ments and with theoretical work on $CdAs_2$. The results will be reported later in a more complete paper on this material.

The author expresses his gratitude to V. J. Lyons and V. J. Silvestri for providing the samples on which these experiments were carried out, to A. S. Fischler for making his results available prior to publication, to J. Swanson for helpful discussions, and to A. J. Landon for his assistance in the experiments.

---

[1] Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. 93, 1418 (1954).

[2] Dresselhaus, Kip, and Kittel, Phys. Rev. 98, 368 (1955); Dexter, Zeiger, and Lax, Phys. Rev. 104, 637 (1956).

[3] Dresselhaus, Kip, Kittel, and Wagoner, Phys. Rev. 98, 556 (1955).

[4] R. N. Dexter, J. Phys. Chem. Solids 8, 494 (1959).

[5] V. J. Lyons and V. J. Silvestri, J. Phys. Chem. (to be published).

[6] A. S. Fischler (to be published).

[7] Turner, Fischler, and Reese, Electrochemical Society Meeting, Columbus, Ohio, October, 1959, Abstract No. 101.

OBSERVATION OF DIRECT TUNNELING IN GERMANIUM

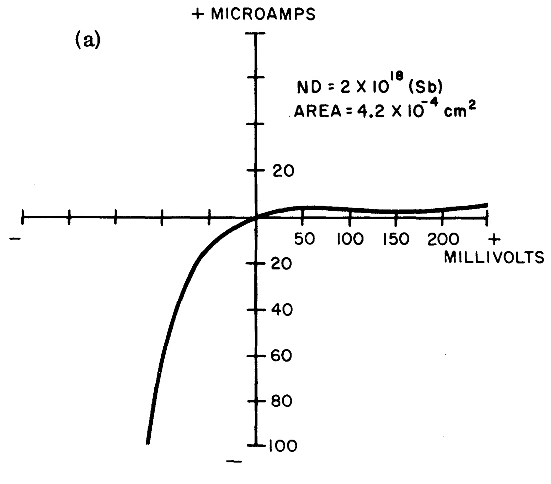
John V. Morgan and Evan O. Kane
Semiconductor Division, Hughes Products Group, Newport Beach, California

(Received October 15, 1959)

Holonyak et al.[1] have demonstrated experimentally the importance of phonons in tunneling from the (111) minimum of the conduction band of germanium to the (000) valence band maximum in accord with the theory of Keldysh.[2] In addition to the phonon process there is a "direct" process, treated by Keldysh[3] and Kane,[4] whereby an electron tunnels from the (000) valence band into the (000) conduction band minimum solely under the influence of the field without any additional perturbing mechanism. The "direct" process cannot occur in the forward bias region of a tunnel diode because there is no occupancy of the (000) minimum. However, in the reverse direction the filled states of the valence band may be made to coincide in energy with the empty states of the (000) minimum and "direct" tunneling will result. A very significant increase in tunneling current should be observed at this point, according to theory.

The transition from "indirect" to "direct" tunneling has been observed experimentally at 77°K in a germanium diode with 2×10^{18} carriers/cc on the n side and 8×10^{18} carriers/cc on the p side. The impurities were Sb and Ga. The diode had a barely discernible negative resistance in the forward direction as shown in Fig. 1(a).

Figure 1(b) shows the reverse characteristic



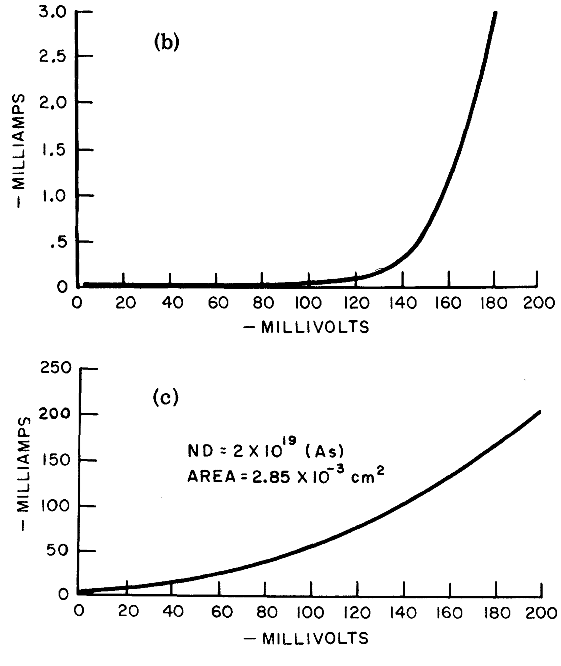


FIG. 1. I-V characteristics of germanium tunnel diodes showing transition from indirect to direct tunneling at 0.13-volt reverse bias. Curves taken at 77°K. p-type impurity is gallium at 8×10^{18} per cm^3. (a) and (b) are same specimen with different scales.

alone. The abrupt rise beginning at about 0.14 ev gives unmistakable evidence of the onset of direct transitions. The magneto-optical data of Zwerdling et al.[5] give 0.15 ev as the separation between the (111) and the (000) conduction band minima.

