It would also be of interest to compare the classification of states and the stress effects with the effect of very strong magnetic fields upon the spectrum. The present authors have conducted experiments with fields up to 21 kOe, and the observed effects were consistent with effective mass $m^* \sim m_0$, but they indicated that fields of $\gtrsim 100$ kOe are required for well-resolved splittings. Such experiments have recently been undertaken.[32]

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[32] D. M. S. Bagguley and G. Vella-Coleiro (private communication).

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Faraday Rotation in ZnO: Determination of the Electron Effective Mass

W. S. Baer

Bell Telephone Laboratories, Murray Hill, New Jersey

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The electron effective mass in ZnO has been determined from free-carrier Faraday rotation. A value of $0.24m_0$ is obtained for the high-frequency band mass, giving a value of $0.29m_0$ for the low-frequency polaron mass. The free-carrier Faraday rotation in a polar compound is well described by a simple Drude theory, although polaron corrections may be important to other optical properties. The interband Faraday rotation in ZnO agrees with theoretical models assuming direct transitions between parabolic valence and conduction bands.

INTRODUCTION

OPTICAL studies[1,2] have shown ZnO to be a direct-gap semiconductor with a single s-like conduction-band minimum at the center of the Brillouin zone. Although this band structure is well established, a number of experiments have given disparate values for the electron effective mass. Measurement of shallow-donor binding energies by Hutson[3] yields a mass of about 0.27 times the free-electron mass, while the exciton binding-energy results of Thomas[1] combined with analysis of the shape of the absorption edge by Dietz, Hopfield, and Thomas[2] give a higher value near 0.38. A different interpretation of the exciton data by Park, Litton, Collins, and Reynolds[4] results in a reduced exciton mass ratio $\mu/m_0 = 0.20$.

The above experiments determine a low-frequency electron effective mass. Since ZnO is a polar compound, one must distinguish between measurements made at frequencies above and below the highest longitudinal optical phonon frequency which occurs at 590 cm^{-1} or 17 μ in ZnO.[5] The low-frequency polaron mass should be larger than the high-frequency bare mass because of coupling of the electron to the longitudinal optical phonons. In ZnO this polaron correction should be, at most, 20%. A determination of the high-frequency electron effective mass was made by Collins and Kleinman,[5] who measured the reflectivity from a ZnO crystal containing 5×10^{18} carriers and applied a Drude-type analysis to the free-electron contribution to the optical constants. Collins and Kleinman reported an effective-mass ratio of 0.06, which is too low to be consistent with the low-frequency results. Recent reflectivity data from $SrTiO_3$,[6] however, suggest that a classical Drude theory may not be adequate to describe free electrons in a polar compound. It may be necessary to calculate polaron contributions to the optical constants in some detail rather than include them in a small effective-mass correction.

Faraday rotation permits an independent measurement of the high-frequency electron effective mass and a test of the Drude theory at high frequencies. Under the conditions $\omega_g > \omega \gg \omega_l$ and $\omega \gg 1/\tau$, where ω is the radiation frequency, $\hbar\omega_g$ the semiconductor band-gap energy, ω_l the longitudinal optical phonon frequency, and τ the electron relaxation time, the interband and free-carrier Faraday rotations should be additive, with the free-carrier rotation displaying a Drude ω^{-2} or λ^2 dependence. This paper reports such results in ZnO and a determination of the electron effective mass in best agreement with that from donor binding-energy measurements.[3] In addition, the interband Faraday rotation is compared with two current theoretical models.

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[1] D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).

[2] R. E. Dietz, J. J. Hopfield, and D. G. Thomas, J. Appl. Phys. **32**, 2282 (1961).

[3] A. R. Hutson, J. Appl. Phys. **32**, 2287 (1961); Phys. Rev. **108** 222 (1957).

[4] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. **143**, 512 (1966).

[5] R. J. Collins and D. A. Kleinman, J. Phys. Chem. Solids **11**, 190 (1959).

[6] A. S. Barker, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Company, Amsterdam, 1965).

EXPERIMENTAL

ZnO single crystals were grown hydrothermally[7] at Bell Telephone Laboratories, either undoped or with $In(OH)_3$ added to the solution. Electron concentrations in the undoped crystals were a few times $10^{15}/cm^3$ and could be increased by subsequent indium diffusion[8] at temperatures above 1000°C. These two methods of indium doping produced crystals with electron concentrations in the 10^{18}–10^{19} cm^3 range having similar electrical and optical properties. Carrier concentrations accurate to about 5% were determined by Hall measurements assuming $R_H=1/Ne$.

