PHYSICAL REVIEW B VOLUME 4, NUMBER 2 15 JULY 1971

Effects of Uniaxial Stress on the Free and Bound Exciton in GaSb at 1.7 °K

Fred H. Pollak*†
Department of Physics, Brown University, Providence, Rhode Island 02912

and

R. L. Aggarwal
Francis Bitter National Magnet Laboratory, ‡
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 15 March 1971)

The effect of a static compressive uniaxial stress on the free and bound excitons in GaSb at 1.7 °K has been measured using wavelength-modulated reflectivity and stresses of up to 5×10^9 dyn cm^{-2} applied along [111], [001], and [110] directions with light polarized parallel and perpendicular to the stress axis. From the observed splittings and shifts of the free-exciton line (α), we have determined the hydrostatic- and shear-deformation potentials of the direct edge. These results are compared with those of other workers. The bound-exciton line (γ) exhibits no splitting but only an isotropic shift to higher energies with stress. The lack of splitting of this line implies that previous suggestions as to the nature of the complex giving rise to this line should be reexamined.

I. INTRODUCTION

The application of a uniaxial stress to a solid produces a strain which, in general, reduces the symmetry of the material and results in significant changes in the electronic energy levels. It is thus possible to determine deformation potentials and to gain information about the symmetry properties of the band-edge optical transitions.[1] In particular, a uniaxial stress results in the splitting of the degenerate valence-band edge at $\vec{k}=0$ in the diamond- and zinc-blende-type semiconductors. The removal of this degeneracy manifests itself in the stress dependence of the optical properties associated with the band-edge transitions. In this paper we report measurements on the effects of static uniaxial stress on the wavelength-modulated reflectivity spectra of the free and bound excitons associated with the direct edge ($\Gamma_8 \rightarrow \Gamma_6$ in double group notation) in GaSb at 1.7 °K. The free exciton is an electron-hole pair in a pure crystal whereas a bound exciton is an electron-hole pair localized near an imperfection in the crystal.

The stress dependence of the free exciton provides information concerning the behavior of the electronic bands of the intrinsic material. From the stress-induced splitting and shifts of the free exciton the hydrostatic- and shear-deformation potentials of the $\Gamma_8 \rightarrow \Gamma_6$ gap can be determined. Although the shear-deformation potentials of this transition in GaSb have been determined by other techniques[2–4] there is a wide discrepancy in some of these values which led us to undertake another independent investigation of these quantities with stresses considerably higher than those used in previous work. In addition, the stress dependence of the bound exciton can be used to gain information concerning the "generic center" to which the electron-hole pair is bound.[5] The results of this experiment are not consistent with the previous identification of the bound-exciton line as being due to an ionized acceptor-exciton complex.[6,7]

II. EXPERIMENTAL DETAILS

The samples used in this investigation were oriented with x rays to ± 1° and cut into parallelepipeds of approximate dimensions $20 \times 1.5 \times 1.5$ mm. The samples were *p* type with a carrier concentration of $\approx 2 \times 10^{16}$ cm^{-3} and a mobility of ≈ 3000 cm^2/V sec at 77 °K. The material was mechanically polished and then etched in a 10 : 1 methanol-bromine solution for approximately 40 sec. The procedures for mounting the sample and applying the stress have been described elsewhere.[8] The stressing frame was lowered into a metal Dewar with sapphire windows; the Dewar was filled with liquid helium and pumped to a vapor pressure corresponding to 1.7 °K. Wavelength modulation of the monochromatic light beam was produced by modifying a Perkin-Elmer single-pass grating monochromator, model No. 99G, as described in Ref. 9. The modulation amplitude was about 0.6 Å at 100 Hz. The entire optical system (monochromator, mirrors, Dewar tail, detector, etc.) was placed inside a large light-tight box which was continuously flushed with dry air in order to minimize the structure in the spectrum due to water vapor. The light was polarized parallel or perpendicular to the stress axis by means of a Glan-Thompson prism. The prism polarizer was used to avoid the large interference fringe effects observed with sheet polarizers such as Polariod HR-2. The light was detected with a PbS photoconductive cell operated at room temperature.

