PHYSICAL REVIEW B VOLUME 10, NUMBER 2 15 JULY 1974

Temperature dependence of the band parameters of bismuth*

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(Received 28 February 1974)

The temperature dependence of the band parameters associated with the electron pockets in bismuth is presented from 4 to 280 K, based on analysis of magnetoreflection data. This first determination of the bismuth band parameters over a wide temperature range shows that the same form of the energy dispersion relation is applicable over the entire temperature range. Above ~60 K a large temperature dependence is found for both the band parameters and the momentum matrix elements coupling the valence and conduction bands.

Of particular interest to the interpretation of transport measurements in bismuth[1-4] is the availability of data on the temperature dependence of the energy-band parameters over a wide temperature range. These energy-band parameters (e.g., effective mass tensor and energy gap) express the characteristics of the energy-dispersion relations for the carriers, and consequently play a dominant role in the determination of the transport properties. In the case of bismuth, the energy gap associated with the electron pockets at the L point in the Brillouin zone is exceptionally small, and consequently all the band parameters associated with the electron carriers are strongly temperature dependent.

The band parameters associated with the electrons in bismuth are well known at liquid-helium temperatures,[5-7] and to a lesser extent up to 75 K.[5,8] In this note, the temperature dependence of the band parameters is extended up to room temperature.

The band parameters for the electrons in the L-point pockets are conveniently expressed in terms of a two-band model that has been shown to describe the electronic properties accurately[6]:

$$E^{\pm}(\vec{k}) = \pm\frac{1}{2}\left(E_g^2 + 2E_g\hbar^2\frac{\vec{k}\cdot\overleftrightarrow{\alpha}\cdot\vec{k}}{m}\right)^{1/2} , \tag{1}$$

where the band parameters are the energy gap E_g and the dimensionless inverse-effective mass tensor $\overleftrightarrow{\alpha}$, defined in terms of the momentum matrix elements

$$\overleftrightarrow{\alpha} = (\overleftrightarrow{m}^*)^{-1} = 2\,\frac{\langle c\,|\vec{p}\,|v\rangle\langle v\,|\vec{p}\,|c\rangle}{E_g m} , \tag{2}$$

in which c, v refer to the conduction (+) and valence (−) bands separated by an energy gap E_g. Magnetoreflection experiments have been shown to provide an excellent technique for determining the temperature dependence of these band parameters.[5] The interpretation of the magnetoreflection data is carried out in terms of the magnetic energy-level structure derived from a two-band model.[5] The magnetic energy levels $E^{\pm}_{j,s}(k_H)$ depend on four quantum numbers: band index (±), magnetic level index ($j = 0, 1, 2, \ldots$), spin numbers ($s = \pm\frac{1}{2}$), and the wave vector in the direction of the magnetic field k_H. For bismuth, the magnetic energy levels have extrema at $k_H = 0$, and it is these energy extrema $E^{\pm}_{j,s}(0)$ that are of greatest importance in the interpretation of the magnetoreflection results[5]

$$E^{\pm}_{j,s}(0) = \pm\left(\tfrac{1}{4}E_g^2 + E_g\beta^* Hj\right)^{1/2} - 2s\,|G\beta^*|\,H,\ j \neq 0, \tag{3a}$$

and

$$E^{\pm}_{0,1/2}(0) = \pm\left[\left(\tfrac{1}{2}E_g - |G\beta^*|\,H\right)^2 + P(\beta^* H)^2\right]^{1/2} , \tag{3b}$$

where H is the externally applied magnetic field. The components of the effective mass tensor are found from a determination of the cyclotron effective mass m_c^* in terms of the parameter β^* in Eq. (3) for several orientations of the magnetic field, using the relation

$$\beta^* = \beta_0\, m/m_c^* , \tag{4}$$

where β_0 is twice the Bohr magneton

$$\beta_0 = e\hbar/mc \tag{5}$$

and the cyclotron effective mass is given by

$$m_c^* = (\det \overleftrightarrow{m}^*/\hat{h}\cdot\overleftrightarrow{m}^*\cdot\hat{h})^{1/2}\, m , \tag{6}$$

where $\hat{h}$ is a unit vector in the direction of the external magnetic field.

The parameter G in Eq. (3) represents the spin splitting of the magnetic energy levels due to the effect of bands outside the two-band model[5,6]; the parameter P represents the coupling between the $j = 0$ levels in the conduction and valence bands that becomes important at magnetic fields large enough to satisfy the condition $\beta^* H \gg E_g$.

