Exciton and Magneto-Absorption of the Direct and Indirect Transitions in Germanium*

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Low-temperature, high resolution experiments on magneto-absorption effects in germanium have resolved fine structure in the direct interband transition and, in addition, have revealed structure in the indirect transition. In each case, exciton absorption was also observed and the experimental binding energy of the lowest exciton level was measured. The values of the direct-transition energy gap found were (1) at 1.5°K and 4.2°K, 0.898±0.001 ev; (2) at 77°K, 0.889±0.001 ev; and (3) at 293°K, 0.805±0.001 ev. The binding energy of the "direct" exciton was 0.0025±0.0005 ev. The magneto-absorption at photon energies slightly greater than the indirect energy gap has the appearance of a series of absorption edges unlike the series of absorption maxima observed in the direct case. The experimental findings are consistent with the theoretical predictions described in the following article. The detailed spectra were observed by means of a new low-temperature, high-resolution magneto-spectrophotometric system providing spectral resolution of the order of 10^{-4} electron volt and steady magnetic fields up to 38.9 kilogauss. An accurate measure of the minimum of the conduction band was obtained by extrapolating a plot of the photon energies of the centers of the absorption edges as a function of magnetic field to zero field. The indirect energy gap, 0.744±0.001 ev at 1.5°K, was then obtained by subtracting the energy of the emitted longitudinal acoustical phonon which is involved in the indirect transition. This accurate value of the energy gap permits the measurement of the exciton binding energy. The "indirect" exciton ground state was found to be split into two components 0.0011 ev apart with a mean value of the binding energy of 0.0025±0.0004 ev. These values are consistent with preliminary theoretical calculations. The Zeeman effect of both the direct and indirect exciton absorptions has also been measured and found to be quadratic in accordance with theory.

I. INTRODUCTION

FROM experimental and theoretical considerations we have selected germanium as the most suitable material for the initial studies of magneto-absorption phenomena. The detailed theory for the oscillatory magneto-absorption of the direct transition[1] indicated that there should be fine structure in the spectrum which had not been observed in the initial room temperature experiments using a prism spectrometer.[2,3] In this paper we shall describe the observation of this fine structure at low temperature using a high-resolution magneto-spectrophotometric system, as well as the observation of the direct-transition exciton lines and their Zeeman effect, together with the determination of the binding energy of the ground state of this exciton.[4] We shall also describe experiments on the magneto-absorption of the indirect transition in germanium and attempts to observe the same in silicon.

The theory which has been worked out for the magneto-absorption of the indirect transition[1] shows that the spectrum does not consist of a series of transmission minima or oscillations as in the direct transition,[3] but rather as abrupt changes in transmission having the appearance of a series of steps. This characteristic "staircase" spectrum has now been observed with the low-temperature, high-resolution system. Perhaps one of the most interesting consequences of these low-temperature measurements was the confirmation of the existence of the indirect-transition exciton absorption reported by Macfarlane, McLean, Quarrington, and Roberts (MMQR),[5] the observation of fine structure in its absorption, and the measurement of its Zeeman effect and binding energy.

The advantage of the magneto-absorption technique is that it yields an accurate experimental determination of the binding energy of the "direct" and "indirect" excitons. In addition, the observation of the quadratic Zeeman effect further demonstrates the existence of these excitons and indicates that their energy level structure is like that of a hydrogen atom in a dielectric medium.

II. EXPERIMENTAL TECHNIQUE

In order to carry out these experiments, it was necessary to rebuild the magneto-spectrophotometric system described previously.[3] A drawing of the present system is shown in Fig. 1. The new apparatus employs a rapid-interchange multiple-source housing which contains the tungsten filament source used in these measurements. The double-pass grating monochromator for these experiments was equipped with a 15 000-line/in. blazed echelette grating used in the first order in the wavelength region between 1.0 and 2.0 microns. Overlapping orders were removed at the entrance slit by means of an antireflection coated silicon filter peaked at 1.3 microns. A linear polarizer inserted in front of the filter permitted orienting the electric vector of the radiation either

* The research reported in this document was supported jointly by the Army, Navy, and Air Force under contract with Massachusetts Institute of Technology.

[1] Roth, Lax, and Zwerdling, following paper [Phys. Rev. **114**, 90 (1959)].

[2] S. Zwerdling and B. Lax, Phys. Rev. **106**, 51 (1957).

[3] Zwerdling, Lax, and Roth, Phys. Rev. **108**, 1402 (1957).

[4] Zwerdling, Roth, and Lax, Phys. Rev. **109**, 2207 (1958), Bull. Am. Phys. Soc. Ser. II, **3**, 16 and 128 (1958).

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

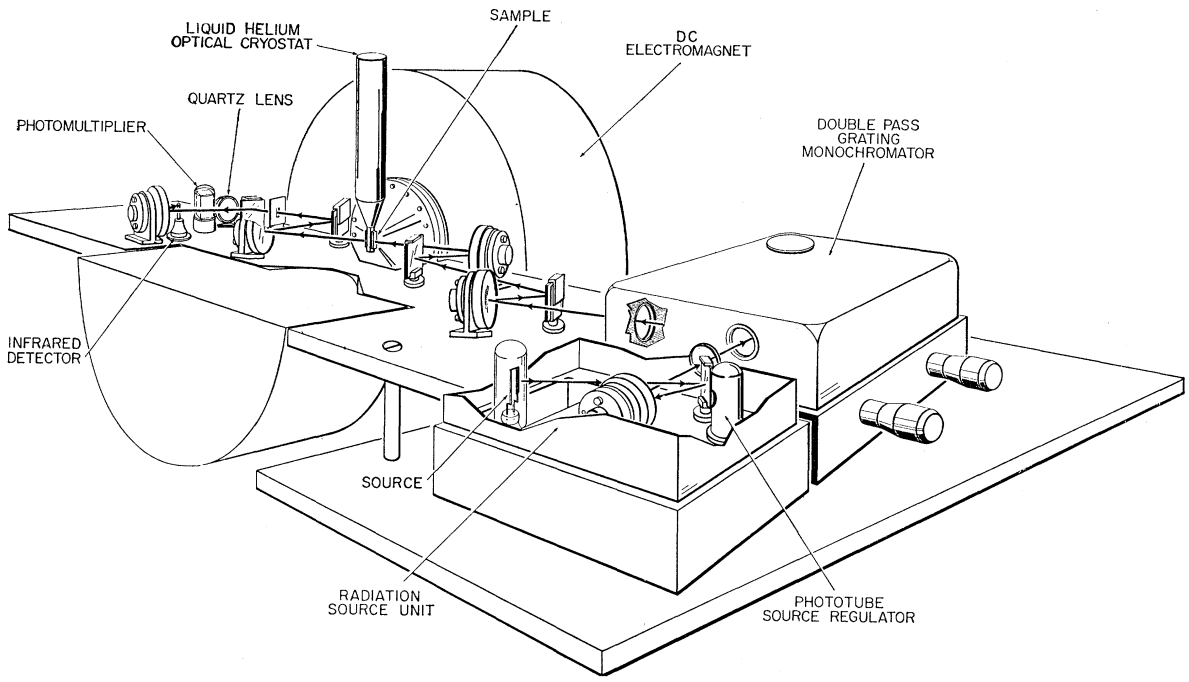


FIG. 1. Cut-away drawing of experimental apparatus used for the observation of fine structure in the oscillatory magneto-absorption of direct transitions and for indirect transition measurements in germanium.