III. MEASUREMENTS AND INTERPRETATION

In the absence of uniaxial stress the valence-band edge in a zinc-blende-type material is a fourfold degenerate multiplet with symmetry $\Gamma_8(J=\frac{3}{2}, M_J=\pm\frac{3}{2}, \pm\frac{1}{2}$ in spherical notation). The application of a uniaxial stress splits this multiplet and shifts the "center of gravity" of the multiplet relative to the Γ_6 conduction band. For the compressive stress used in this experiment the lower split band at $\vec{k}=0$ (v_2 in the notation of Refs. 1 and 8) is a pure $|\frac{3}{2}, \pm\frac{3}{2}\rangle$ state while the upper band (v_1) is mainly $|\frac{3}{2}, \pm\frac{1}{2}\rangle$ with a stress-induced admixture of $|\frac{1}{2}, \pm\frac{1}{2}\rangle$ (spin-orbit split band v_3).[10] It has been shown that for stress X parallel to [001] or [111] the stress-induced change in the $\Gamma_8 \rightarrow \Gamma_6$ energy gap, to second order in stress, is given by[1]

$$\Delta(E_c - E_{v1}) = \delta E_H - \tfrac{1}{2}\delta E_s + \tfrac{1}{2}(\delta E_s')^2/\Delta_0 + \cdots , \qquad (1)$$

$$\Delta(E_c - E_{v2}) = \delta E_H + \tfrac{1}{2}\delta E_s , \qquad (2)$$

where Δ_0(= 0.75 eV[11]) is the spin-orbit splitting of the valence bands at $\vec{k}=0$ and

$$\delta E_H = a(S_{11}+2S_{12})\, X = -\frac{\partial E_g}{\partial P} P , \qquad (3)$$

$$\delta E_s = \begin{cases} 2b(S_{11}-S_{12})X , & X \parallel [001] \\ (d/\sqrt{3})S_{44}X , & X \parallel [111] \end{cases} \qquad (4)$$

$$\delta E_s' = \begin{cases} 2b'(S_{11}-S_{12})X , & X \parallel [001] \\ (d'/\sqrt{3})S_{44}X , & X \parallel [111] . \end{cases} \qquad (5)$$

In the above equations δE_H is the shift of the gap E_g due to the hydrostatic pressure component of the strain, while δE_s and $\delta E_s'$ represent the effect of the shear component of the strain,[1,12] and S_{ij} are elastic compliance constants.[13] The difference between the primed and unprimed quantities is due to the stress dependence of the spin-orbit interaction.[12] Although we have observed the nonlinear shift due to the quadratic term in Eq. (1) we have not been able to measure it with sufficient accuracy to determine the difference between the unprimed and primed parameters. Since we have determined only the parameters associated with the linear splitting, only the unprimed quantities will be considered in the following discussion.

For the case of stress parallel to [110] the situation is somewhat more complex since for this stress direction the crystal is, in general, biaxial (i.e., M_J is not a good quantum number). However, in the case that there is equal band splitting under [001] and [111] stress ($\delta E_s^{001} = \delta E_s^{111}$) the crystal is uniaxial also for stress along [110]. Since this is only approximately the case for GaSb the stress dependences of the bands for this stress direction are given by[8,10]

$$\Delta(E_c - E_{v1}) = \delta E_H - \tfrac{1}{4}[(\delta E_s^{001})^2 + 3(\delta E_s^{111})^2]^{1/2} - \tfrac{1}{32}(\delta E_s^{001} + 3\delta E_s^{111})^2/\Delta_0 + \cdots , \qquad (6)$$

$$\Delta(E_c - E_{v2}) = \delta E_H + \tfrac{1}{4}[(\delta E_s^{001})^2 + 3(\delta E_s^{111})^2]^{1/2} + \cdots , \qquad (7)$$

where we have neglected terms of the order $(\delta E_s^{001} - \delta E_s^{111})^2/\Delta_0$ and higher.

The effects of the stress on the free exciton are expected to be very nearly equal to those of the electronic bands, as discussed above, since the band splittings and shifts are considerably larger than any stress-induced changes in the exciton binding energy.[3,14,15]

Shown in Fig. 1 are the wavelength-modulated reflectance spectra of GaSb at 1.7 °K in the energy range 0.78–0.86 eV for $X=0$, 1.95×10^9 dyn cm^{-2}, and 5.85×10^9 dyn cm^{-2} along a [111] direction with the electric vector of the incident radiation polarized parallel and perpendicular to the stress axis. No polarization effects were observed at $X=0$. In the zero stress spectrum the line at 0.8090 eV corresponds to the free-exciton transition. Following the notation of Johnson *et al.*[6] this line has been labeled α. The line observed at 0.7947 eV in the zero stress spectrum corresponds to the bound exciton γ in the same notation.