Rectangular samples about 10×3×1 mm were cut and polished with the crystal c axis perpendicular to the polished faces. All Faraday-rotation measurements were made with the direction of light propagation and the magnetic field along the c axis, since in other geometries the Faraday rotation is quenched by the natural birefringence of ZnO.[9]

An ac experimental system, shown in Fig. 1, was developed to measure rotations accurately to much less than 1°. Light from a tungsten source and a Jarrell-Ash $\frac{1}{4}$-m monochromator was linearly polarized and focused on the sample in the magnetic field. The light transmitted by the sample passed through a Glan-Thompson calcite polarizer rotating at frequency ω and was focused on a PbS detector. The polarizer was mounted in the inner race of a thrust ball bearing which was driven by a synchronous motor. A reference signal was derived simply from light chopped by a two-bladed chopper attached to the rotating polarizer and detected by a solar cell. The signal and reference, both at frequency 2ω, were amplified and compared in phase using an amplitude-independent phase meter.[10] The frequency could be varied between 20 and 300 cps by varying the speed of the synchronous motor; an optimum signal-to-noise ratio was found at about 200 cps. Rotation of the plane of polarization by the sample thus produced a phase shift between signal and reference which could be measured to better than 0.05°.

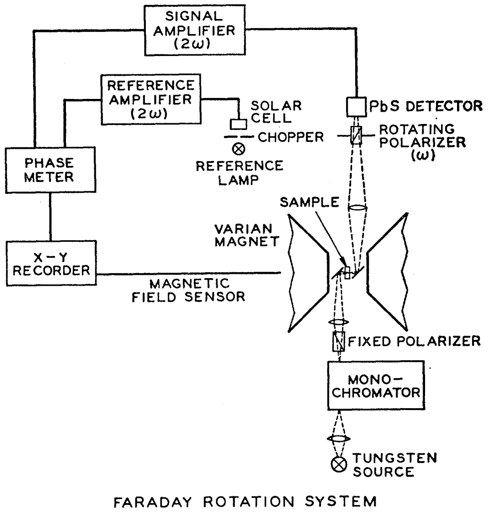

FIG. 1. Schematic of Faraday rotation experimental arrangement.

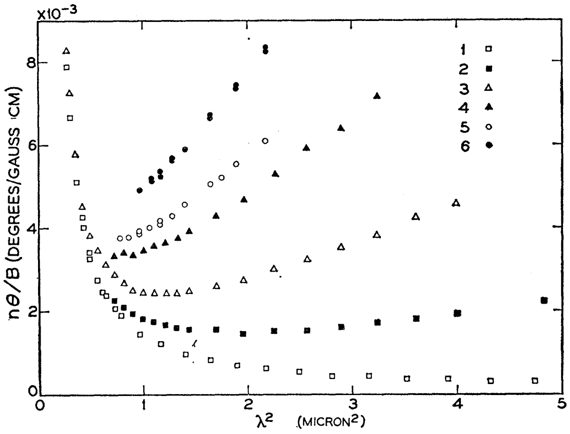

FIG. 2. Faraday rotation versus λ^2 at room temperature and 15 kG for undoped ZnO and five doped samples.

RESULTS

Faraday-rotation measurements made at room temperature on an undoped ZnO sample and five indium-doped samples are shown in Fig. 2. The rotations are normalized to sample thickness and magnetic field strength B and multiplied by the index of refraction n as measured by Bond.[11] All rotations were linear with magnetic field up to the 15 kG maximum. Attenuation due to free-carrier absorption in the doped samples prevented data from being taken beyond 2.4 μ. The carrier concentration and Hall mobility for each sample, measured with the current density perpendicular to the c axis, are given in Table I.

The free-carrier Faraday rotation per unit length θ_c can be determined by subtracting the rotation of the

TABLE I. Electron effective mass in ZnO.