parallel or perpendicular to the magnetic field. The chopped monochromatic radiation from the exit slit was then focused on a sample in a specially designed cryostat with transparent windows, located between the poles of a twelve-inch electromagnet. The tapered pole pieces of the electromagnet were cast from Hiperco alloy and machined to have a $\frac{7}{8}$-in. pole face diameter. A field of 38 900 gauss could be produced in the $\frac{5}{16}$-in. gap. The infrared radiation transmitted through the sample entered the multiple detector housing and was then focused on a lead sulfide detector. The output signal was amplified and recorded automatically as a function of photon energy on a strip chart recorder.

The cryostat assembly is shown in Fig. 2. This consisted of a cylindrical container having a liquid nitrogen jacket and its radiation shield surrounding a liquid helium chamber which extends down into the region of maximum magnetic field by tapering into a copper nose piece which holds the sample. The cryostat has a common vacuum for both liquid nitrogen and liquid helium compartments and has an operating capacity of 2.5 liters of liquid helium. Pumping on the liquid helium is accomplished through crossed holes in a pair of upper radiation shields and temperatures down to less than 1.5°K can be reached. Very high vacuum is maintained by the pumping action of the liquid helium container and operating times of 12 hours and longer were possible with one filling. The helium chamber is removable permitting the replacement of samples. Teflon O rings are used to provide vacuum seals for the removable sections and to permit adjustment of their relative positions to prevent internal contact. One pair of transparent windows, in this case CaF_2, was used cemented to the nose piece of the outer wall which was $\frac{9}{32}$-in. wide in the direction perpendicular to the pole faces.

For the direct-transition experiments, the samples consisted of polished single crystals of germanium, 4 microns thick and mounted on a glass substrate. The samples for the indirect transitions were 6 millimeters thick in the direction of transmission and had plane-parallel polished surfaces.

III. DIRECT TRANSITION IN GERMANIUM

A. Oscillatory Magneto-Absorption

The initial observations of the fine structure were carried out with unpolarized radiation at 4.2°K using a magnetic field intensity of 38.9 kilogauss, and the result is shown in Fig. 3. Comparison of this figure with the data obtained earlier with a prism spectrometer[3] shows that the first two minima, which are now clearly resolved, correspond to a single minimum in the earlier results. It can also be seen that, in addition to the grouping of the prominent transmission minima corresponding to single lines, the fine structure is clearly visible. Further resolution of the spectral fine structure was obtained by using linearly polarized radiation. This is consistent with theoretical predictions. The 4.2°K spectrum is shown in Fig. 4 for the electric vector parallel and also perpendicular to the dc magnetic field. The measurements at 4.2°K were carried out to photon energies as large as 1.07 ev, although the entire spec-

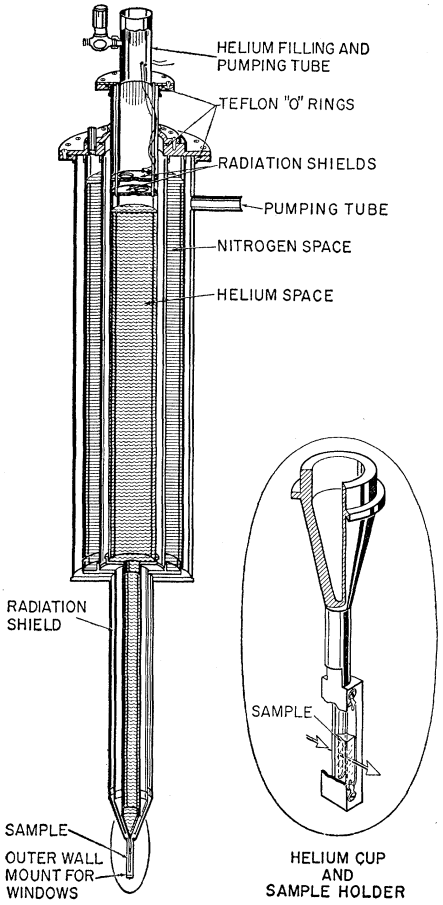


FIG. 2. A cross-section drawing of the liquid helium optical cryostat.

trum is not shown in the figures. The numerals designating each of the transmission minima represent those lines which have been correlated theoretically with the transitions between Landau levels of the valence band and those of the conduction band except lines 1, 1′ and 3, 3′. The selection rules for the Landau transitions are $\Delta n=0$, $\Delta n=-2$, and $\Delta m=0$ for the $\mathbf{E}\|\mathbf{B}$ and $\Delta m=\pm 1$ for $\mathbf{E}\perp\mathbf{B}$. The detailed correlation between theory and experiment has been given by Roth, Lax, and Zwerdling.[1] An important consequence of this correlation was that the lines 1, 1′ and 3, 3′ did not fit the theoretical pattern for the Landau transitions. Similar measurements were also made at 1.5°K, 77°K, and 293°K, and in each case, the energy gap was determined from the convergence of the Landau transition lines on a plot of photon energy of absorption maxima *vs* magnetic field.[3] The values of the energy gap found were (1) at 1.5°K and 4.2°K, 0.898±0.001 ev; (2) at 77°K, 0.889±0.001 ev; and (3) at 293°K, 0.805±0.001 ev. The average rate of change of the direct gap with temperature below 77°K is therefore 1.2×10^{-4} ev/°K and from 293°K to 77°K, 3.9×10^{-4} ev/°K.

