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# Magneto-optical determination of the $T$-point energy gap in bismuth

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We have carried out infrared magnetotransmission measurements on a 5000-Å-thick bismuth film grown by molecular beam epitaxy onto a CdTe substrate. The data for photon energies below 300 meV display at least ten orders of minima due to interband transitions at the $L$ points. In contrast to previous results from magnetoreflectivity experiments on bulk Bi, two concurrent series of resonances separated by a nearly constant energy of $\approx 5$ meV are observed. An additional series of strong oscillations emerges at somewhat higher photon energies, due to interband transitions at the $T$ point. The energy dispersion of these resonances are fit quite well by a simple nonparabolic model, allowing us to directly determine the $T$-point energy gap (407 meV) and the electron-hole reduced mass ($0.027m_0$, which implies an electron mass of $0.048m_0$).

The group-V element bismuth is a semimetal, whose three conduction-band minima at the $L$ points overlap the valence-band maximum at the $T$ point by about 40 meV.[1,2] It is well known that each of the electron valleys is accompanied by a mirror-image valence extremum lying $\approx 55$ meV below the primary maximum at $T$, i.e., the direct energy gap at $L$ ($E_g^L$) is only $\approx 15$ meV.[3,4] A schematic of this band alignment is illustrated in Fig. 1. Partly because the relevant interband transition energies fall in a convenient range for far infrared (FIR) magneto-optical experiments, $E_g^L$ has been accurately known for over 30 years.

By contrast, previous work has failed to yield a reliable characterization of the energy gap $E_g^T$ between the valence-band maximum at $T$ and the corresponding conduction valley at that symmetry point. Previous experimental determinations have been wildly inconsistent, yielding a nearly homogeneous distribution of values between 15 meV and 720 meV.[2,5–10] Apart from a tunneling spectroscopy study[5] which is now known to have been misinterpreted,[11,12] those experiments provided only indirect determinations of $E_g^T$, since they relied on fits to the nonparabolicity or $g$ factors of $T$-point holes. In fact, Smith, Baraff, and Rowell pointed out that one expects the nonparabolicity approach to have high uncertainty in this case because the two-band model is inappropriate.[1] Theoretical results from band structure calculations[7,11,13–16] have spanned nearly as broad a distribution (60–745 meV), although more recent work has tended to yield values in the slightly more restricted range between 200 and 600 meV.[7,15,16] These calculations have confirmed the importance of multiband interactions, since two additional conduction bands at $T$ lie in close proximity to the lowest-lying band. Both Golin[7] and Gonze, Michenaud, and Vigneron[16] find the actual conduction-band minimum to be slightly displaced from the $T$ point, although the latter authors obtain an energy difference of only 21 meV between the indirect and direct gaps at $T$.

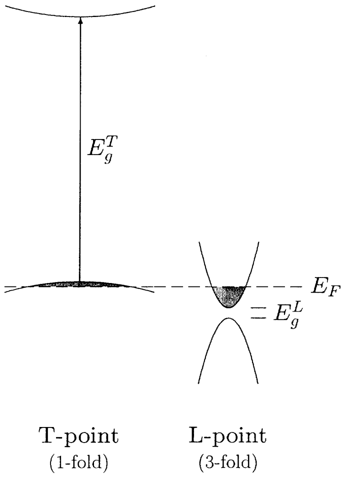

FIG. 1. Schematic of the $L$-point and $T$-point band alignments in Bi.

We report here the results of infrared magnetotransmission measurements on a Bi film whose thickness of 5000 Å is large enough that quantum confinement effects may be ignored. At photon energies below 300 meV, previously-observed resonances due to interband transitions at the $L$ points are prominent. However, the region above 350 meV, which had not been probed in previous magneto-optical studies of Bi, yields an additional series of minima which may be attributed to interband transitions at $T$. From the dispersion of the resonance energies as a function of magnetic field, we have directly determined the $T$-point energy gap and the electron-hole reduced mass.

The Bi film was grown by molecular beam epitaxy onto a (111)B CdTe substrate, as has been described elsewhere.[17] Following deposition of a 3000-Å CdTe buffer layer at 250 °C, the substrate temperature was lowered to 150 °C and the Bi film was grown at a rate of 0.2–0.5 Å/s. The structure was then covered with a 100-Å CdTe cap. Reflection high energy electron diffraction (RHEED) patterns for the Bi growth were streaked, with clear Kikuchi lines evident. X-ray diffraction data ($\Theta/2\Theta$) and high-resolution transmission electron microscopy (HRTEM) also confirmed the excellent crystallinity of the film. A mixed-conduction analysis of the field-dependent Hall and conductivity data indicates that the sample is slightly $n$-type, with a net donor concentration of $7\times10^{16}$ cm$^{-3}$. The low-temperature mobilities for both electrons and holes are $\approx 2\times10^4$ cm$^2$/V s.[18]

The magneto-optical experiments were carried out using a Mattson Fourier transform infrared (FTIR) spectrometer. Low-temperature (4.2 K) transmission spectra as a function of photon energy were obtained at constant magnetic fields ($B$) between 2 and 12 T, with both the field direction and the light propagation coincident along the trigonal growth axis. The photon energy was varied from $\approx$ 90 meV to $\approx$ 540 meV, these boundaries being determined by limitations of the detector, beam splitter, and IR source.