The application of the uniaxial stress causes the α line to split into two components, labeled α_1 and α_2. The α_1 line is observed for both polarizations while α_2 is seen for the perpendicular polarization only. From this we identify α_1 and α_2 as corresponding to the free-exciton transitions associated with valence bands v_1 and v_2, respectively. It should be pointed out that for both polarizations the α_1 line is observed at the same energy, within the experimental error of about 0.3 meV. The γ line does not split under the action of the stress but moves to higher energies, eventually merging with the α_1 line at stresses above $\approx 3\times10^9$ dyn cm^{-2}. Similar results have been obtained for the α and γ lines for stress parallel to [001] and [110].

In Figs. 2–4 are plotted the energies of the γ, α_1, and α_2 lines as a function of uniaxial stress along [111], [001], and [110]. For all three stress directions the energy of α_2 varies linearly with stress while α_1, which has a linear stress dependence at low stresses, exhibits a nonlinear behavior at stress above $\approx 2\times10^9$ dyn cm^{-2}. The linear stress dependence of α_1 and α_2 is indicated by the solid lines, which have been obtained from a least-squares fit (linear for α_2 and quadratic for α_1).

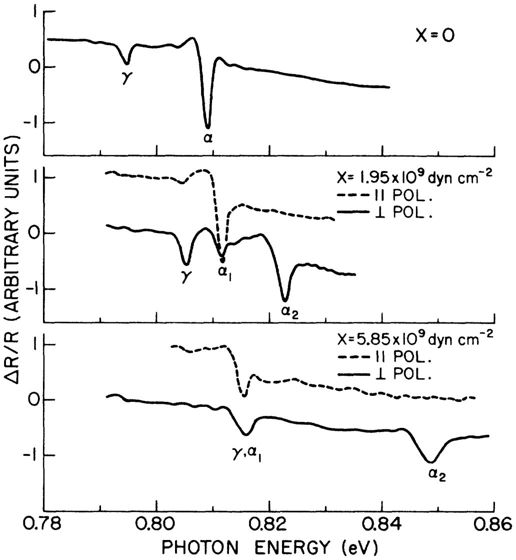

FIG. 1. Wavelength-modulated reflectance spectra for the free (α) and bound (γ) excitons of GaSb at 1.7 °K at $X=0$, 1.95×10^9, and 5.85×10^9 dyn cm^{-2} along [111] for light polarized parallel and perpendicular to the stress axis. At the highest stress γ and α_1 have already merged. The vertical displacement between the parallel- and perpendicular-polarization spectra is due to a polarization-dependent background.

The stress dependence of the γ line is very nearly the same for all three stress directions.

Listed in Table I are the values of the deformation potentials $(\partial E_g/\partial P)$, d, and b as determined from a least-squares fit of the experimental data

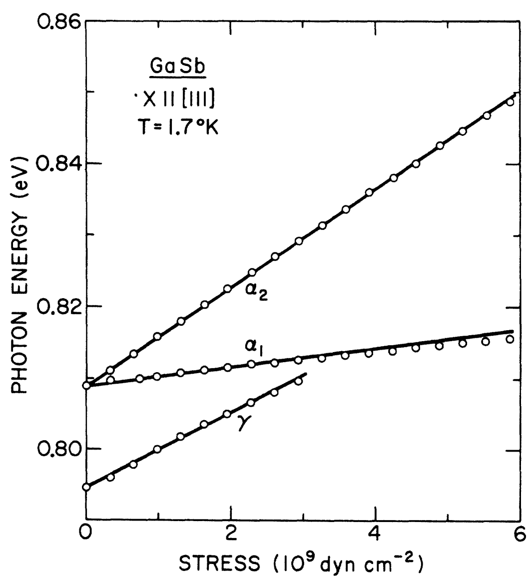

FIG. 2. Energies of the γ, α_1, and α_2 spectral lines as a function of uniaxial stress along [111].