B. Exciton Absorption

The existence of the additional minima mentioned above was not completely unexpected at this temperature and was assumed to be due to exciton absorption of the direct transition, a problem which has been treated theoretically by Dresselhaus[6] and by Elliott.[7] To verify this hypothesis, a careful study of these two minima was made as a function of magnetic field intensity down to zero field, as shown in Fig. 5. At zero magnetic field these two peaks persisted with 1′ quite prominent and 3′ considerably weaker. Therefore, these lines could not be associated with Landau transitions. To provide additional evidence for the existence of the exciton, these transmission minima were plotted in terms of photon energy as a function of magnetic field as shown in Fig. 6(a). The first two magneto-absorption lines of the Landau transitions are also shown. The exciton lines exhibited nonlinear behavior at small magnetic field intensities in accordance with the theory of the quadratic Zeeman effect. Since the extrapolation of the Landau lines to zero field establishes the energy gap,[3] the binding energy of the exciton ground state corresponds to approximately 0.0025 electron volts at 4.2°K. The measurements were also carried out at 77°K and 1.5°K as shown in Fig. 7. The significant features of the spectra were approximately the same at all temperatures, but the line width appears to be slightly narrower at 1.5°K. It is interesting to note that for the ground state of the exciton, the line width increased almost threefold from zero field to 38.9 kilogauss. This implies that the exciton fine structure which is primarily due to the complex nature of the valence band was not resolved, although at 1.5°K, there was a slight indication of a double minimum. The data at 77°K for $\mathbf{E}\|\mathbf{B}$ was taken at intervals of three kilogauss, and the detailed plot is shown in Fig. 6(b). The first two exciton lines behave almost as expected, and have a ground-state binding energy (which is apparently smaller than

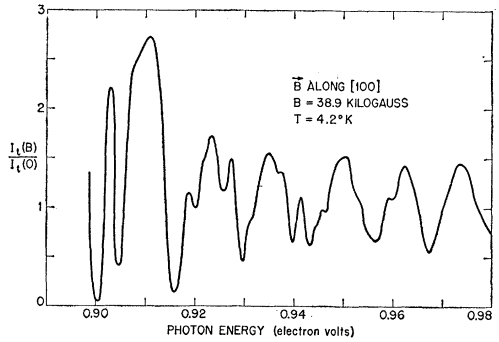


FIG. 3. The fine structure of the oscillatory magneto-absorption spectrum in germanium using unpolarized incident radiation. The trace of the transmission through a sample 4 microns thick in a field of 38.9 kilogauss has been normalized by the transmission at zero field.

[6] G. Dresselhaus, J. Phys. Chem. Solids **1**, 14 (1956).
[7] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

at 4.2°K) of approximately 0.0020 electron volt in reasonable agreement with the theoretical value of 0.0017 ev obtained from the expression

$$\mathcal{E}_n^{ex} \approx 13.6\mu^*/\kappa^2 n^2 m_0, \quad (1)$$

for a simple hydrogen-like model of the exciton. Here we have used a dielectric constant $\kappa=16$ and a reduced effective mass $\mu^*=0.031m_0$ obtained from the determination of the $k=0$ electron mass[1] at 4.2°K of $0.037m_0$ and an effective hole mass[8] of $0.20m_0$. The binding

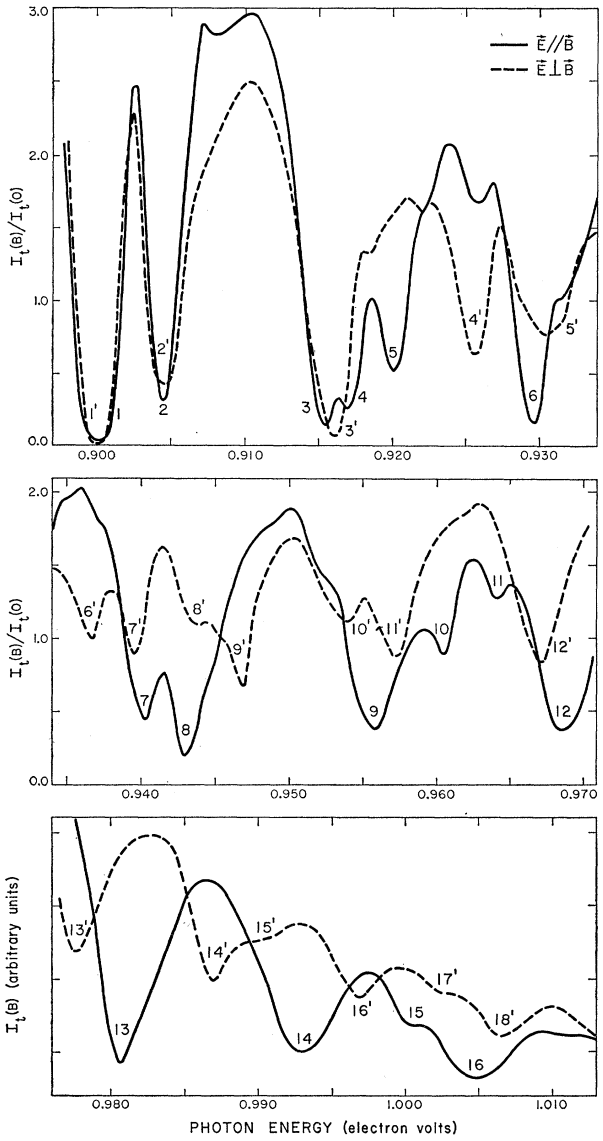


FIG. 4. The fine structure of the oscillatory magneto-absorption spectra for two orientations of the linearly polarized incident radiation. $B=38.9$ kilogauss and $T=4.2$°K. Sample thickness 4μ. $\mathbf{B}\|[100]$.

[8] This is the mass which gives the value of binding energy of the lowest acceptor state of a hole when compared with experiment, using an expression similar to that in Eq. (1). An upper limit for ϵ_n^{ex} can be obtained by using the maximum heavy-hole mass of 0.38 m_0, which yields a binding energy of 0.0018 electron volt.

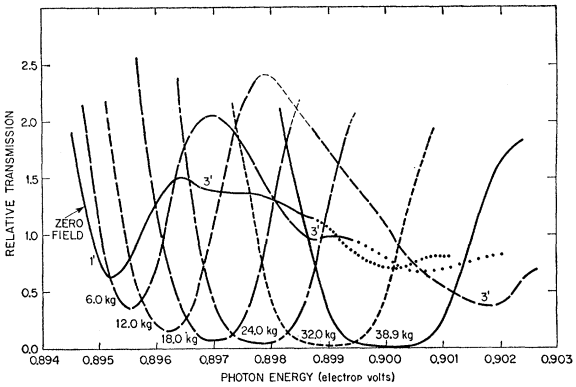


FIG. 5. Detailed traces at 4.2°K of line 1′ with the magnetic field intensity as a parameter. Line 3′ also persists down to zero field. Therefore, 1′ and 3′ have been identified as exciton absorptions.

energy at high fields by analogy with the definition by Yafet, Keyes, and Adams[9] for an impurity state in a large magnetic field is the difference between the lowest state and the first Landau level. This difference corresponds to approximately 0.0043 ev at 4.2°K and about 0.0035 ev at 77°K as compared to a theoretical estimate of 0.0045 ev, using the curves of YKA and the above reduced mass. The behavior of the lowest exciton state with magnetic field is in fairly good agreement with this theory. An anomalous feature in this spectrum which was observed with two different samples at all temperatures was an absorption persisting down to zero field at an energy above the gap. This is shown as a solid line in Fig. 6(b) starting at 0.891 ev and apparently coalesces with the lowest Landau line at high fields. This absorption is shown dotted in Fig. 5. Its origin at the moment is unexplained.

