vector parallel to the trigonal axis and the dashed curve for the electric vector parallel to the bisectrix axis.

Quite clearly from the geometry of the sample in Fig. 1, it is not possible to obtain completely normal incidence of the radiation upon the sample. Consequently, consideration must be given to the question as to whether or not the lack of normal incidence will affect the results of the measurements which are assumed to be normal incidence for comparison with theory.

First, it is noted that the large dielectric constant will result in a large index of refraction; therefore, the angle of refraction should be much smaller than the angle of incidence. Consequently, the radiation propagation vector in the metal should be almost parallel to the crystallographic axis.

Secondly, it is possible to experimentally check whether the small, but finite, angle of incidence gives significantly different results than would normal incidence. This check may be achieved by measuring the absorptance of a trigonal sample, first with unpolarized radiation and second with radiation polarized perpendicular to the plane of incidence. If the two measurements give the same result then the assumption of normal incidence is a valid one. A test of this type on an antimony sample with the trigonal axis normal showed identical results for both measurements.

V. DISCUSSION

The absorptance curves in Figs. 3 and 4 fit a theoretical dielectric anomaly model absorptance curve derived from Eqs. (1) and (2) well in the region beyond $3.5\ \mu$, provided one introduces *ad hoc* a relaxation time much shorter than theoretically expected. The minimum absorptance at $2.9\ \mu$, likewise is not contained in the theoretical expressions. This minimum is possibly due to a rise in the extinction coefficient at this wavelength due to an interband absorption edge.

As mentioned above, the dielectric constant ϵ_0 is difficult to determine precisely since the imaginary part of the index of refraction k is nonvanishing in the short-wavelength region. If k is known, however, ϵ_0 may be determined. For example, the broadening of the maximum at $5.7\ \mu$ requires that $k\approx3.5$. Measurements on antimony films by Shkliarevskii, *et al.*[11] and Beattie and

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[10] In general, shorter relaxation times are found at optical frequencies than at microwave frequencies and dc [e.g., D. Brust, and J. C. Phillips, Phys. Rev. Letters 9, 94 (1962)]. The relaxation time observed in the present infrared work falls between the observed optical and dc relaxation times.

[11] I. N. Shkliarevskii, A. A. Avdeenko, and V. G. Padalka, Opt. Spectr. (U.S.S.R.) 6, 336 (1959).

Conn[12] give values of k between 3.3 and 4.0 in this wavelength region, which is in agreement with the above estimate. From this and other estimates the value of the "static" dielectric constant is found to be $\epsilon_0 = 80 \pm 5$. Furthermore, ϵ_0 appears to be very nearly isotropic.

Using a dielectric constant of eighty we determine for the expressions in Eqs. (3) and (4) the following values:

$$(N\alpha')_{1,2} = 7.30 \times 10^{20} \text{ cm}^{-3}, \tag{6}$$

$$(N\alpha')_{1,3} = 27.2 \times 10^{20} \text{ cm}^{-3}. \tag{7}$$

Beyond these results it is difficult to proceed further without making certain assumptions. For example, in the infrared studies of bismuth,[7] it was assumed that the masses of the holes were so large that they did not contribute in Eqs. (3) and (4). Although Shoenberg has suggested that the holes in antimony might be heavy to account for the large electronic specific heat, the observation[3] that antimony has a positive Hall coefficient makes it unlikely that the holes can be neglected. Furthermore, the holes cannot be light and the electrons heavy since Dexter and Datars[4] work indicates that Shoenberg's light carriers are electrons. This evidence indicates that in all probability there are at least three bands in antimony, consisting of a set of light holes and light electrons, and an additional heavy band of some kind. Since the carrier concentration in Shoenberg's electron band is very nearly that determined by the galvanomagnetic measurements as the total electron concentration, it is reasonable to assume that the second and third bands are both holes. This point of view is supported by recent work by Datars[5] which indicates the existence of three sets of carriers, assumed by him to be light holes, light electrons and heavy holes. In addition he states the light holes are a majority carrier as compared to the heavy holes.