Typical results are illustrated in Fig. 2, which shows spectra for $B = 6$ T and 12 T. Two series of transmission minima are evident in each spectrum, one occupying the region below 300 meV (labeled $L$ points) and the other beginning above 350 meV (labeled $T$ point). The greater noise in the higher-energy features is due primarily to limitations of the beam splitter in that region.

The most prominent aspect of the lower-energy ($L$ points) portion of the spectrum is the series of principal minima which extend for at least ten orders. The resonance energies $\hbar\omega_r$ are plotted vs magnetic field as the solid curves in Fig. 3 (the curves were obtained by interpolating between the data for discrete fields). These dispersion relations are in good agreement with the $L$-point interband energies reported previously by Maltz and Dresselhaus from magnetoreflectivity measurements on bulk Bi with the magnetic field along the trigonal axis.[19] In addition to the principal features, however, we also note that with increasing order the $L$-point minima in Fig. 2 first show a shoulder, then a splitting into a doublet, and finally a complete resolution into two distinct minima (particularly the data for $B = 6$ T). In fact, the "secondary" resonances actually become stronger than the "principal" resonances at higher orders and lower fields. Resonance energies as a function of field for the secondary features are plotted as the dashed curves in Fig. 3. Note that the two series remain closely correlated, with a nearly constant energy separation of $\approx$ 5 meV, under all conditions for which both are resolvable.

The origin of the second series of $L$-point resonances is unclear at this time. Maltz and Dresselhaus[19] observed only a single series, while Mendez, Misu, and Dresselhaus[20] found that the application of a hydrostatic pressure shifted the transition energies but did not introduce additional lines. Measurements on heavily-doped $p$-type samples by Misu *et al.*[21] did in fact produce a second series of resonances, which were attributed to a breakdown of the usual selection rule ($\Delta j = 1$, where $j = n+1/2-s$ is the sum of the Landau quantum number $n = 0,1,2...$ and the spin quantum number $s = \pm1/2$) due to impurity-assisted intervalley transitions. Unlike the results in Fig. 3, however, all of the secondary features from those data lay approximately midway between the two adjacent primary resonances. Although it is not unreasonable to suppose that intervalley transitions induced by boundary scattering in the present thin film

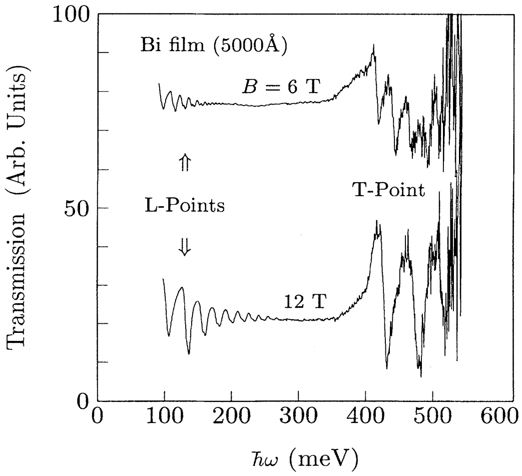

FIG. 2. Magnetotransmission spectra for the Bi film at magnetic fields of 6 T and 12 T. The lower-energy and higher-energy resonances correspond to interband transitions at the $L$ points and $T$ point, respectively.

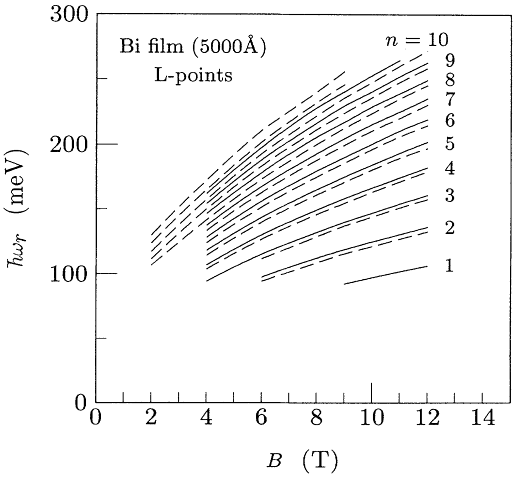

FIG. 3. Experimental resonance energies vs magnetic field for interband transitions at the $L$ points. The solid curves represent the principal resonances corresponding to those observed previously by Maltz and Dresselhaus (Ref. 19), while the dashed curves correspond to a second series of minima whose origin is uncertain. Indices for the participating electron and hole levels are labeled as in Ref. 19.

could lead to selection rules similar to those resulting from impurity scattering in the heavily-doped sample of Misu *et al.*, the close spacing of the solid and dashed curves at low Landau indices in Fig. 3 is inconsistent with that interpretation.