Because of the chromatic resolving power available, the line widths observed in these spectra are natural widths for the samples used. The minimum line width of the first exciton level is about 0.001 electron volt which yields a lower limit of the lifetime of the exciton of about 8×10^{-12} second. The maximum line width shown in Fig. 5 corresponds to approximately 4×10^{-12} second.

IV. INDIRECT TRANSITION IN GERMANIUM

A. Magneto-Absorption Spectrum of Landau Transitions

In the early experiments carried out at room temperature with a prism spectrometer which provided resolution of the order of 10^{-3} electron volt, the magneto-absorption spectrum of the indirect transition was not observed in germanium. It was necessary to carry out the experiments at low temperatures using spectral resolutions of the order of 10^{-4} ev. The expected maximum separation between Landau transitions with the magnetic field along the [100] direction at about 40 kilo-

[9] Yafet, Keyes, and Adams, J. Phys. Chem. Solids **1**, 137 (1956).

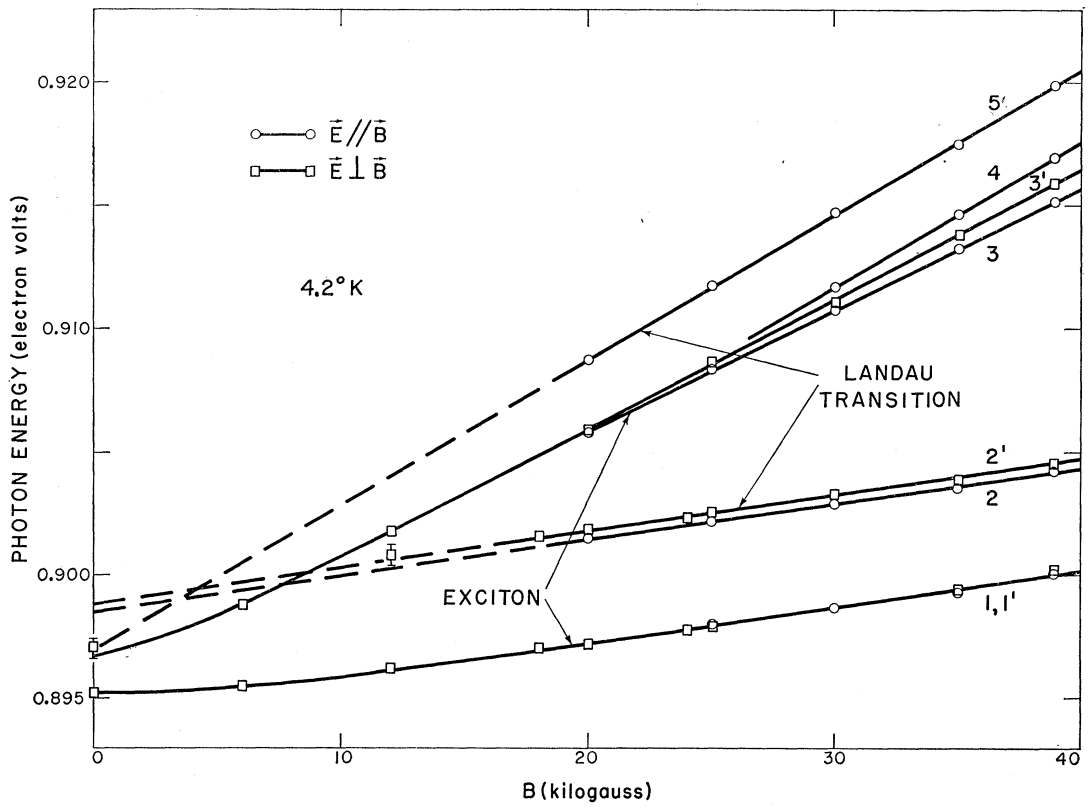


FIG. 6 (a)

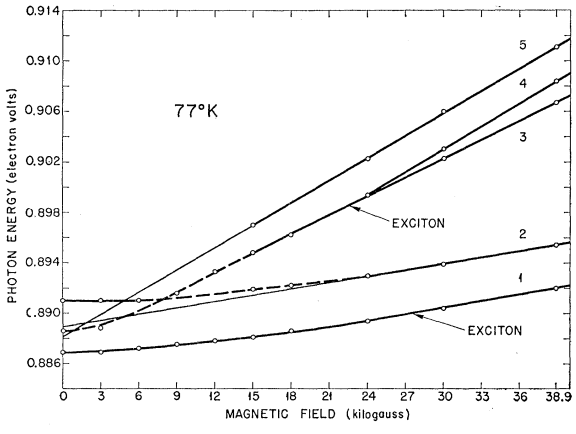


FIG. 6 (b)

FIG. 6. Positions of exciton absorptions and Landau transitions as a function of magnetic field intensity for (a) 4.2°K and (b) 77°K. The Landau transitions (straight lines) extrapolated to zero field yield the energy gap. The exciton absorptions (nonlinear) persist to zero field at an energy below the gap. $\mathbf{E}\|\mathbf{B}$ for Fig. 6(b).

gauss would be of the order of 0.001 ev if the detailed nature of both the valence and conduction bands is taken into account. Furthermore, the theory worked out by RLZ[1] showed that the spectrum should not be oscillatory, but consists of a series of steps where the absorption coefficient is represented by the function

$$\alpha_H = K_{\pm}\left(\frac{eH}{c}\right)^2 (m_1 m_2)^{\frac{1}{2}} \sum_{nn'} F(h\nu - \mathcal{E}_{nn'}), \qquad (2)$$

where

$$\mathcal{E}_{nn'} = \mathcal{E}_g \pm k\theta + (n+\tfrac{1}{2})\hbar\omega_{c1} + (n'+\tfrac{1}{2})\hbar\omega_{c2},$$

and $F\ (h\nu - \mathcal{E}_{nn'})$ is a step function. $K_{\pm}$ is a constant[10] involving the phonon matrix element and an oscillator strength. $k\theta$ is the energy of the phonon where the plus sign refers to emission and the minus sign to absorption. This expression is somewhat simplified and assumes spherical bands at the center and edges of the Brillouin zone. However, it does predict the appropriate form of the spectrum because the experiments carried out at low temperatures with the high-resolution system did indeed show a series of "steps." The relaxation processes broadened each absorption line so that the observed "step" had a finite slope. Figure 8(a) shows the spectrum of the transmission through a sample 6 millimeters thick at 1.5°K. The dashed line is the transmission at zero field and shows the indirect exciton line discovered by Macfarlane and co-workers.[5] In addition, the solid line contains two regions of absorption due to transitions between the Landau levels in the valence band and the conduction band. These transi-

[10] Bardeen, Blatt, and Hall, *Proceedings of the Atlantic City Photoconductivity Conference, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley and Sons, Inc., New York, 1955).

tions appear as distinct decreases in transmission when compared to the transmission at zero magnetic field. A detailed experimental study was made of the discontinuities in the slope indicated in Fig. 8(a) as Landau transitions. The resulting transmission traces are shown in Fig. 8(b) for different values of magnetic field intensity. The motion with field of one such Landau transition between 0.773 ev and 0.774 ev is particularly noticeable.