Assuming a three-band model, Eq. (3) may be rewritten in the form

$$(N\alpha')_{1,2} = \tfrac{1}{2}N_e(\alpha_1+\alpha_2) + \tfrac{1}{2}N_h[r_\beta(\beta_1+\beta_2)+r_\gamma(\gamma_1+\gamma_2)], \tag{8}$$

where charge neutrality requires $N = N_e = N_h$, and $r_\beta = n_\beta/N_h$ and $r_\gamma = (1-r_\beta) = n_\gamma/N_h$. We assume Shoenberg's[1] results $N = 3.6 \times 10^{19}$ cm^{-3} and $(\alpha_1+\alpha_2)/2 = 12.7$. Since Datars[5] reports the light holes as being approximately isotropic it is assumed for the purposes of calculations $\beta_1 = \beta_2 = \beta_3 = 9.1$. Using these results it is readily found from Eqs. (6) and (8) that

$$9.1 r_\beta + (1-r_\beta)(\gamma_1+\gamma_2)/2 = 7.5. \tag{9}$$

If, indeed, the light holes are a majority[5], i.e., $r_\beta > 0.5$, we find for, say, $0.6 < r_\beta < 0.8$ the result

$$5.0 > (\gamma_1+\gamma_2/2 > 1.0.$$

The mass values of Datars' third set of carriers ("heavy holes") also lie within this range; that is, $(\gamma_1\gamma_2)^{1/2} = 3.1$. [If $\gamma_1 \approx \gamma_2$, then the approximation may be made that

$$(\gamma_1\gamma_2)^{1/2} \approx (\gamma_1+\gamma_2)/2. \tag{10}$$

For the time being this assumption is made.]

Stated in other words, the three-band model assumed by Datars is in agreement, within experimental error, with the infrared data in the binary-bisectrix plane.

Equation (4) may be rewritten in a manner after Eq. (8) as

$$(N\alpha')_{1,3} = N_e\alpha_3 + N_h[r_\beta\beta_3 + r_\gamma\gamma_3]. \tag{11}$$

Again using Shoenberg's result of $\alpha_3 = 10.0$ and the assumption that $\beta_3 = 9.1$, from Eqs. (7) and (11) it is found, for $0.6 < r_\beta < 0.8$, that

$$140 < \gamma_3 < 280. \tag{12}$$

Finally, going one step further using the preceding ranges of r_β and the assumption $(\gamma_1+\gamma_2)/2 = 3$ the following ratio is obtained:

$$47 < 2\gamma_3/(\gamma_1+\gamma_2) < 94. \tag{13}$$

While the exact ratio is not determined very precisely, it is safe to draw the qualitative conclusion, nevertheless, that the ratio in Eq. (13) is quite large.

Recently Ketterson[13] and Eckstein[14] have observed a ratio like that in (13) to be of the order of 50 to 300 for a new set of carriers observed in antimony with magnetoacoustic attenuation experiments. Consequently, we tentatively identify Ketterson and Eckstein's carriers with Datars' third band, although the designation "heavy holes" may not be a good one in view of Eq. (12).

Ketterson[13] gives the result $\gamma_1 = 0.0146\gamma_2$, which makes it apparent that Eq. (10) above was not a good assumption. It would be possible in principle to take Ketterson's result and use Eq. (9) to determine r_β. However, the uncertainty in $N\alpha'$, β_1, β_2, ϵ_0, etc., coupled with the fact that a determination of r_β involves taking small differences, would permit r_β to assume any value between about 0.5 and 1.0. Nevertheless, r_β must be less than unity in order to account for the value of $(N\alpha')_{1,3}$. Consequently, we take $r_\beta = 0.70 \pm 0.25$.

