processes may be seen independently by the use of infrared filters. The method is essentially an extension of the phase method of measuring radiative lifetimes. To measure the relaxation rates for the first process, the infrared and optical pumps should be chopped at the same frequency and then any phase shift in the fluorescent output will be a measure of the relaxation rate. For the second process the pumps should be chopped so that the beat frequency is constant and then a change in the beat frequency amplitude will occur when the infrared chopping frequency is approximately the relaxation rate. This assumes the relaxation times are less than the fluorescent lifetime.

(b) As can be seen from Scheme 1, provided the levels are thermally populated, then absorption transitions from these levels can be detected even though direct absorption to these levels is masked by the host lattice absorption.

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QUANTUM EFFECTS IN THE INFRARED REFLECTIVITY OF BISMUTH

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Recent experiments[1] have shown unequivocally that the energy-momentum relation for electrons in Bi is nonparabolic. In addition, the small Fermi energy, E_F, and light cyclotron masses in this material make it possible, with modest magnetic fields, to achieve Landau-level spacings which are comparable to E_F. Such a situation is ideally suited to the observation of quantum effects in cyclotron resonance. We report here on infrared reflectivity measurements which show pronounced effects of this type. These are of particular interest since they give information about the band structure away from the point $k_z = 0$. The data are analyzed in terms of Lax's[2] two-band model for Bi and are consistent with it.

In the two-band model, the energy of the nth Landau level in a conduction band of Bi is given by the expression

$$E_n = \{(\tfrac{1}{2}E_G)^2 + E_G[\hbar^2 k_z^2/2m_z + nh\omega_c]\}^{1/2} - (\tfrac{1}{2}E_G), \quad (1)$$

in which E_G is the band gap, ω_c the cyclotron frequency, and k_z the electron momentum in the magnetic field direction as measured from the band minimum. Figure 1 shows the corresponding variation with k_z of the three lowest Landau level energies. The magnetic field, B, has been chosen in such a way that the $n = 2$ Landau subband lies entirely above the Fermi surface, whereas the $n = 1$ subband cuts it. Such were the circumstances under which the most pronounced quantum effects were observed. For B parallel to the binary axis in Bi, they are

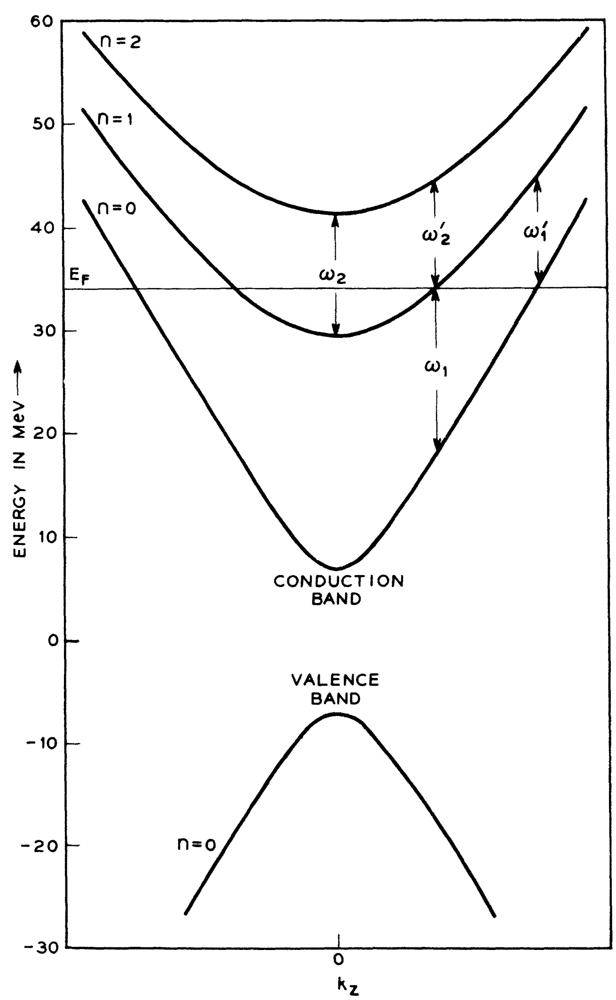

FIG. 1. Plot of Landau-level energy versus k_z.

achieved when 6.8 kG $\leq B \leq$ 13.6 kG, and in the bisectrix direction for 5.7 kG $\leq B \leq$ 11.4 kG.