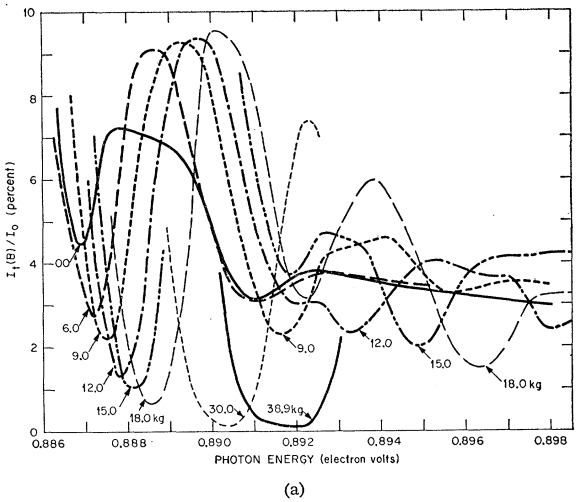
Utilizing different traces for magnetic field intensities between 10 000 and 38 900 gauss, we selected the center of all resolvable Landau transition lines and plotted them in terms of energy as a function of magnetic field intensity. The midpoint of the slopes shown in Fig. 8(a) and (b) is interpreted as the difference in energy between the Landau levels in the valence and conduction bands. In the absence of relaxation, the theory indicates that these transitions are abrupt changes. We have interpreted the finite slope of the experimental line as relaxation broadening on either side of the center. The "line width" is then defined as the difference in energy between the onset of absorption and the foot of the step[11] (see Fig. 9). Figure 10(a) shows lines drawn through the points corresponding to a given transition for different values of the magnetic field. They all extrapolate to a point 0.7713 ± 0.0004 ev which is an accurate measure of the bottom of the conduction band. MMQR have shown that at these temperatures, an indirect transition in this range of energies involves the emission of a longitudinal acoustical phonon whose Debye temperature is given by $\theta=321°\text{K}\pm6°\text{K}$ which corresponds to 0.0276 ± 0.0005 ev. Consequently, the actual location of the energy gap is given by

$$\mathcal{E}_g=0.744\pm0.001 \text{ ev at } 1.5°\text{K}. \quad (3)$$

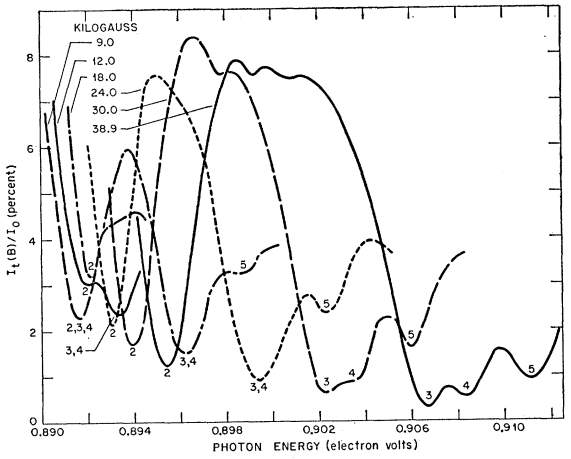
A similar plot has also been developed for the magnetic field along the [111] direction as shown in Fig. 10(b).

Another representation of these data is shown in Fig. 11. Here we have compared the experimental spectrum with the theoretical spectrum which has been calculated by taking transitions from the Landau levels of the valence band to those of the conduction band. A generalization of Eq. (2) was used, which is discussed in RLZ. Since the indirect transition is a two-step process, the selection rules governing transitions to the intermediate state (which we assume to be the $k=0$ conduction band) are the same as those for the direct transition. For the phonon matrix element, there is no selection rule on n and only the condition that the spin be conserved. The transition probabilities were evaluated by a procedure similar to that used for the direct transition.[1] The density of states factor $(m_1m_2)^{\frac{1}{2}}$ was calculated for each transition by using an average light or heavy mass for the hole (with $n=0$ treated as

[11] Overlapping lines were resolvable since the shape readily indicated the synthesis of two such lines as shown in the sketch of Fig. 9.



(a)



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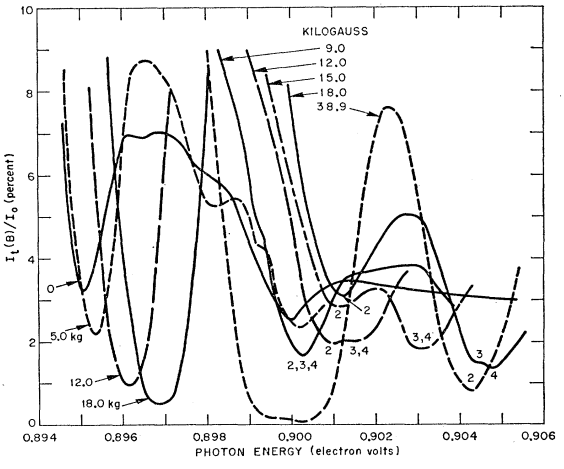

(c)

FIG. 7. Detailed magneto-absorption traces for $\mathbf{E}\|\mathbf{B}$ with the magnetic field intensity as a parameter. The lowest energy exciton line is shown in (a) at 77°K. The higher energy transitions at 77°K are shown in (b). Similar traces for 1.5°K are shown in (c) where the first exciton begins to show a double transmission minimum at 38.9 kilogauss.