Ketterson lists the parameters[15] γ_{11}, γ_{22}, γ_{23}, γ_{33} in terms of the Fermi energy and Datars gives the result $(\gamma_1\gamma_2)^{1/2} = 3.1$. If these are the same set of carriers the two results may be combined to determine the Fermi energy of Ketterson's and Eckstein's carriers to be $E_F = 56.6 \times 10^{-14}$ erg. Knowing the Fermi energy, one determines from Ketterson's results that

$$\gamma_{11} = 0.38, \quad \gamma_{22} = 26,$$
$$\gamma_{23} = 370, \quad \gamma_{33} = 5400.$$

(According to Ketterson[16] his numbers result from a force fit of his data to an ellipsoidal model and should be taken with considerable caution.)

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[12] J. R. Beattie and G. K. T. Conn, Phil. Mag. **46**, 222 (1955).

[13] J. Ketterson, Phys. Rev. **129**, 18 (1963).

[14] Y. Eckstein, Phys. Rev. **129**, 12 (1963).

[15] Here $\gamma_{11} = \gamma_1$, $\gamma_{22} = \gamma_2$, $\gamma_{23} = \gamma_4$, $\gamma_{33} = \gamma_3$.

[16] J. Ketterson (private communication).

TABLE I. Tentative band structure of antimony based on a three-band model.

	Electrons	Holes–I	Holes–II
Carriers per cm^3	3.6×10^{19a}	2.5×10^{19}	1.1×10^{19}
α_{11}	$16.7^{a,b}$	9^{c}	$0.38^{c,d}$
α_{22}	$5.98^{a,b}$	9^{c}	$26^{c,d}$
α_{33}	$11.61^{a,b}$	9^{c}	$150\text{–}6{,}000^{d}$
α_{23}	$7.54^{a,b}$	...	...
Tilt angle	$35°^{a}$	?	$3.5°^{b,d}$
No. ellipsoids assumed	3	3	3
Fermi energy (10^{-14} erg)	18^{a}	23	$56^{c,d}$

[a] Reference 1.
[b] Reference 14.
[c] Reference 5.
[d] Rerefence 13.

A tentative estimation of the band parameters of antimony on the basis of a three-band model is given in Table I. It is of interest to note that if the carriers in Table I are assigned the relaxation times noted in the cyclotron resonance studies,[5] antimony would be expected to exhibit a positive Hall coefficient. This is indeed the sign of the observed[3] Hall coefficient.

The electronic specific heat of antimony has been given as 6300 erg/°K-mole by Wolcott.[17] Table I may be used to estimate the specific-heat contribution by these carriers. A calculation based on Table I shows that these carriers can be expected to contribute only about 10% of the experimental value. This discrepancy remains unresolved.

VI. LONG WAVELENGTHS

The absorptance was observed to become constant at a very small value for wavelengths greater than approximately twice that of the maximum absorptance. The Holstein[18] theory of the anomalous skin effect absorptance should be applicable in this wavelength range. Accurate measurements of the absorptance in this region should provide another set of numbers related to the band parameters in addition to those given by the dielectric anomaly theory. Unfortunately, no theory has been published for a nonspherical Fermi surface, although a paper is in preparation.[19]

In the present work the absorptance of a trigonal sample of bismuth (Fig. 2) was found to be constant at $A=(0.39\pm0.02)\%$ in the far infrared. An approximate calculation of the theoretical absorptance was made based on the theory of Holstein,[18] assuming a spatially averaged effective mass and an isotropic relaxation time. For specular reflection of the electrons at the surface of the sample a value of $A=0.31\%$ was found. Assuming diffuse reflection of the carriers the theoretical absorptance becomes $A=0.41\%$. This agreement with experiment is probably fortuitous considering the approximations made in the calculations.

The absorptance in antimony for a trigonal axis normal to the surface was observed to be constant in the region 15 to 20 μ and to have a value of $A=(0.90\pm0.10)\%$. A calculation, similar to the one made for bismuth, based on Table I gave a value of absorptance to be $A=0.24\%$, assuming specular reflection. For diffuse reflection of the carriers the absorptance was calculated to be $A=0.69\%$, which is in better agreement with the observed value.