The tunneling calculations[3,4] were based on a two-band approximation and a constant electric field. The spin-orbit splitting in germanium invalidates the two-band approach and the junction field is linear rather than constant. In applying the formulas we attempt to correct for these errors by treating the field as a parameter to be determined by matching to the absolute current density. The theory gives

$$j=\frac{em_r\bar{E}_\perp}{9\hbar^3}\left\{eV_d-\bar{E}_\perp\left[1-\exp\left(\frac{-eV_d}{\bar{E}_\perp}\right)\right]\right\}\times\exp\left(\frac{-\pi m_r^{1/2}E_{000}^{3/2}}{2\hbar F}\right),\qquad(1)$$

$$\bar{E}_\perp=\hbar F/2\pi m_r^{1/2}E_{000}^{1/2},\qquad(2)$$

where m_r is the reduced mass, $0.02m$, E_{000} is the band gap at $k=0$, F is the force on the electron, and V_d is the continuation of the p-side Fermi level measured from the bottom of the (000) minimum on the n side. (See Fig. 2.) $\bar{E}_\perp$ is the average kinetic energy of the tunneling carriers perpendicular to the junction field. Carriers with perpendicular energies much larger than $\bar{E}_\perp$ have greatly reduced tunneling probabilities. In deriving Eq. (1), ζ_p, the p-side Fermi level, was assumed much greater than $\bar{E}_\perp$. Temperature effects were also ignored. Neglecting the variation of F with V_d, Eq. (1) shows that the current increases quadratically for $V_d \ll \bar{E}_\perp$ and linearly for $V_d \gg \bar{E}_\perp$. Extrapolation of the linear slope back to $j=0$ gives a voltage intercept $+\bar{E}_\perp$. Calling ζ_n the Fermi level on the n-type side, we calculate that for $n=2\times10^{18}$ carriers/cc and $T=77°\mathrm{K}$, $\zeta_n=0.006$ ev. The separation of the minima will then be given by

$$E_{000}-E_{111}=eV_0-\bar{E}_\perp+\zeta_n,\qquad(3)$$

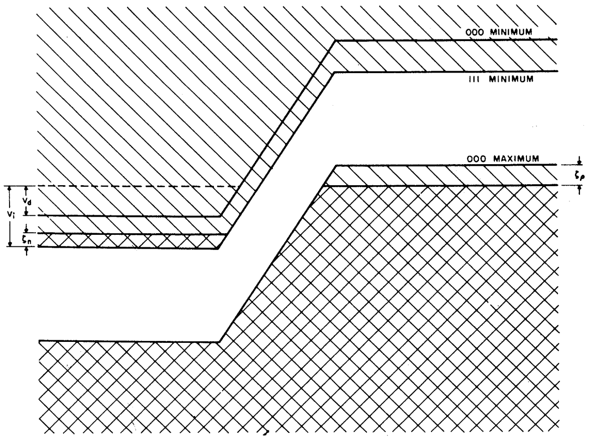


FIG. 2. Band edge contours in a tunnel diode with illustration of symbols.

where V_0 is the voltage intercept extrapolating linearly back to zero current. Taking a current density of 3.1 amp/cm² at 0.16 volt applied voltage from Fig. 1(b), we compute that $F=6\times10^5$ ev/cm, $\bar{E}_\perp=0.019$ ev. Using these values in Eq. (3), we find

$$E_{000}-E_{111}=0.13\text{ ev.}$$

The discrepancy between this value and the magneto-optical value of 0.15 lies well outside the experimental error. It does not appear correct to ascribe the difference to an impurity-induced shift of the bands since measurements on an As-doped sample with 2×10^{19} carriers per cc on the n side as shown in Fig. 1(c), also give a separation of 0.13 ev. The latter value is less reliable, however.

In order to test the reasonableness of the assumed parameter F, we calculated the "effective" field for an abrupt junction with the measured carrier concentrations using parabolic energy bands. The effective field was defined to be the constant field which would give the same exponential attenuation factor as the variable field. The computed value was 3.5×10^5 ev/cm.