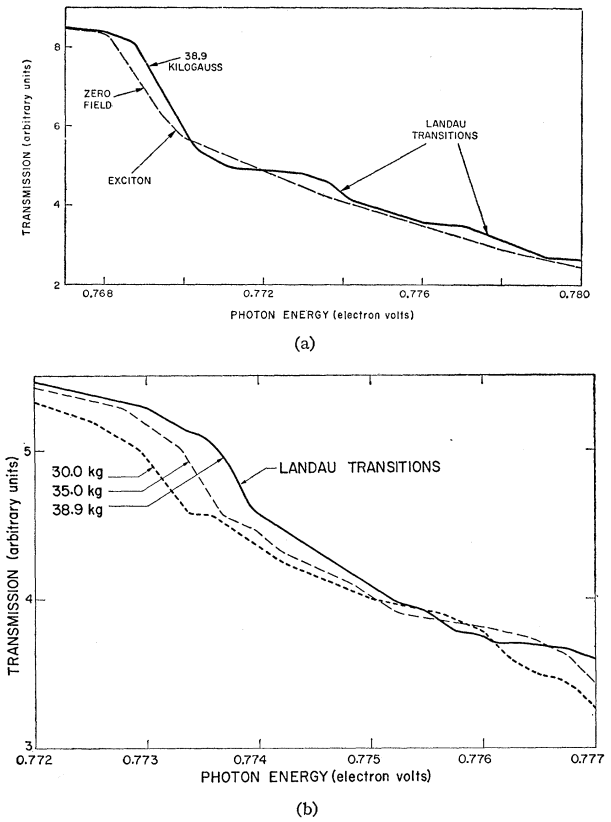

FIG. 8. The series of absorption edges or "staircase" spectrum at 1.5°K characteristic of magneto-absorption for indirect transitions. The traces for zero field and full field are shown in (a) demonstrating the exciton absorption and subsequent transitions between magnetic levels in the valence bands and the conduction band. The center portion of (a) is shown magnified in (b) for three values of the magnetic field intensity.

"heavy" and $n=1$ treated as "light") and, using for each ellipsoid, the mass in the direction of **B**:

$$m_2 = m_l \cos^2\theta + m_t \sin^2\theta,$$

where θ is the angle between **B** and the axis of the ellipsoid. The level structure for the valence band was derived by using the Luttinger-Kohn expressions[12] for the levels and the cyclotron resonance parameters for germanium. For the conduction band the levels for **B** along the [100] and [111] directions, respectively, were evaluated using the cyclotron resonance masses obtained experimentally[13] for these directions. In addition, spin splitting of each of these levels has been taken into account assuming a spin of $\frac{1}{2}$ and a g value of 2. This g value may have to be corrected to account for the influence of spin-orbit coupling and the presence of higher and lower bands at the edges of the Brillouin zone. In the absence of detailed information, this correction is not yet possible.

[12] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955); J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[13] Dexter, Zeiger, and Lax, Phys. Rev. **104**, 637 (1956).

The spectral lines in the [100] direction shown in Fig. 11(a) are reasonably well resolved experimentally and correspond closely with the lines of the theoretically derived spectrum. The experimental lines for higher energy transitions are not fully resolved because of the multiplicity, reduced intensity, and considerable overlapping. However, the grouping of lines is quite distinct.

The spectrum for **B** along the [111] direction is shown in Fig. 11(b). This pattern is further complicated by the splitting of the conduction band Landau levels into one ellipsoid which is parallel to the applied magnetic field and three others which are along the other [111] directions, making angles of approximately 70° with the magnetic field. It is impossible to resolve some of the lines because of the complexity of the overlapping lines of the spectrum as shown by the theoretical spectrum of Fig. 11(b). The over-all correspondence of the groupings, however, does indicate some agreement between theory and experiment. In order to resolve the detailed spectrum and obtain the good correlation observed for the direct transitions, it will be necessary to go to much higher magnetic field intensities to increase the separation of the individual lines. Higher fields would have the added advantage of increasing the intensity of the lines considerably because Eq. (2) predicts a quadratic increase in absorption coefficient with increasing magnetic field intensity.

B. Indirect Exciton and Its Zeeman Effect

In analyzing our magneto-absorption spectrum at one field intensity, 38.9 kilogauss, it is necessary in practice to distinguish between the transition of an electron from the valence band to a conduction band Landau level or to an exciton level. In analyzing such a situation, we have developed several criteria in the case of the direct exciton which we proceeded to apply also to the indirect case. The first of these was to examine

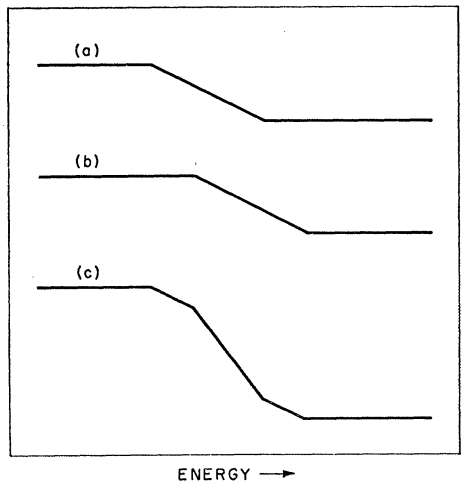

FIG. 9. A sketch of steps in the transmission traces showing the method used for interpreting the positions of two overlapping absorptions. Two individual lines, a and b, form the composite line c.