These results indicate that diffuse scattering gives better agreement between theory and experiment for both antimony and bismuth. However, both Smith[20] and Koenig[21] report specular reflection in bismuth to give better agreement with their measurements of the anomalous skin effect and size effects of dc conductivity, respectively. The disagreement of the present work in the case of bismuth is probably not significant, since the observed infrared absorptance differs by only about 20% from the value calculated assuming specular reflection. Furthermore, as pointed out above, the calculations are based on a severe approximation. Nevertheless, the infrared results for antimony strongly indicate that diffuse scattering is the appropriate description of the electron-surface interaction. It is not unreasonable that a difference in the type of scattering should exist between antimony and bismuth, since the electron wavelength of antimony is almost an order of magnitude less than in bismuth.

It is worth noting that an examination of the absorptance in the longer wavelengths with high resolution and precise measurements might possibly reveal fine structure related to indirect transitions in antimony and bismuth. As is well known, previous studies[22,23] of indirect transitions in germanium and silicon were valuable in elucidating the positions of the band edges in k space, and provided information about phonon energies and exciton levels. In bismuth, as noted above, there were indications of fine structure in the far infrared, but no careful study was made of these. In antimony, at room temperature, there was indication of fine structure at 15.2 μ. However, none could be found at helium temperatures in the region 10 to 18 μ with the accuracy available in this experiment.

Note added in proof. The optical data combined with Shoenberg's antimony data (independently substantiated by Eckstein and Ketterson) indicate that Shoenberg's assumption of *three*, rather than six, electron ellipsoids was the correct one. This is easily seen since an assumption of six ellipsoids for Shoenberg's carriers results in an $N\alpha_{1,2}$ for these carriers alone in excess of the value permitted by Eq. (6). We also note in passing

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that a similar conclusion [A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962)] has been advanced recently with regard to the number of electron ellipsoids in bismuth. This latter conclusion is based on a reevaluation of extensive bismuth data.

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Rydberg Function as an Interatomic Potential for Metals

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The Rydberg potential has been applied to a number of body-centered and face-centered cubic metals. The parameters of the potential were calculated using the experimental values for the energy of vaporization, the lattice constant, and the compressibility. Results have been obtained for the elastic constants, for the equation-of-state curves, and for the volume dependence of the cohesive energy. They are compared with those obtained using the Morse potential, and with the experimental data. For the elastic constants, the results by the two potentials are not very different, but a significant improvement has been obtained in several cases for the equation of state and for the volume dependence of the cohesive energy.

INTRODUCTION

ONE approach to the theoretical study of the properties of solids is through the assumption of a central pairwise potential function. This approach was initiated in the early part of this century by the work of Mie[1] and Grüneisen[2,3] and has been developed in subsequent years by various people. Although in the case of molecules a large number of potential energy functions have been examined,[4] for solids very few have been investigated.

The conditions that a satisfactory interatomic potential in a crystal must satisfy have been discussed recently by Girifalco and Weizer.[5,6] Varshni[4] has discussed the requisite shape of a potential for the case of diatomic molecules and the same general requirements also apply here.

Born and his collaborators[7] have made a detailed analysis of the stability of crystal lattices and have given conditions that must be satisfied among the elastic constants. For cubic crystals these are: (1) All elastic constants are positive. (2) $C_{11}-C_{12}>0$.

For metals, two potential energy functions have been used by different workers:

1. The Mie-Grüneisen potential,

$$\phi(r)=-a/r^m+b/r^n;\quad (m<n), \tag{1}$$

where a, b, and m, and n are constants. This potential function has been used extensively[8] by workers in solid-state physics. Grüneisen employed this function in his early investigations on the theory of solids. Fürth,[9] and more recently Dayal and Sharma[10] and Cole,[11] have discussed the applicability of the function for a number of solids. Fürth finds that this equation gives reasonable results for the equation of state, but the values of m and n determined by him violate the stability conditions for body-centered cubic metals. The causes of this anomaly have been discussed by Girifalco and Weizer.

2. The Morse potential,[12]

$$\phi(r)=D[e^{-2\alpha(r-r_0)}-2e^{-\alpha(r-r_0)}], \tag{2}$$

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