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Photovoltaic effect and interband magneto-optical transitions in InP

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A study is made of the oscillatory spectral distribution of the photovoltaic (PV) effect of a gold-indium phosphide Schottky barrier in magnetic fields of up to 70 kG. Spectra are obtained for both the direct and wavelength-modulated PV signals, the latter being compared to the wavelength-modulated reflectivity data. The spectra are taken at 4.2 K in the Faraday configuration for both circular polarizations. The transition energies associated with the spectral oscillations are corrected for exciton-binding effects, and are analyzed as Landau levels in terms of the Pidgeon and Brown coupled-bands theory of interband magnetoabsorption. The fit to the data gives a conduction-band effective mass $m_c/m_0 = 0.079 \pm 0.001$ and Luttinger parameters $\gamma_1^L = 5.15 \pm 0.05$, $\gamma_2^L = 0.94 \pm 0.03$, and $\gamma_3^L = 1.62 \pm 0.03$. The direct observation of the split-off valence-band–to-conduction-band transition gives $\Delta_0 = 0.108 \pm 0.003$ eV and an approximate effective mass of $m_{so}/m_0 = 0.21 \pm 0.02$.

I. INTRODUCTION

The study of interband magneto-optical transitions has been extensively used in order to determine accurate band parameters for many semiconductors. The theory for the quantization of electronic levels in a magnetic field was first developed by Landau.[1,2] It was refined by Luttinger and Kohn[3] to include valence-band degeneracy and further refined by Pidgeon and Brown[4] to include the nonparabolicity of the conduction band. However, in interband magneto-optics, one can only use the latter theory directly in cases where the exciton contributions to the spectra are negligible. Exciton effects can be included by using the theories developed by Elliott and Loudon,[5] and more recently by Altarelli and Lipari.[6,7] The problem of the exciton in a magnetic field has been solved for the cases of low and high fields (i.e., $\gamma \ll 1$ and $\gamma \gg 1$, where $\gamma = \hbar\omega_c/2R_0$, the ratio of the cyclotron energy to the exciton binding energy). No explicit solution for degenerate nonparabolic bands at intermediate fields has yet been presented.

The determination of the band parameters of indium phosphide through magneto-optics presents both experimental and theoretical difficulties. Due to the relatively high effective masses involved, high magnetic fields are required to produce observable energy quantization, and even at 70 kG only the transitions from the light-hole valence band will produce any observable effects, these effects being small in comparison to the background. The exciton contributions to the spectrum are large because of the exciton's large binding energy; thus the observed quantum oscillations must be corrected for these effects. The correction in the case of indium phosphide is difficult to perform explicitly since the field involved is in the intermediate region ($\gamma \simeq 1$).

In order to circumvent the problems of excitonic participation, the data presented below are empirically corrected for the exciton contributions by a method used by Vrehen[8] for GaAs. The data were obtained by using the photovoltaic effect which has recently been used with some success in interband magneto-optics.[9,10] This method was used for detection because of its high signal-to-noise ratio and its experimental simplicity, and also because it can be easily coupled to wavelength modulation to obtain the first derivative of the observed signal directly.

In the following paragraphs a brief review of the theory of the effects involved and used here is presented, followed by a description of the experimental setup and a discussion of the results. The data are analyzed and fitted to the Pidgeon and Brown theory for Landau levels. The parameters obtained from the fit are used to analyze the energy shift of the transition from the split-off valence band to the conduction band (hereafter referred to as S.O.).

II. THEORY

A. Photovoltaic effect

The open-circuit zero-bias photovoltage V_{pv} across an illuminated Schottky barrier can be shown[11] to be

$$V_{pv} = (kT/e)\ln(J/J_0 + 1)\,, \tag{1}$$

where J_0 is the equilibrium dark-current density in the semiconductor and J is the nonequilibrium current density caused by the illumination. In the case of a metal-semiconductor junction where the contribution to the photocurrent from the semi-

transparent metal film can be ignored, the photocurrent is given by[10]

$$J = e\beta N\,(1 - e^{-2W\alpha})\,, \tag{2}$$

where β is the quantum efficiency, N is the number of photons crossing the film per unit area, α is the absorption coefficient of the semiconductor, and W is the thickness of the space-charge region, which in the case of an abrupt junction is approximately given by[11]

$$W = (2\epsilon_S \phi_B / eN_0)^{1/2}\,, \tag{3}$$

Here ϵ_S is the effective permittivity of the semiconductor, ϕ_B is the barrier height, and N_0 is the density of ionized donors.