From Fig. 1, it is clear that in these field ranges there are two different types of transitions, $n=0$ to $n=1$ and $n=1$ to $n=2$, that can contribute to the optical properties of the solid. The frequencies of these two types of transitions differ by a considerable factor with ω_1 always greater than ω_2 (see Fig. 1). Detailed calculations show that the principal contribution to the real part of the dielectric constant comes from transitions of the 1-2 type, since they benefit from the large density of states at $k_z=0$. Thus, as far as the reactive properties of the plasma are concerned, the effective cyclotron frequency of the electrons is about ω_2. The 0-1 transitions do not greatly influence Re(ϵ) except very near ω_1, but do produce an absorption band, that is, an imaginary contribution to ϵ, for $\omega_1' \leq \omega \leq \omega_1$.

An important feature of this absorption is the fact that its high-frequency onset, ω_1, occurs well away from the effective cyclotron frequency, and corresponds to transitions with $k_z \neq 0$. One expects, therefore, that as the field is increased, the reflectivity should change abruptly at the value of field, B_1, for which ω_1 is equal to the experimental infrared frequency, ω, since the sample suddenly becomes dissipative. The magnitude of the effect is determined by both Re(ϵ) and Im(ϵ) at $\omega \leq \omega_1$; calculations show that the reflectivity decreases for $\omega_1 > \omega$ should be at least 10% under favorable circumstances. In addition, for B along a given crystallographic axis, the value of B_1 should be the same for B parallel or perpendicular to the sample surface. On the other hand the values of field at which magnetoplasma effects occur are different for the field in the surface or normal to it. The most prominent of these effects is the reflection minimum which occurs close to the plasma frequency where Re$\epsilon = 0$.

Bismuth samples were oriented, cut, and polished following procedures of Smith, Hebel, and Buchsbaum,[3] and were glued at one corner to a mask attached to a cold finger. The operating sample temperature was 2.0 to 2.2°K. Infrared radiation between 80 cm^{-1} and 240 cm^{-1} was obtained from a globar source using a grating spectrometer with suitable filters and scattering plates. The instrument was operated double-beam by mounting two doped-germanium detectors on the cold finger which held the sample. A germanium beam splitter was used to divide the radiation, such that one bolometer monitored the direct radiation, the other detected the radiation reflected from the sample at normal incidence at about $f/2.2$ solid angle. The ratio of the two bolometer signals was plotted directly to obtain normalized reflectivity versus either B or ω.

Figure 2 is a plot of reflectivity versus B for $\omega = 205$ cm^{-1} with B parallel to the binary axis and perpendicular to the sample surface. As B is increased, the reflectivity goes through its usual minimum where Re$\epsilon = 1$ near the plasma frequency, then rises to unity as Reϵ becomes negative and the sample cuts off. The new feature of our data is the sharp drop in reflectivity at a higher field, which we identify as B_1 discussed earlier. Similar curves are obtained for B parallel to the bisectrix axis; in either case the values of B_1 observed were the same whether B was parallel or perpendicular to the surface. At a finite temperature the reflectivity should start to drop just below the B_1 which was calculated for $T=0$. Since the sample was at about 2.0°K, a correction of 2.5% was made in the values of B_1 read from the data, corresponding to using the dashed curve of Fig. 2.

A plot of the measured values of ω_1 versus B_1/B_0 is shown in Fig. 3, where B_0 is the field at which the bottom of the $n=1$ Landau subband crosses the Fermi level. The values of B_0 used were 13.6 kG for B along the binary axis and 11.4 kG for B along the bisectrix axis. The er-