It is also of interest to check the magnitude of the indirect tunneling current, shown most clearly in Fig. 1(a). Using Keldysh's[2] result, we find

$$j=\frac{F^{3/2}(m_1m_2)^{3/2}(2n+1)(M^2V)}{32(2)^{3/4}\pi^{5/2}\hbar^{9/2}m_{rx}^{5/4}E_{111}^{7/4}}\left\{eV_i+\bar{E}_\perp\left[\exp\left(-\frac{(eV_i+\zeta_n)}{\bar{E}_\perp}\right)-\exp\left(\frac{-\zeta_n}{\bar{E}_\perp}\right)\right]\right\}\exp\left(\frac{-4(2m_{rx})^{1/2}E_{111}^{3/2}}{3\hbar F}\right),\qquad(4)$$

$$\bar{E}_\perp = \hbar F/2(2m_{rx})^{1/2} E_{111}^{1/2}, \qquad (5)$$

where m_1, m_2 are density of states masses, m_{rx} is the reduced mass in the field direction, E_{111} is the indirect energy gap, n is the average number of phonons, and M^2V is the square of the phonon matrix element times the volume. Again we have assumed $\zeta_p \gg \bar{E}_\perp$. The right-hand side of Eq. (4) should be summed over the 4 conduction band minima but we assume that just one minimum is most favorably aligned for tunneling. For this minimum $m_{rx}^{-1} = 0.08^{-1} + 0.04^{-1}$. We have determined M^2V from the magnitude of indirect optical absorption[6] to be

$$M^2V = 1.3\times10^{-47}\ \mathrm{erg}^2\ \mathrm{cm}^3.$$

Using the above values together with the value of F determined for the direct case, we calculate a current density of 4×10^{-3} amp/cm^2 at 0.05 volt reverse bias, which is to be compared with the experimental value of 2×10^{-2} amp/cm^2. The factor of 5 discrepancy is within the uncertainty of the theoretical estimate. However, it is clear from Fig. 1(a) that the experimental curve shape does not agree with theory in the region between 0.05 ev and 0.12 ev since the slope increases rapidly with energy instead of becoming constant for $V_i \gg \bar{E}_\perp$. ($\bar{E}_\perp = 0.015$ ev in this case.) The current increase is not rapid enough to be due to thermal excitation to the energy of the (000) minimum. We suggest that the increase is due to the impurity admixture of states in the (111) and (000) minima. In perturbation terminology, the particle tunnels into a virtual state in the (000) minimum and is then impurity-scattered into the (111) minimum. The rapid increase in current with voltage would then be due in part to the decrease of the energy denominator.

Holonyak et al.[1] have observed phonon-assisted tunneling in Sb-doped junctions of germanium but not in P- and As-doped junctions. A possible interpretation is that impurity scattering dominates phonon scattering for the latter two impurities. Since the k-vector change is a large one, a variation with the specific impurity is to be expected. Their results are also consistent with the observation that Sb has the smallest ionization energy of the column V impurities, hence the wave function is least concentrated at the core. A good test of this interpretation would be a comparison of direct and indirect tunneling currents in the reverse characteristic for Sb, As, and P. The latter two should have the smaller ratio.

---

[1] Holonyak, Lesk, Hall, Tiemann, and Ehrenreich, Phys. Rev. Letters 3, 167 (1959); L. Esaki, J. Phys. Soc. Japan (to be published).

[2] L. V. Keldysh, J. Exptl. Theoret. Phys. U.S.S.R. 34, 962 (1958) [translation: Soviet Phys. JETP 34(7), 665 (1958)].

[3] L. V. Keldysh, J. Exptl. Theoret. Phys. U.S.S.R. 33, 994 (1957) [translation: Soviet Phys. JETP 33(6), 763 (1958)].

[4] E. O. Kane, J. Phys. Chem. Solids (to be published).

[5] Zwerdling, Roth, and Lax, Phys. Rev. 109, 2207 (1958).

[6] Macfarlane, McLean, Quarrington, and Roberts, Phys. Rev. 108, 1377 (1957).

OPTICAL DETECTION OF PARAMAGNETIC RESONANCE SATURATION IN RUBY*

Irwin Wieder
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received June 24, 1959; revised manuscript received October 12, 1959)

In order to extend the technique of optical pumping to solids, it is convenient to employ a solid system with sharp optical lines.[1] One such material is ruby which consists of Cr^{+++} ions in a host crystal of Al$_2$O$_3$. The optical spectrum of ruby has been studied extensively[2-6] and includes two sharp lines denoted by R_1 and R_2 which appear in both absorption and emission. The Zeeman effect of these lines was also observed and has recently been investigated both theoretically and experimentally in detail.[7,8] The results of the above-mentioned work are shown in the high-field transition diagrams of Fig. 1. The expected zero-field intensities were obtained by assuming[9] that the optical matrix elements are magnetic-field independent and adding the appropriate values for the degenerate levels. It is apparent that many possibilities exist for preferentially depopulating one of the sublevels of the ground state. For example, a mixture of R_1 and R_2 radiation polarized with the electric vector along the optic axis can be expected to depopulate pref-