Sample	Carrier concentration (cm^{-3})	Hall mobility $j\perp c$ axis, 300°K (cm^2/V sec)	m^*/m_0
1	6.4×10^{15}	226	…
2	1.6×10^{18}	85	0.24
3	3.6×10^{18}	77	0.23
4	8.6×10^{18}	54	0.25
5	1.1×10^{19}	46	0.25
6	1.5×10^{19}	55	0.25

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[7] R. A. Laudise, E. D. Kolb, and A. J. Caporaso, J. Am. Ceram. Soc. **47**, 9 (1964).

[8] D. G. Thomas, J. Phys. Chem. Solids **9**, 31 (1958).

[9] M. Balkanski and J. J. Hopfield, Phys. Status Solidi **2**, 623 (1962).

[10] Ad-Yu type-524 phase meter, Ad-Yu Electronics, Inc., Passaic, New Jersey.

[11] W. L. Bond, J. Appl. Phys. **36**, 1674 (1965).

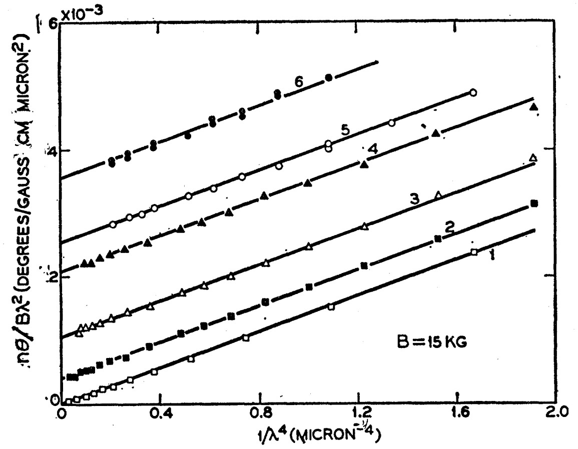

FIG. 3. Graphical separation of the free-carrier and interband Faraday rotations for the samples of Fig. 2. The y intercept for each sample is proportional to $N/(m^*)^2$.

undoped sample from that of each doped sample. This should then be described by the expression derived from Drude theory[12]:

$$\frac{\theta_c n}{B}=\frac{Ne^3}{2\pi c^4(m^*)^2}\lambda^2, \qquad (1)$$

where N is the electron concentration, m^* is the effective mass, and the other symbols have their usual meanings. A more graphic separation of interband and free-carrier rotations is obtained[9] by plotting $\theta n/B\lambda^2$ versus $1/\lambda^4$, as seen in Fig. 3. Away from the band gap the interband rotation goes as λ^{-2}, so that this plot should give parallel straight lines with the results for the undoped sample extrapolating to zero. The effective masses, determined from Eq. (1) and the y intercepts of the lines for each doped sample, are presented in Table I. The interband rotation for samples 1 and 3 is shown in more detail in Fig. 4.

DISCUSSION

Electron Effective Mass

The high-frequency electron effective-mass ratio in ZnO determined from free-carrier Faraday rotation is thus 0.24±0.02. Although the experimental accuracy would permit an estimated error of ±0.01, due primarily to uncertainties in measurement of the carrier concentration, the more conservative estimate is due to three factors. First, the assumption $R_H=1/Ne$ used to calculate carrier concentrations from the Hall data is certainly naive. Actually, $R_H=r/Ne$, where r is a statistical factor near unity determined by the dominant electron-scattering mechanism(s). The relatively low mobilities of the doped ZnO samples would indicate that impurity scattering is important, in which case r might be significantly greater than 1. However, the near degeneracy of these samples even at room temperature implies that r is close to 1. Our best estimate[13] is that r is no greater than 1.1, and, since the effective mass is proportional to $r^{1/2}$, this means an upward correction of no more than 5%, or 0.01.

Second, because of the large electron concentrations required to observe free-carrier Faraday rotation, this effective mass is measured at a Fermi energy up to 0.05 eV above the bottom of the conduction band. Should the conduction-band energy be nonparabolic, due, for example, to the piezoelectric electron-phonon interaction,[14] the effective mass at the bottom of the band