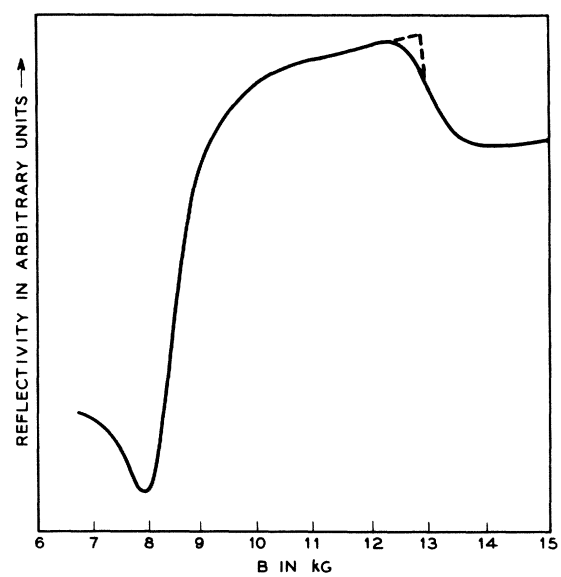

FIG. 2. Experimental reflectivity versus magnetic field, B, for B along a twofold axis.

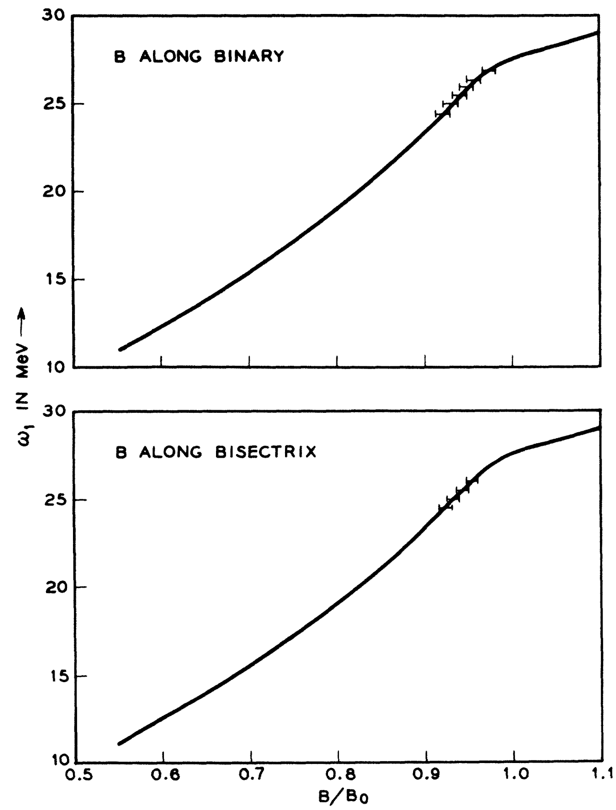

FIG. 3. Frequency of absorption edge versus B/B_0. Comparison of experiment and theory.

ror bars shown arise primarily from the temperature correction.

An expression for ω_1 versus B_1/B_0 can also be obtained for the two-band model from Eq. (1). For $B_1 \leqslant B_0$, one finds

$$h\omega_1 = \tfrac{1}{2}(2E_F + E_G)\left\{1 - \left[\frac{4E_F(E_F+E_G)}{(2E_F+E_G)^2}\left(\frac{B_1}{B_0}\right)\right]^{1/2}\right\}. \quad (2)$$

Equation (2) is plotted in Fig. 3. The solid curve takes into account a small (<4%) variation of the Fermi level with B near B_0 obtained from work of Smith.[4] The parameters used were $E_G = 14$ meV and $E_F(B=0) = 27$ meV. These values are consistent with the experiments of Brown, Mavroides, and Lax[1] and also with those of Boyle and Rodgers.[5] In addition, the relation between B_0, E_G, and E_F obtained from Eq. (1) is consistent with the cyclotron masses of Smith, Hebel, and Buchsbaum.[3] The curves are relatively insensitive to E_G but very sensitive to E_F; the often quoted value $E_F = 25$ meV gives a poor fit.

The excellent agreement indicates that we have correctly identified the absorption edges. Though our data are consistent with Lax's two-band model, they can also be reconciled with other models of the conduction-band structure in Bi. In particular, Cohen's[6] model A, which has the conduction-band minimum at the same point in k space as the corresponding valence-band maximum, gives an equally good fit. It is much harder to obtain agreement with his other two models (B and C) in which the band edges are displaced with respect to one another. Thus our experiment suggests, as does that of reference 1, that the conduction and valence-band extrema occur at the same positions in k space.

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