At various temperatures between room temperature and 4.2 K we have measured the magnetic-field dependence of the optical reflectivity of bismuth for several fixed incident photon energies. Magnetic fields up to 150 kG were obtained using

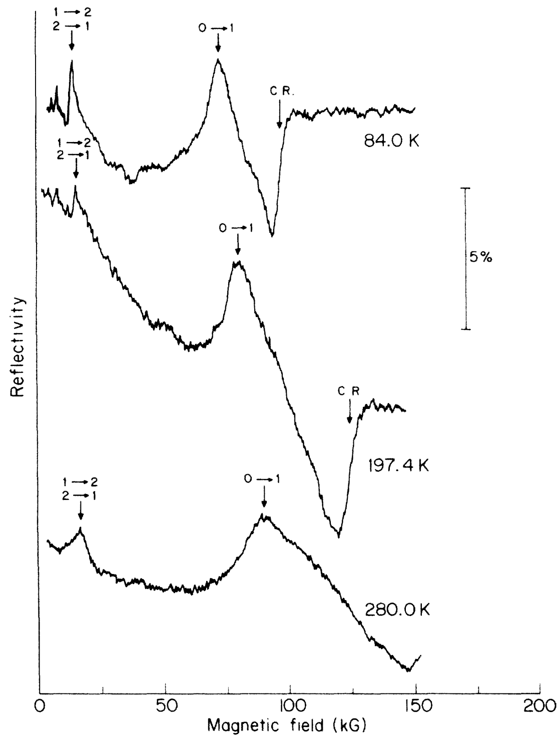

FIG. 1. Typical experimental traces for $\vec{H}$ parallel to the binary axis at three different temperatures. The incident photon energy is $\hbar\omega = 82.16$ meV. The resonances are labeled according to the convention used in Ref. 5. The strong temperature dependence of the band parameters is evident, especially by looking at the cyclotron-resonance (C.R.) transition.

a Bitter solenoid. The photon source was a globar, and a standard grating spectrometer allowed continuous tuning between 7 and 15 μm. The bismuth

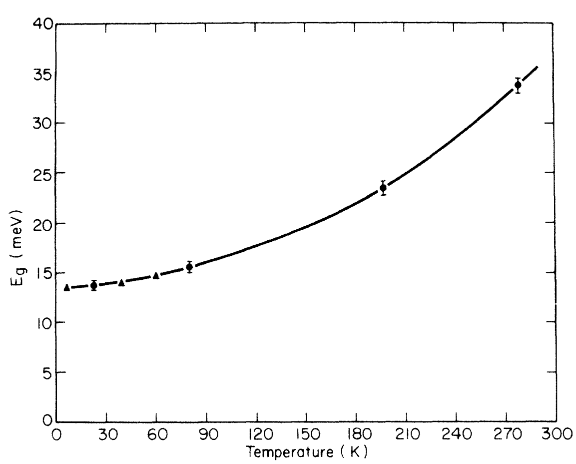

FIG. 2. Temperature dependence of the energy gap E_g. The circles represent the experimental results of the present work, and the triangles are taken from Ref. 5. The solid line represents a least-squares fit to the data.

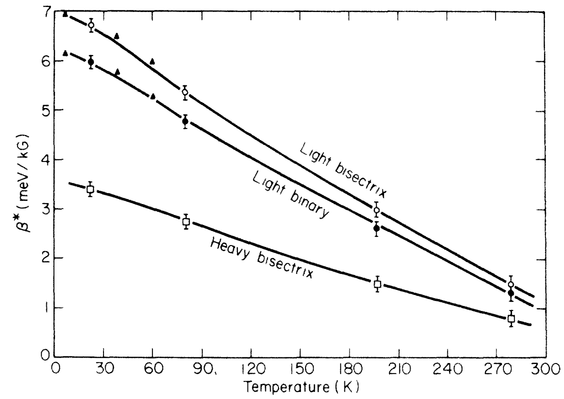

FIG. 3. Temperature dependence of β^* for the light-binary, light-bisectrix, and heavy-bisectrix electrons. The triangles are points taken from Ref. 5. The solid lines are least-squares fits to the experimental results.

single crystals were prepared using the same technique described in Ref. 5. The samples were mounted on a cold-finger inside a low-temperature Dewar. By using liquid helium, liquid nitrogen, and dry ice with acetone, we were able to span the temperature range $22.5 < T < 280$ K,[9] while data in the range $4.2 < T < 75$ K were available from previous work.[5] The exact temperature was measured by mounting a chromel-constantan thermocouple on the optical faces of the samples. The temperature was always measured at zero magnetic field in order to avoid any distortion in the thermocouple reading due to the magnetic field. It is estimated that the uncertainty in the temperature measurement is less than ~0.5 K, the main errors arising from slow thermal drifts during an experimental run and possible temperature gradients in the samples. Typical experimental traces taken at different temperatures are shown in Fig. 1. Of particular significance is the fact that at all temperatures the magnetoreflection data can be interpreted quantitatively in terms of the magnetic energy-level structure given by Eq. (3). Such an analysis has been carried out for the magnetic field along the binary and the bisectrix directions. In the case of the bisectrix direction, results are obtained for both the light and heavy electrons. The results of these magnetoreflection experiments are summarized in Figs. 2–4. It is seen that the temperature dependence of the band parameters is a large effect, particularly for temperatures above ~60 K. A least-squares fit to the experimental results using a second-order polynomial yields the following temperature-dependent expressions:

$$E_g = 13.6 + (2.1\times10^{-3})\,T + (2.5\times10^{-4})\,T^2; \qquad (7)$$

for the light binary electrons,

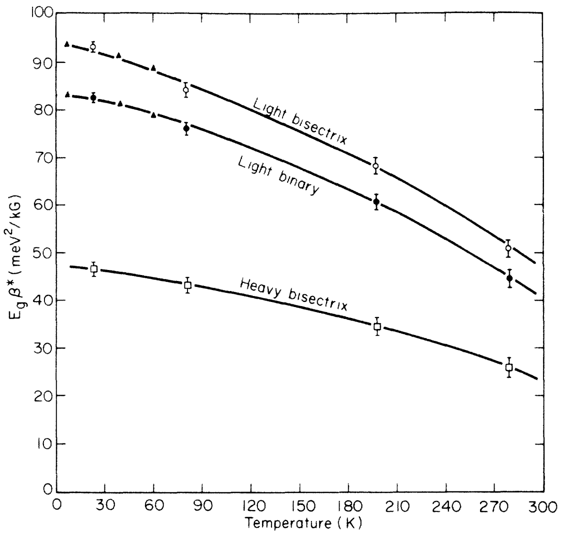

FIG. 4. Temperature dependence of $E_g\beta^*$ for the light-binary, light-bisectrix, and heavy-bisectrix electrons. The triangles are taken from Ref. 5 and the solid lines represent least-squares fits to the experimental results.

$$\beta^*_{\rm lbn} = 6.26 - (1.8\times10^{-2})\,T + (2.1\times10^{-6})\,T^2, \quad (8a)$$

$$E_g\beta^*_{\rm lbn} = 83.5 - (5.7\times10^{-2})\,T - (2.9\times10^{-4})\,T^2; \quad (8b)$$

for the light bisectrix electrons,

$$\beta^*_{\rm lbx} = 7.06 - (2.2\times10^{-2})\,T + (7.4\times10^{-6})\,T^2, \quad (9a)$$

$$E_g\beta^*_{\rm lbx} = 94.1 - (8.5\times10^{-2})\,T - (2.4\times10^{-4})\,T^2; \quad (9b)$$

and for the heavy bisectrix electrons,

$$\beta^*_{\rm hbx} = 3.53 - (1.0\times10^{-2})\,T + (1.0\times10^{-6})\,T^2, \quad (10a)$$

$$E_g\beta^*_{\rm hbx} = 47.1 - (3.3\times10^{-2})\,T - (1.5\times10^{-4})\,T^2. \quad (10b)$$

Here the quantities T, E_g, and β^* are respectively given in units of degrees K, meV, and meV/kG. It should be pointed out that the effective masses measured in magnetoreflection experiments—i.e., the parameter β^* [see Eq. (4)]—correspond to the curvatures at the *extrema* of the conduction and valence bands at $H=0$. Because of the nonparabolicity of the bands, the effective masses at the Fermi level will exhibit a temperature dependence due to both the temperature-dependent band parameters, as shown in Figs. 2–4, and the temperature dependence of the Fermi energy. It is of interest to observe that the temperature dependence of the band parameters is weak below liquid-nitrogen temperatures and much stronger at higher temperatures.

The perturbation parameters G and P [see Eq. (3)] have been determined previously at low temperatures for the light-binary and light-bisectrix electrons.[5] It was not possible in the present work to resolve a temperature dependence for either the parameter G or the parameter P. Since the energy gap increases very significantly as the temperature is raised, the coupling parameter P becomes less important in determining the $j=0$ magnetic energy levels at higher temperatures. Also, for the heavy-bisectrix electrons the contributions to the energy from terms involving the parameters G and P are very small in magnitude and even at the highest available magnetic fields it was not possible to determine these parameters. On the other hand, the present work does represent the first determination of the temperature dependence of the cyclotron effective mass for the heavy-bisectrix electrons. For $\vec{H}$ parallel to the trigonal axis, the experimental magnetoreflection resonances are of small magnitude and have large linewidths.[6] No temperature dependence of the magnetoreflection spectrum for the trigonal field orientation has yet been obtained.

Work is currently in progress to relate the observed temperature dependence of the band parameters to the energy-band structure at the L point in the Brillouin zone. Of particular interest is the observation of a large temperature dependence of the product $E_g\beta^*$, which is directly related to the square of the momentum matrix elements coupling the conduction and valence bands.[5]

ACKNOWLEDGMENTS

We would like to thank Dr. R. L. Aggarwal for his help with the experiments and for valuable discussions. Special thanks are also due to Dr. J.-P. Issi and Dr. G. A. Saunders for stimulating the present work.

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*Work supported by the National Science Foundation.
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‡Visiting Scientist, Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, Mass. 02139, supported by the National Science Foundation.
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[9]The low-temperature limit was determined by the thermal losses due to the cold-finger geometry. Also, the cooling water of the Bitter magnet established an effective room temperature for the bismuth sample of ~280 K.