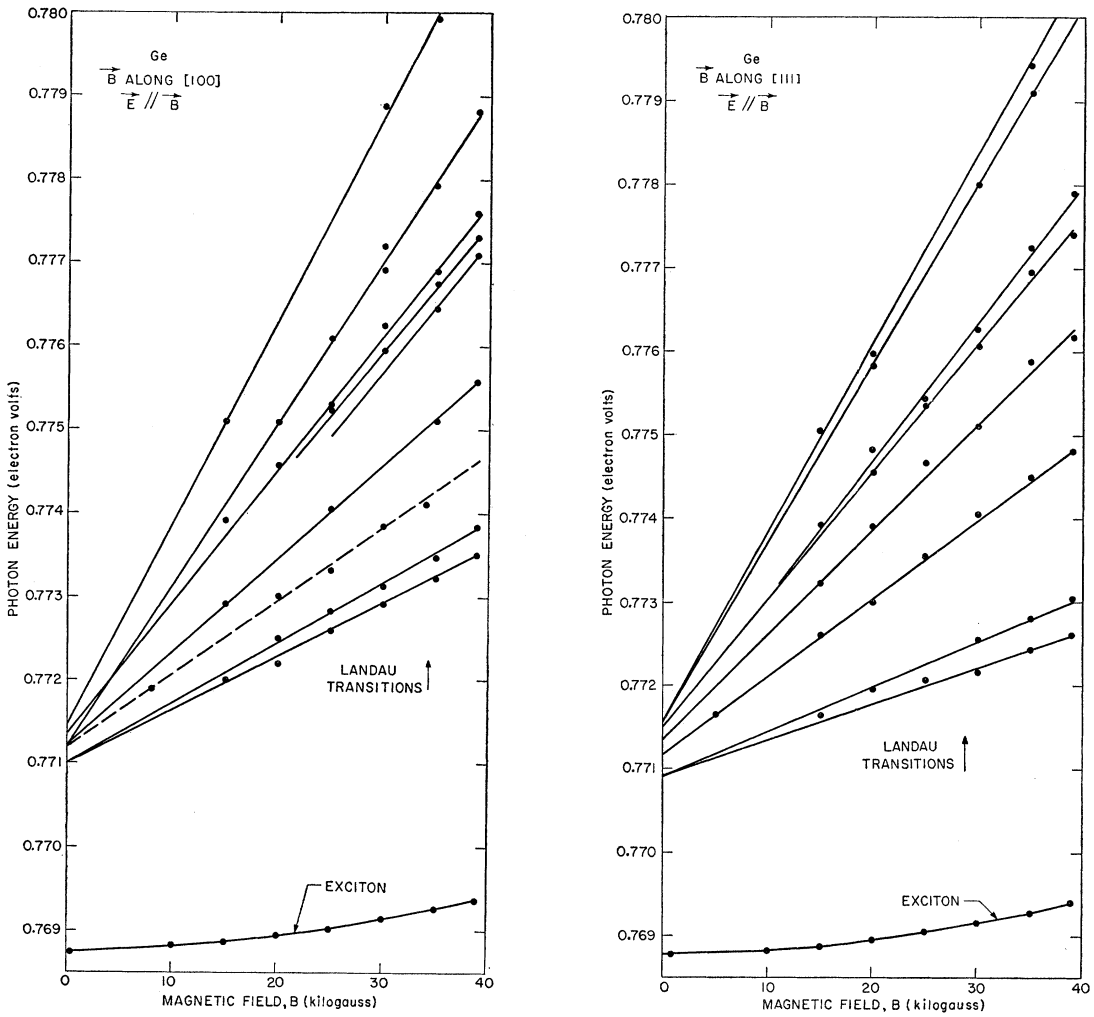

FIG. 10. Plots of the positions of indirect transitions at 1.5°K *versus* magnetic field intensity, for (a) **B** along the [100] crystal direction and (b) **B** along the [111].

each line as a function of magnetic field intensity down to zero field. Figure 12 shows the motion of the indirect exciton absorption line with field. The line persists to zero field and shifts nonlinearly. The motion of this exciton line with field is shown in Fig. 10. The difference between its energy value at zero field and the convergence point of the Landau levels is finite and was interpreted as the exciton binding energy.

$$\mathcal{E}^{\text{ex}}=0.0025\pm0.0004 \text{ ev at } 1.5^\circ\text{K}. \qquad (4)$$

This value, which was obtained by taking the center position of the exciton line is smaller than the estimate of 0.005 ev made theoretically by Dresselhaus[6] and Elliott[7] and experimentally by MMQR.† We have made a somewhat more detailed approximation to the binding energy. A variational solution to the problem is obtained by replacing the 4×4 effective mass Hamiltonian for the valence band by its diagonal elements. Using a representation with the z axis along the [111] direction, these diagonal elements are equal in pairs, and correspond to two ellipsoids, one prolate with effective masses

$$m_{1t}=\frac{m_0}{\gamma_1+\gamma_3}=\frac{m_0}{18.6},$$
$$m_{1l}=\frac{m_0}{\gamma_1-2\gamma_3}=\frac{m_0}{2.1}, \qquad (5)$$

† *Note added in proof.*—We have learned since our report of these results early in 1958 at a meeting of The Physical Society, Malvern, England, that a re-evaluation by MMQR of their experimental results[5] now gives a value of the indirect exciton binding energy in very close agreement with ours. For the indirect energy gap at these temperatures, both our value and theirs are also in complete agreement within experimental error.

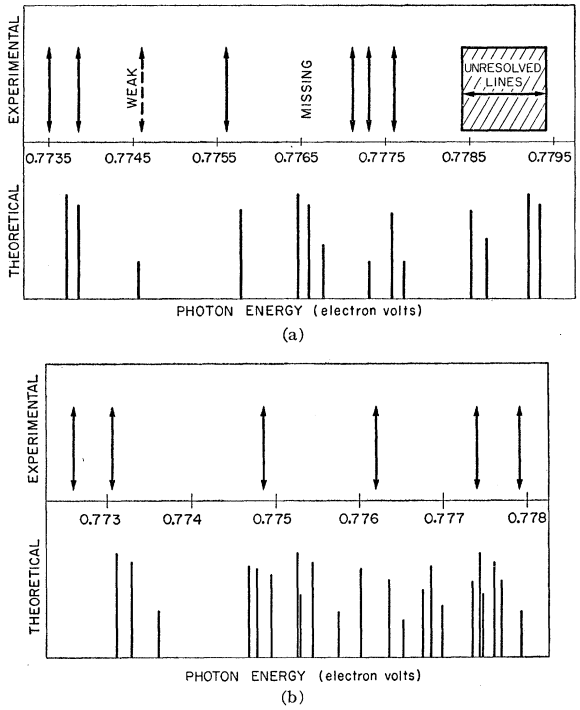

FIG. 11. Line spectrum of indirect Landau transitions at 38.9 kilogauss for (a) **B** along the [100] crystal direction and (b) **B** along the [111] direction. The experimental lines, observed at 1.5°K, correlate reasonably well with the theoretical spectrum for the [100] direction. It was only possible to identify groups from the many closely-spaced lines in the [111] spectrum.

and the other oblate with effective masses

$$m_{2t}=\frac{m_0}{\gamma_1-\gamma_3}=\frac{m_0}{7.6},$$
$$m_{2l}=\frac{m_0}{\gamma_1+2\gamma_3}=\frac{m_0}{24.1}, \tag{6}$$

where γ_1 and γ_3 are valence band parameters as defined by Luttinger[12] and the values are obtained from cyclotron resonance data.

The electron moves on an ellipsoid with effective masses $m_t=0.083m_0$ and $m_l=1.69m_0$. If we transform to center-of-mass coordinates for the exciton, we then obtain two sets of reduced masses corresponding to the two reduced ellipsoids:

$$1/\mu_{1t}=1/m_t+1/m_{1t}=12.2+18.6=30.8,$$
$$1/\mu_{1l}=1/m_l+1/m_{1l}=0.6+2.1=2.7,$$

and similarly,

$$1/\mu_{2t}=19.9, \quad 1/\mu_{2l}=24.7.$$

In the variational problem, if we approximate the wave functions for the two states by $\exp\{-[a^2z^2+b^2(x^2+y^2)]^{\frac{1}{2}}\}$ and vary $\mathcal{E}$ with respect to a and b in each case as in the donor problem,[14] the binding energies obtained are 0.0025 and 0.0033 electron volt, with the prolate ellipsoid giving the larger binding energy. The mean value is 0.0029 electron volt, in reasonable agreement with the experiment. As a matter of fact, the indirect exciton does show fine structure which we have analyzed in detail by plotting the derivative of the transmission. Figure 13 shows two peaks which we interpret as corresponding to the splitting of the exciton ground state. The experimental binding energies at zero field are 0.0021 ev and 0.0032 ev. We may expect that a more accurate calculation including the off-diagonal elements for the matrix of the valence band would increase the calculated value of the splitting and the estimate of the mean binding energy. The existence of the splitting of the lowest exciton level in this case can be deduced from symmetry arguments since the introduction of an ellipsoid for the electron removes the cubic symmetry from the valence band matrix. The over-all cubic symmetry of the exciton wave function is restored by taking linear combinations of the four ellipsoids[15];