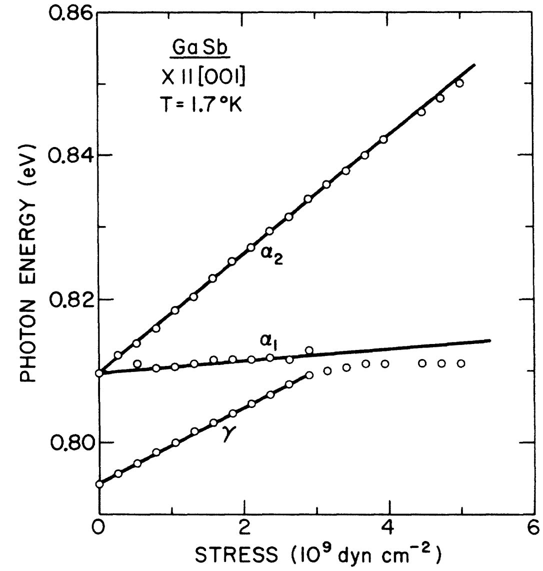

FIG. 3. Energies of the γ, α_1, and α_2 spectral lines as a function of uniaxial stress along [001].

for the free exciton for stress parallel to [111] and [001] as shown in Figs. 2 and 3, respectively, using Eqs. (1)–(4). Also listed are the results of other workers. Our values of b and d are in good agreement with those of Ref. 3. The value of $[b^2(S_{11}-S_{12})^2+\frac{1}{4}d^2S_{44}^2]^{1/2}$ is also given for comparison with the [110] data. Also given in Table I are the values of $(\partial E_g/\partial P)$ and $[b^2(S_{11}-S_{12})^2+\frac{1}{4}d^2S_{44}^2]^{1/2}$ as obtained

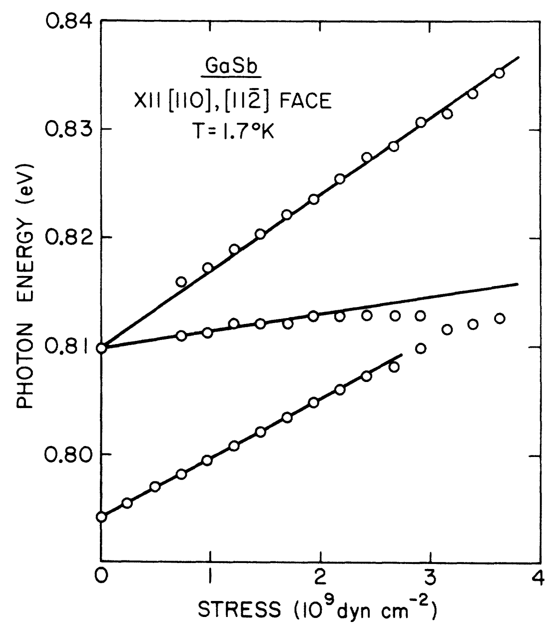

FIG. 4. Energies of the γ, α_1, and α_2 spectral lines as a function of uniaxial stress along [110].

TABLE I. Deformation potentials of the direct edge of GaSb obtained in this experiment and in previous work.

Deformation potential	This work	Previous work
$(\partial E_g/\partial P)$	12.2 ± 0.6[a]	14.5[b]
(10^{-6} eV bar^{-1})	13.6 ± 0.6[c]	14 (Ref. 3)
	13.0 ± 0.6[d]	
d (eV)	-4.2 ± 0.2[a]	-4.6 (Ref. 3)
		-8.35 ± 1.7 (Ref. 2)
		-3.5 ± 0.4 (Ref. 4)
b (eV)	-1.8 ± 0.1[c]	-2 (Ref. 3)
		-3.3 ± 0.6 (Ref. 2)
		-2.2 ± 0.2 (Ref. 4)
$[b^2(S_{11}-S_{12})^2+\frac{1}{4}d^2S_{44}^2]^{1/2}$	-5.5[d]	
(10^{-12} eV cm^2 dyn^{-1})	-6.0[a,c]	

[a][111] stress measurements.
[b]R. Zallen and W. Paul, Phys. Rev. 155, 703 (1967).
[c][001] stress measurements.
[d][110] stress measurements.

from the [110] data (Fig. 4) and Eqs. (6) and (7). The measurement of the latter quantity provides an internal check on the values of b and d.