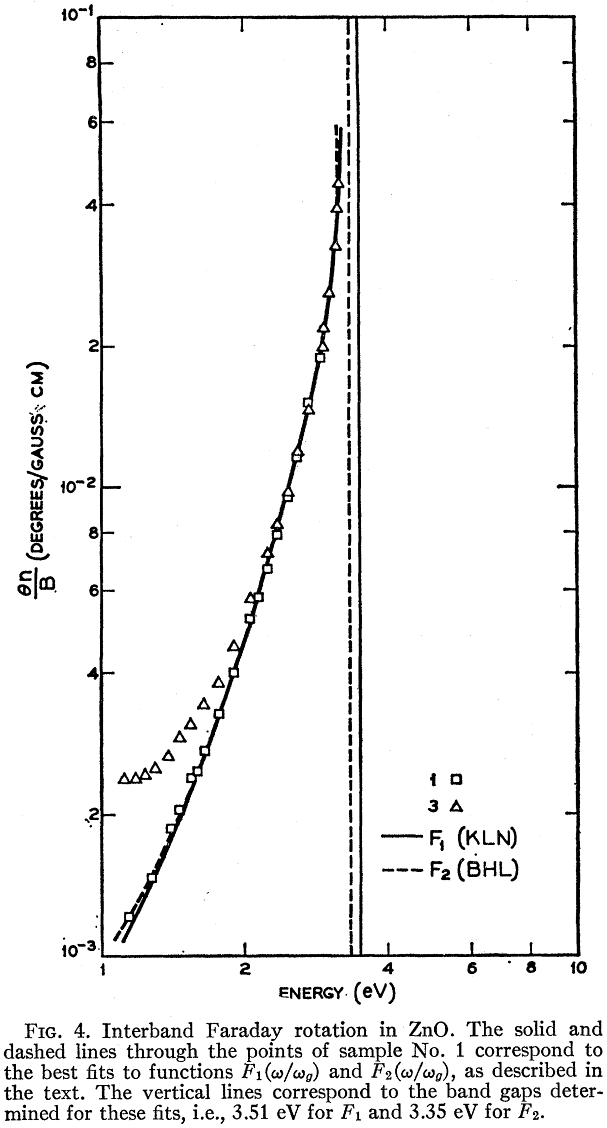

FIG. 4. Interband Faraday rotation in ZnO. The solid and dashed lines through the points of sample No. 1 correspond to the best fits to functions $F_1(\omega/\omega_g)$ and $F_2(\omega/\omega_g)$, as described in the text. The vertical lines correspond to the band gaps determined for these fits, i.e., 3.51 eV for F_1 and 3.35 eV for F_2.

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[12] M. J. Stephen and A. B. Lidiard, J. Phys. Chem. Solids **9**, 43 (1958).

[13] A. C. Beer, *Galvanomagnetic Effects in Semiconductors* (Academic Press Inc., New York, 1963), p. 111ff.

[14] W. S. Baer and R. N. Dexter, Phys. Rev. **135**, A1388 (1964); G. D. Mahan and J. J. Hopfield, Phys. Rev. Letters **12**, 241 (1964).

might differ slightly from our quoted value. Cyclotron resonance would be the best method of measuring the effective mass at the conduction-band minimum. Unfortunately, since the low-temperature mobility in ZnO is intrinsically limited by piezoelectric scattering,[3] the cyclotron-resonance criterion $\omega\tau>1$ will be difficult to realize. Using Hutson's estimate[3] for the piezoelectric relaxation time in ZnO,

$$\tau_p=1.6\times10^{-12}(m^*/m)^{-1/2}T^{-1/2}, \tag{2}$$

where T is the Kelvin temperature, one finds that even at 1°K a working frequency of more than 200 Gc/sec would be required to make $\omega\tau\approx4$ in order to observe a well-defined cyclotron resonance.

Finally, these Faraday rotation experiments measure the transverse effective mass in an ellipsoidal valley whose major axis is along the crystal c axis. The conduction band in ZnO should be nearly spherical, but a small effective-mass anisotropy may exist. An anisottropy similar to that seen in CdS [14] $(m_l^*/m_t^*=0.9)$ would make the density-of-states effective mass about 4% smaller than the transverse mass.