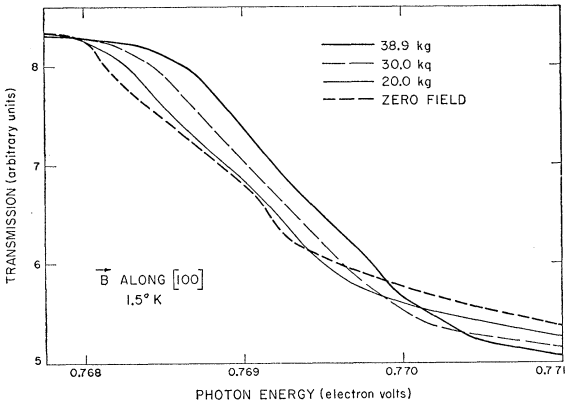

FIG. 12. The transmission trace in the region of indirect exciton absorption at 1.5°K for several values of the magnetic field intensity. Exciton absorption persists at zero field and the absorption edge shifts nonlinearly with magnetic field intensity.

nevertheless, the splitting of the original states is retained.

The third criterion for identifying the exciton is found by studying its Zeeman effect in a large magnetic field. The motion of the absorption line is a nonlinear function of magnetic field intensity and with the fields and masses involved here would show a quadratic behavior. This was confirmed experimentally as shown in Fig. 10. For the Zeeman effect, the energy shift for a simple hydrogenic model is given by

$$\Delta\mathcal{E}=\hbar^4H^2\kappa^2/(4\mu^{*3}c^2e^2). \tag{7}$$

We can make an estimate of this quantity by using a reduced effective mass which is a mean of the two values, about $0.08m_0$. This mean value can be justified in a problem such as this when the fine structure is not considered, in a manner analogous to that in which one treats it in a mobility problem. This has been evaluated[16] taking into account the density of states and the

[14] W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

[15] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 883 (1955).

[16] B. Lax and J. G. Mavroides, Phys. Rev. **100**, 1650 (1955).

warping of the energy surfaces and is equal to $0.25m_0$. Again, using the expression for the reduced effective mass for the transverse and longitudinal components and taking into account the reduced mass, we obtain $\mu^*=0.08m_0$. If we substitute this in Eq. (7), using a field of 38.9 kilogauss, we then obtain $\Delta\mathcal{E}\approx0.001$ electron volt. Considering the crudeness of the approximation, the mean shift of the exciton absorption peak is apparently of the right order of magnitude. An interesting thing to note about the exciton line at high fields is the two main peaks of the fine structure in Fig. 13 and in addition there appears small but definite structure at either side of the main absorptions.

V. CONCLUSIONS

The results presented in this paper are ample proof of the tremendous value of high-field, high-resolution, and low-temperature measurements in providing extensive information on the behavior of holes and electrons in semiconductors with complex band structure. We have shown that the direct transition magneto-absorption spectrum, in addition to having an oscillatory character according to the theory for simple bands, does exhibit fine structure which can be directly attributed to the valence band. These data have been correlated with the theory[1] which takes into account spin-orbit effects and curvature of the bands. Although in germanium, such information was predicted from cyclotron resonance, a spectrum in other new materials could be used conversely to obtain the parameters of the energy surfaces such as the valence band, particularly when use is made of the anisotropy of the magneto-absorption. The ability to observe the indirect magneto-absorption spectrum with high-resolution equipment has also been demonstrated and its characteristics have been shown to be in agreement with the theoretical predictions. From the study of both spectra, we have obtained very accurate measurements of both the direct and indirect energy gaps. The line widths in the well-resolved magneto-absorption spectra could be determined and indicated scattering times from 3×10^{-12} to 8×10^{-12} second.

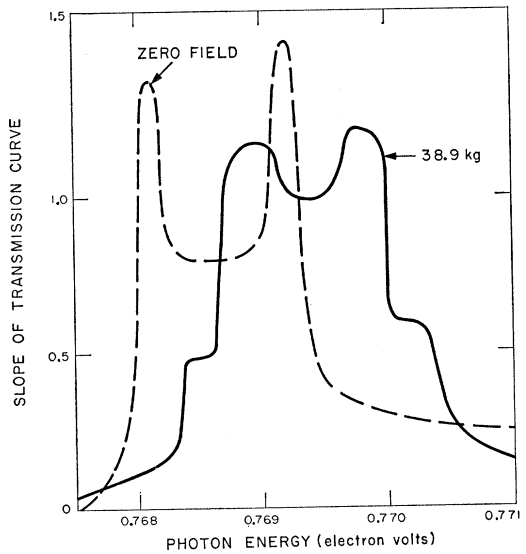

FIG. 13. The derivative of two of the exciton absorption edges shown in Fig. 12. The two peaks correspond to the splitting of the exciton ground state.

The demonstrated experimental capabilities of this system have shown that it should now be possible to study the transitions between the split-off valence band of germanium and the two degenerate bands at $\mathbf{k}=0$. This should provide an accurate measure of the effective mass in the split-off band and its energy position.

In addition to studying the magneto-absorption, a useful method for identifying and studying the quantitative behavior of excitons has been demonstrated. We have shown that the comparison of the zero-field data provides a very accurate measure of the binding energy of the excitons and the quadratic behavior of the Zeeman effect establishes their existence conclusively. The experimental data on the indirect exciton showed no anisotropy and no dependence on the polarization of the incident radiation. The observed fine structure of the indirect zero-field exciton due to the combined effect of the degenerate valence bands and the ellipsoidal surfaces was predicted theoretically. In addition, for both types of excitons, there were indications of fine structure at high magnetic fields but these presently available field intensities were not sufficiently large to resolve this structure. However, this indicates the necessity of performing these experiments at field intensities up to 100 000 gauss. Not only will the higher magnetic fields resolve the fine structure of the excitons but the intensity of the magneto-absorption spectrum will also be increased permitting the observation of the "steps" much deeper into the band. Then the curvature of these bands could be mapped in some detail as a function of energy. Another argument for the use of higher fields is that in attempting to study the magneto-absorption of the indirect transition in silicon, although there were indications of some magnetic effect, the resolution of the lines or any quantitative measurements of magnetically induced shifts were not possible. This can be attributed to the relatively large effective masses in silicon. However, the presence of the "step" in the transmission curve corresponding to the indirect-transition exciton formation at zero field was clearly observed, the position of the center being at 1.2053 ± 0.0006 ev. Fields of much higher intensity will undoubtedly lead to success in this and other materials with semiconducting properties.

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