When $\alpha W < 1$, changes in the absorption coefficient will give rise to changes in the photocurrent and thus in turn to changes in the photovoltage. For example, when $\alpha W < 1$ Eq. (2) reduces to

$$J \propto \alpha\,, \tag{4}$$

such that

$$V_{pv} \propto \ln\alpha \tag{5}$$

and

$$\Delta V_{pv} \propto (1/\alpha)\,\Delta\alpha\,. \tag{6}$$

Thus, in order to observe changes in the absorption coefficient of a semiconductor due to an imposed external magnetic field, the sample must be selected in such a way that the condition $\alpha W < 1$ is satisfied. For a given case, this can be accomplished by selecting the parameters ϕ_B and N_0 of Eq. (3).

B. Magneto-optics

Interband magneto-optical effects usually observed in absorption or reflectivity spectra can thus be displayed, in the proper circumstances, in the spectral distribution of the photovoltaic effect and such spectra can be analyzed to give band parameters of the semiconductor. The Pidgeon-Brown[4] theory for interband magneto-optical transitions is to date the most realistic theory for the displacement of the Landau-level-associated transitions as a function of magnetic field. The theory takes into account the valence-band degeneracy as well as the interaction between the valence bands, conduction band, and the upper bands. Thus a fit to the experimental transition energies gives the approximate functional parameters of the theory.

The experimental results, however, include contributions not only from Landau-like transitions but also reflect the participation of excitons associated with each Landau level. The theory of the behavior of excitons in a magnetic field has been developed for the cases of low and high magnetic fields.[5–7] Unfortunately in the intermediate-field region ($\gamma \simeq 1$, the case of InP here) the theory has yet to be explicitly developed. In order to circumvent this difficulty, the experimental data can be empirically corrected using the method suggested by Vrehen.[8] This correction involves shifting the experimental points to higher energies by $R(H)/(2n+1)$, where $R(H)$ is the binding energy of the exciton associated with the first Landau level as a function of magnetic field, and n is the Landau-level quantum number. The value of $R(H)$ can be obtained by taking the difference between the experimental data for the first exciton level and the approximately calculated position of the first Landau level. The new data are then fitted to the Pidgeon-Brown theory.

III. EXPERIMENTAL

The samples are obtained from a monocrystalline block of n-type InP with a room-temperature impurity concentration of $2\times10^{15}\,\mathrm{cm}^{-3}$. This material should be pure enough to obey the condition $\omega\tau > 1$ (where ω is the cyclotron frequency and τ the relaxation time), necessary for the observation of magneto-optical structure associated with the light-hole valence-band–to–conduction-band transitions. At the same time the impurity concentration should be sufficient to satisfy the barrier width condition, as well as to provide a moderate electric field at the junction. This material seemed to satisfy all the conditions, since quantum oscillations were observed and no Franz-Keldysch effect could be observed at 4.2 K. A rough estimate, assuming the ionized-impurity concentration at 4.2 K to be of the order of $10^{13}\,\mathrm{cm}^{-3}$, with $\epsilon_S = 12.09$,[12] and $\phi_B = 0.56$ V,[11] gives the barrier width $W \simeq 5\times10^{-4}$ cm, with a maximum electric field of $E = 2\times10^3\,V/\mathrm{cm}$ at the barrier.

The samples were polished with Al_2O_3 powder, etched in a methanol 10-vol.% Br solution and kept in an inert atmosphere or high vacuum during the remainder of the preparation in order to minimize surface oxidation and the resultant changes in the spectrum.[13] The contacts on the photovoltaic samples were placed in a "sandwich" configuration, the back contact being made by evaporating indium and alloying in a nitrogen-atmosphere furnace at 300 °C, and the front contact consisting of an evaporated semitransparent gold film. The samples were mounted in the Faraday configuration in such a manner that $\vec{S} \| \vec{B} \| \langle 111 \rangle \| \vec{E}$, where $\vec{S}$ is the incident-radiation propagation vector, $\vec{B}$ the magnetic field, and $\vec{E}$ the junction electric field. (Note $\vec{E} \| \vec{B}$ in order to avoid crossed-field effects.)