Our value of the high-frequency electron effective mass can be combined with the expected polaron correction[15] in ZnO to give a low-frequency polaron mass m_p^*. For weak coupling between electrons and longitudinal optical phonons, the polaron mass is given by $m_p^*/m^*=(1-\alpha/6)^{-1}$, where α is the familiar Frohlich coupling constant

$$\alpha=\frac{e^2}{\hbar}\left(\frac{m^*}{2\hbar\omega_l}\right)^{1/2}\left(\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right),$$

ϵ_0 is the low-frequency dielectric constant, and $\epsilon_\infty=n^2$. For ZnO, $\alpha\approx2.0\ (m^*/m_0)^{1/2}$, so that for a high-frequency mass ratio of 0.24, $\alpha\approx1.0$ and $m_p^*/m_0=0.29\pm0.02$. This value is in good agreement with the donor binding-energy results of Hutson,[3] but it lies between the masses derived from the two interpretations of the exciton data. Dietz, Hopfield, and Thomas[2] point out, however, that the ZnO exciton binding energy may be larger than the hydrogenic value by a substantial central-cell correction. Such a correction would bring their electron effective mass to a value consistent with these Faraday rotation results.

Drude and Polaron Theories

The free-carrier Faraday rotation in ZnO is well described by the simple Drude theory of Eq. (1). Any discrepancy would show up as a wavelength dependence different from the observed λ^2 dependence. For example, the free-carrier absorption in ZnO varies as $\lambda^{2.5-3.0}$ in the 1–10-μ region.[15] Theories which treat electron scattering from longitudinal optical phonons[16,17] predict a $\lambda^{2.5}$ dependence of the high-frequency free-carrier absorption coefficient.

It is easy to see why a Drude theory is adequate for free-carrier Faraday rotation but not for free-carrier absorption. Faraday rotation measures the difference in index of refraction between right and left circular polarizations, which, in regions of low absorption, depends only on the real part of the dielectric function ϵ'. Absorption, on the other hand, is proportional to the imaginary part of the dielectric function ϵ''. A classical high-frequency expansion of the dielectric function in powers of $1/\omega\tau$ gives a zeroth-order term which is purely real. For the case of electron scattering from polar phonons, McCumber[17] has derived expressions for the free-carrier dielectric function:

$$\begin{aligned}\epsilon'&=-\frac{\omega_p{}^2}{\omega^2}\left[1+\frac{2\alpha}{3}P\left(\frac{\omega}{\omega_l},\frac{\omega_p}{\omega_l},\frac{\epsilon_\infty}{\epsilon_0}\right)\right],\\ \epsilon''&=-\frac{\omega_p{}^2}{\omega^2}\left[\frac{1}{\omega\tau}+\frac{2\alpha}{3}I\left(\frac{\omega}{\omega_l},\frac{\omega_p}{\omega_l},\frac{\epsilon_\infty}{\epsilon_0}\right)\right],\end{aligned} \tag{3}$$

where $\omega_p{}^2=4\pi Ne^2/m^*$ and the functions $P(\omega/\omega_l,\cdots)$ and $I(\omega/\omega_l,\cdots)$ each go as $(\omega/\omega_l)^{-3/2}$ at high frequencies. In both expressions the first term is the classical Drude term and the second represents the polaron correction. Thus, at high frequencies the polaron term may be small compared to unity in ϵ' but still dominate the Drude $1/\omega\tau$ term in ϵ''.

Reflectivity depends on both real and imaginary dielectric constants, so that considerable care must be exercised in determining an effective mass from the high-frequency reflectivity if polaron contributions are important.[18] Free-carrier Faraday rotation, however, remains an accurate method of measuring effective masses even in strongly polar materials.

Interband Faraday Rotation

The interband Faraday rotation in II-VI compounds has been investigated previously by Ebina, Koda, and Shionoya[19] and by Balkanski, Amzallag, and Langer.[20] ZnO was included only in the former study. The results of both groups were interpreted in terms of theoretical models developed by Boswarva, Howard, and Lidiard[21] (BHL) and by Kolodziejczak, Lax, and Nishina[22] (KLN).

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[15] D. G. Thomas, J. Phys. Chem. Solids **10**, 47 (1959).

[16] V. L. Gurevich, I. G. Lang, and Yu. A. Firsov, Fiz. Tverd. Tela **4**, 1252 (1962) [English transl.: Soviet Phys.—Solid State **4**, 918 (1962)].

[17] D. E. McCumber (to be published).

[18] Preliminary reflectivity measurements on a ZnO sample from the same boule as our sample No. 3 ($N\sim3.6\times10^{18}/\text{cm}^3$) show a minimum near 12 μ, indicating an electron effective mass greater than 0.2 m_0. These experimental data differ significantly from those of Collins and Kleinman (Ref. 5), who reported a reflectivity minimum near 6 μ for a ZnO sample containing 5×10^{18} carriers [A. S. Barker, Jr. (private communication)].