Recently Gavini and Cardona (GC)[2] as well as Lawaetz[16] have developed theories for the shear-deformation potentials. The former authors have proposed a simple point-ion model to explain the observed trend of the deformation potentials with ionicity while Lawaetz has developed a theory on the basis of Phillip's ionicity scheme. Gavini and Cardona find that the change in b and d in going from the group IV to III-V semiconductors is given by

$$\Delta b = -0.23 \text{ eV} \tag{8}$$

and

$$\Delta d = -0.69 \text{ eV} . \tag{9}$$

The parameters of the group IV material corresponding to GaSb are an average of the parameters of Ge and α-Sn. While for Ge both b and d have been measured for α-Sn only b ($= -2.3\pm0.5$ eV[17]) has been determined. Taking $b=-2.6\pm0.2$ eV for Ge[8] and the above value of b for α-Sn the theory of GC predicts $b=-2.7\pm0.35$ for GaSb, which is higher than our experimentally determined value. However, the GC theory is more successful in predicting the ratio d/b. Since d for α-Sn has not been determined by taking the b and d values of Ge from Ref. 8, Eqs. (8) and (9) yield $d/b=1.9\pm0.3$ as compared with our measured ratio of 2.3 ± 0.2. The theory of Lawaetz predicts $b=-2.3$ eV and $d=-5.2$ eV for GaSb. While these values are slightly higher than those measured in this experiment, Lawaetz's ratio of $d/b=2.3$ is in good agreement with our measurements.

It has been observed by Langer *et al.*[18] and Gilleo *et al.*[19] that the energy of the α_1 line for several zinc-blende-type materials is somewhat different for the two polarizations; the perpendicular-polarization line occurs at the lower energy. This difference has been attributed to the combined effects of the uniaxial stress and the electron-hole spin-exchange interaction.[18,19] Since we have not observed this effect (to within our experimental error of 0.3 meV) we conclude that the spin-exchange parameter in GaSb is less than about 0.3 meV.

As mentioned above, the main features of the stress dependence of the γ line are (a) lack of observed splitting for any of the three stress directions, (b) almost isotropic motion to higher energies with a slope approximately equal to that of the center of gravity for the α_1 and α_2 components in the low-stress region ($X < 3\times10^9$ dyn cm^{-2}), and (c) observed merging with the α_1 line (within the linewidth of 2 meV) at higher stresses. The above results, particularly the lack of splitting, appear to be somewhat surprising in view of the previous experimental work[6,7] and theoretical considerations[5,20] of the bound excitons in these materials. The consideration common to all this previous work has been the identification of a bound exciton as being a free exciton bound to one of the following centers: neutral or ionized donor or acceptor. Based on group-theoretical analysis, Bailey[21] has shown that the line associated with any one of these four complexes (bound excitons) is expected to split into two or more components and exhibit polarization effects under the action of uniaxial stress. The fact that we have not observed any splitting of the γ line suggests that the identification of this optical structure should be reexamined. The present data should stimulate further theoretical interest in this problem.

ACKNOWLEDGMENTS

We are grateful to R. Ranvaud and L. V. Sousa for valuable assistance with the measurements and sample preparation. The authors have benefited from discussions with Professor M. Cardona, Professor A. K. Ramdas, and K. J. Button.

*Work supported in part by the Advanced Research Projects Agency.
†Visiting Scientist, Francis Bitter National Magnet Laboratory, MIT., Cambridge, Mass.
‡Supported by the U. S. Air Force Office of Scientific Research.

[1]See, for example, F. H. Pollak, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge*, 1970 (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1970), p. 407.
[2]A. Gavini and M. Cardona, Phys. Rev. B 1, 672 (1970).
[3]C. Benoit á la Guillaume and P. Lavallard, J. Phys. Chem. Solids 31, 411 (1970).
[4]R. L. Aggarwal and M. Reine (private communication).

[5]For a discussion of bound-exciton complexes see, for example, J. J. Hopfield, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris*, 1964 (Dunod, Paris, 1964), p. 725.

[6]E. J. Johnson, I. Filinski, and H. Y. Fan, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter*, 1962 (The Institute of Physics and the Physical Society, London, 1962), p. 375; E. J. Johnson and H. Y. Fan, Phys. Rev. 139, A1991 (1965).