Other modifications of the selection rules similarly fail to account for the present data. For example, a relaxation of the spin selection rule ($\Delta s = \pm 1$) should break the degeneracy of the transition energies into three distinct series rather than two, while a slight inequality of the electron and hole effective masses will produce four concurrent series. An obvious difference between our thin-film experiment and those on bulk Bi is the presence of in-plane strain due to the small lattice-constant mismatch ($\approx 0.7\%$) between the CdTe substrate/buffer layer and the Bi film. It is unclear why such a strain should lead to the observed results, however, since it should in principle be symmetric for the three $L$-point valleys. In order to simulate the effects of a slight unintentional tilt of the magnetic field orientation from the trigonal axis, the magnetotransmission experiment was repeated with the sample tilted into the plane by $\approx 10^\circ$ along an arbitrary axis. Those conditions produced approximately three times as many resonances as in the untilted bulk case, presumably because the degeneracy of the three $L$-point valleys was lifted. At the same time, any close correlation (analogous to the 5 meV splitting in Fig. 3) between the various series of lines was lost. These observations suggest that the second series of resonances in the untilted thin-film data resulted from some type of two-against-one breaking of the threefold valley degeneracy, perhaps due to a preferential strain relaxation along one of the three binary axes.

The higher-energy features in Fig. 2 may be straightforwardly interpreted in terms of interband transitions at the $T$ point. Figure 4 illustrates that when the experimental resonance energies (points) are plotted against magnetic field, the Landau series is easily identified. The curves in the figure represent a fit to a simple nonparabolic model:[19]

$$\hbar\omega_r = \left[\left(\frac{E_g^T}{2}\right)^2 + \frac{j_e e\hbar B E_g^T}{m_{e0}}\right]^{1/2} + \left[\left(\frac{E_g^T}{2}\right)^2 + \frac{j_h e\hbar B E_g^T}{m_{h0}}\right]^{1/2}, \tag{1}$$

where $m_{i0}$ is the effective mass at the bottom of a given band, $j_i = n_i + 1/2 - s_i$ as for $L$-point carriers, and $\Delta j \equiv j_e - j_h \rightarrow \pm 1$ for allowed transitions. Rather than being independently sensitive to the electron and hole effective masses, the dispersion of the resonance energy with field is instead sensitive to the reduced mass: $m_r \equiv 1/(m_{e0}^{-1} + m_{h0}^{-1})$. In modeling the data, we have therefore set both masses equal to $2m_r$. The fit, which is seen to be quite good, gives $E_g^T = 407$ meV and $m_r = 0.027m_0$. If we take the hole mass at the bottom of the band to be $0.059m_0$ from previous Alfven-wave experiments on bulk samples,[2] the reduced mass from the fit yields a $T$-point electron mass of $0.048m_0$. Since the two-band model is known to be unreliable at $T$ due to interactions with the higher conduction bands,[1,7,16] the slight inequality of the electron and hole masses is not surprising. We also note that the transmission spectrum at zero magnetic field displays a weak inflection near $\hbar\omega \approx 400$ meV.

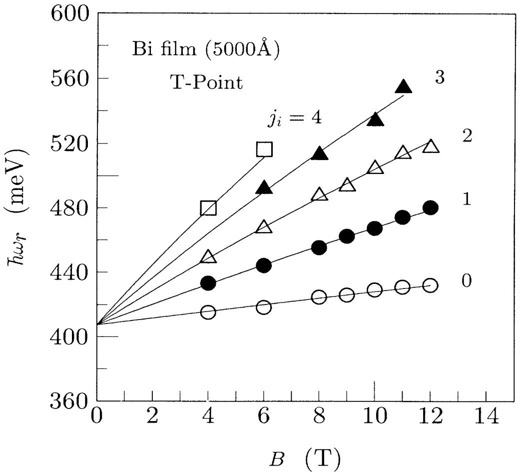

FIG. 4. Resonance energies vs magnetic field for interband transitions at the $T$ point. Both experimental data (points) and the results of a nonparabolic model (curves) are given. The indexing of the lines identifies transitions $j_i \rightarrow j_i + 1$.

Experimental uncertainty in the present magneto-optical determination of the $T$-point energy gap is estimated to be no more than a few meV. While previous experimental[2,5–10] and theoretical[7,11,13–16] results have covered a wide range both below and above the observed value of 407 meV, none was more than approximately correct (closest was 350 meV from the recent calculation of Gonze, Michenaud, and Vigneron[16]). However, we emphasize that our measured $E_g^T$ should correspond to that for direct optical transitions, whereas the indirect gap at $T$ may be slightly smaller.[7,16]

We have also observed interband transitions at the $T$ point in recent magnetotransmission experiments on two Bi-CdTe superlattices. Those data will be discussed elsewhere.

Summarizing, we have used a FTIR spectrometer to study the infrared transmission properties of a Bi thin film in the presence of variable magnetic fields oriented along the trigonal axis. At photon energies below 300 meV, the data yield two concurrent series of closely-correlated resonances due to interband transitions at the $L$ points. It is presently unclear why we observe twice as many lines as were seen in most previous magnetoreflectivity experiments on bulk Bi. At somewhat higher photon energies, additional oscillations emerge due to interband transitions at the $T$ point. A fit of the field-dependent resonance energies to a nonparabolic model has allowed us to directly determine the energy gap and reduced effective mass at the $T$ point.

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