[19] A. Ebina, T. Koda, and S. Shionoya, J. Phys. Soc. Japan **26**, 1497 (1965).

[20] M. Balkanski, E. Amzallag, and D. Langer, J. Phys. Chem. Solids **27**, 299 (1966).

[21] I. M. Boswarva, R. H. Howard, and A. B. Lidiard, Proc. Roy. Soc. (London) **A269**, 125 (1962).

[22] J. Kolodziejczak, B. Lax, and Y. Nishina, Phys. Rev. **128**, 2655 (1962).

The rotation arising from direct interband transitions between parabolic valence and conduction bands can be expressed in the general form

$$\theta n/B = KF(\omega/\omega_g)\,, \tag{4}$$

where K is a constant independent of the radiation frequency and band-gap energy. The function $F(\omega/\omega_g)$ must vanish at low frequencies as ω^2. Assuming that transitions from each valence band individually give the proper low-frequency dependence, KLN derive a function (following the notation of Roth[23])

$$F_1(x) = \frac{1}{x}\left(\frac{1}{(1-x)^{1/2}} - \frac{1}{(1+x)^{1/2}}\right) - \frac{4}{x^2} \times [2-(1-x)^{1/2}-(1+x)^{1/2}]\,. \tag{5}$$

BHL, on the other hand, assume that a summation over all valence bands is required. They obtain

$$F_2(x) = \frac{1}{x}\left(\frac{1}{(1-x)^{1/2}} - \frac{1}{(1+x)^{1/2}}\right) - 1\,. \tag{6}$$

These two functions differ only slightly in their spectral dependence, but F_2 is greater than F_1 at all frequencies below ω_g and approaches $2F_1$ for small ω.

The interband rotation of Fig. 4 was fitted to both F_1 and F_2 in the sense of least squares, using K and ω_g as adjustable parameters. The values of K and ω_g thus obtained are given in Table II. A good fit can be made for either function. Ebina *et al.* did not report a fit to F_1 for their ZnO data, but their value of $\hbar\omega_g$ for F_2, 3.35 eV, agrees with the present results. Both Ebina *et al.* and Balkanski *et al.* favored F_2 over F_1, chiefly because F_2 in most II-VI compounds gave a band-gap value closer to that determined from other optical data. In the case of ZnO, however, the band-gap value corresponding to F_1 appears to give somewhat better agreement with the band gap accurately measured from exciton experiments.[1,4]

TABLE II. Interband Faraday rotation parameters.

	K (deg/G cm)	$\hbar\omega_g$ (eV)
Faraday rotation fit to F_1	3.1×10^{-2}	3.51
Faraday rotation fit to F_2	1.5×10^{-2}	3.35
$\hbar\omega_g$ from exciton data	···	3.44
K calculated from Eq. (7)	3.4×10^{-2}	···

The calculated value of K for ZnO also agrees best with the experimental value for function F_1. According to BHL, this constant is given by

$$K = \frac{e^2|p_{cv}{}^x|^2\beta}{\sqrt{2}m_0{}^2c\hbar^2}\left(\frac{\mu}{\hbar\omega_g}\right)^{3/2}(g_c+g_v)\,, \tag{7}$$

where β is the Bohr magnetron, μ is the reduced effective mass for electrons and holes, g_c and g_v are the conduction- and valence-band g factors, respectively, and $p_{cv}{}^x$ is the matrix element of $-i\hbar(\partial/\partial x)$ between valence and conduction states at the zone center. To compute K we take a reduced effective mass of 0.20, obtained from the electron effective mass of 0.24 and the mass ratio $m_v/m_h = 0.21$ determined by Dietz *et al.*[2] Using $|p_{cv}{}^x| = 1.53\times10^{-38}$,[20] $\hbar\omega_g = 3.44$ eV,[1,4] and $(g_c+g_v) = 3.7$,[24] a value of $K = 3.4\times10^{-2}$ is obtained. This is in good agreement with the value determined from the fit to F_1, but does not agree well with the F_2 fit. The data in ZnO thus support the theoretical results of KLN[22] and of Roth[23] in which transitions from each valence band to the conduction band contribute individually to the interband Faraday rotation.

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[24] J. J. Hopfield and D. G. Thomas, Phys. Rev. Letters **15**, 22 (1965).