[7]E. J. Johnson, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1967), Vol. 3, p. 153.

[8]F. H. Pollak and M. Cardona, Phys. Rev. 172, 816 (1968); in the second of Eqs. (13), the coefficient in front of the term "$(\delta E_{001}+3\delta E_{111})^2/\Delta_0$" should read $-\frac{1}{32}$ instead of $-\frac{1}{4}$.

[9]R. L. Agarwal and M. Reine, Bull. Am. Phys. Soc. 14, 736 (1969).

[10]H. Hasegawa, Phys. Rev. 129, 1029 (1963).

[11]M. Reine, R. L. Aggarwal, and B. Lax, Solid State Commun. 8, 35 (1970).

[12]K. Suzuki and J. C. Hensel, Bull. Am. Phys. Soc. 14, 113 (1969).

[13]For the values of the S_{ij} used in this work see H. B. Huntington, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7.

[14]I. Balslev, Phys. Rev. 143, 636 (1966).

[15]L. D. Laude, F. H. Pollak, and M. Cardona, Phys. Rev. B (to be published).

[16]P. Lawaetz, Phys. Rev. B (to be published).

[17]B. J. Roman and A. W. Ewald, Bull. Am. Phys. Soc. 13, 408 (1968); and private communication.

[18]D. W. Langer, R. N. Euwema, K. Era, and T. Koda, Phys. Rev. B (to be published).

[19]M. A. Gilleo, P. T. Bailey, and D. E. Hill, J. Luminescence 1/2, 562 (1970).

[20]R. R. Sharma and S. Rodriguez, Phys. Rev. 153, 823 (1967); 159, 649 (1967).

[21]P. T. Bailey, Phys. Rev. B 1, 588 (1970).

PHYSICAL REVIEW B VOLUME 4, NUMBER 2 15 JULY 1971

Study of the Shape of Cyclotron-Resonance Lines in Indium Antimonide Using a Far-Infrared Laser

J. R. Apel* and T. O. Poehler
Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910

and

C. R. Westgate and R. I. Joseph
The Johns Hopkins University, Baltimore, Maryland 21218
(Received 18 May 1970)

An experimental and theoretical study of the shape of cyclotron-resonance lines in high-purity n-type InSb has been conducted at cryogenic temperatures, using a repetitively pulsed far-infrared gas laser at $\lambda = 336.8$, 118.6, 78.4, 55.1, and 47.5 μm. Measurements of the 4.2 °K effective mass and scattering times have been obtained as a function of frequency via transmission through a thin sample arranged in the Faraday configuration. For carriers at a concentration of 1×10^{14} cm^{-3}, one obtains a zero-field 4.2 °K effective-mass ratio of 0.0139 ± 0.0002. At laser frequencies below the optical-phonon frequencies, an anomalous narrowing of the lines was observed whose width implies a collision time τ near 10^{-11} sec, which is about 160 times longer than the value derived from dc magnetoconductivity at 20 kG. The theoretical analysis uses the quantum plasma dielectric tensor $\overleftrightarrow{\epsilon}(\vec{q}, \omega)$ complete with a collisional energy term of the form $\Delta + i\Gamma$ and a nonparabolic energy expression for conduction-band electrons. The dispersion equations for photon propagation in the Faraday and Voigt geometries are then solved to obtain the cyclotron-resonance line shape, using both constant- and energy-dependent collision times. It is shown that the observed line shapes and widths may be predicted without adjustable parameters to within the experimental error by a scattering time $\tau(\vec{B}, k_z)$, which describes adiabatic and nonadiabatic Coulomb scattering. Thus the narrowed lines are attributed to the reduced scattering rate from long-range ionized impurities that occurs in the quantum limit $\hbar\omega_c > k_B T$. Another experiment, done in the Voigt configuration at 77 °K using $\lambda = 336.8$ μm, yielded at 4.5-kG mass ratio of 0.0132 ± 0.0002 and a scattering time of 2.75×10^{-12} sec, which is within a factor of 2 of the zero-field mobility time.

I. ON INTENT AND EXTENT

There is much information on the nature of carrier states to be obtained from a detailed examination of the shape of a cyclotron-resonance curve. In principle, a single precise measure of cyclotron resonance that is used in conjunction with a suitable theory would allow one to deduce the numerical