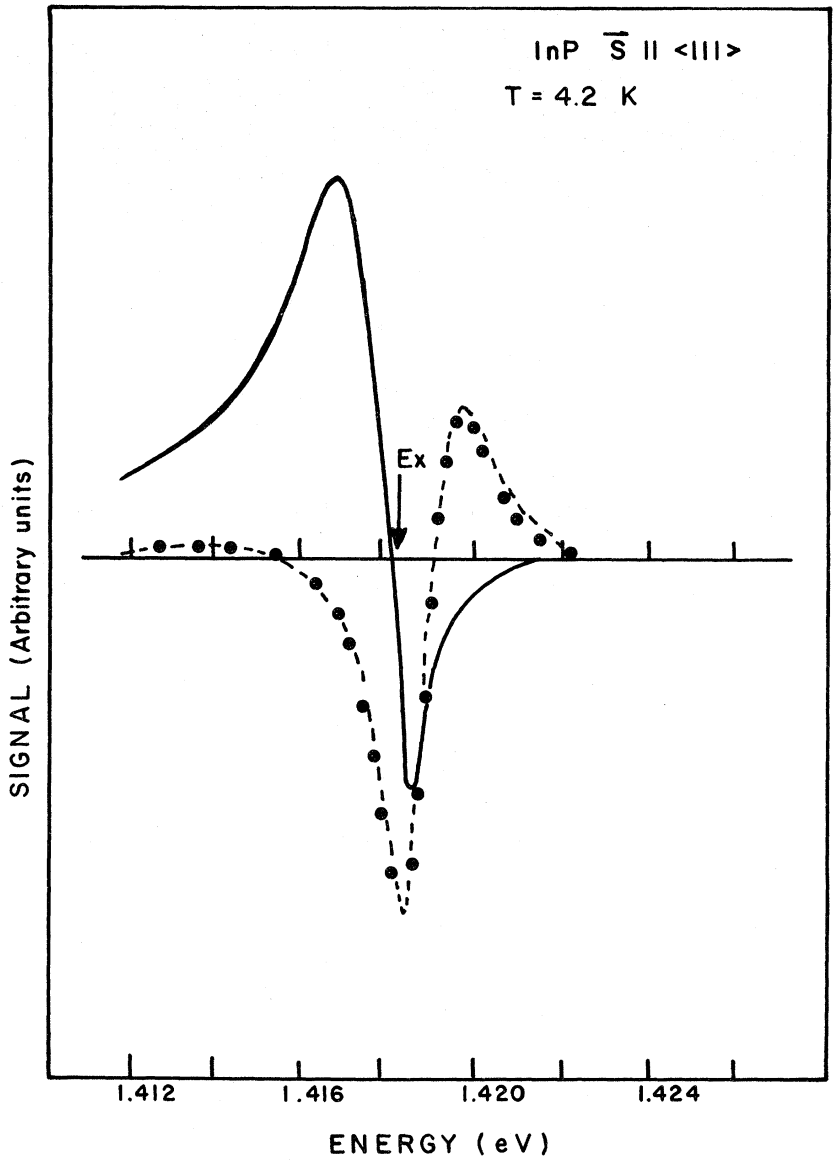

FIG. 1. Wavelength-modulated reflectivity ($\Delta R/R$) and wavelength-modulated photovoltaic (ΔV_{pv}) effect near the 1S exciton line: solid line, ΔV_{pv} experimental; dashed line, $\Delta R/R$ fit; ●, $\Delta R/R$ experimental.

These samples were placed in an independent chamber within a superconducting magnet and kept at 4.2 K by a He exchange gas at a pressure of 10 Torr.

The optical system consisted of a $\frac{3}{4}$-m grating monochromator mounted in a double-beam geometry and coupled to an HR polarizer and a Fresnel rhomb, thus providing monochromatic radiation circularly polarized at better than 90% over the spectral range of interest. The beam was chopped at 85 Hz and synchronous detection was used throughout. The wavelength modulation was provided by a vibrating refractor plate placed in the monochromator. A low-noise silicon photodiode (EG and G type HAD-1000) was used as detector in order to obtain the reflectivity data. A more complete description of the apparatus can be found elsewhere.[14]

IV. RESULTS AND DISCUSSION

A. Comparison of wavelength-modulated photovoltaic effect and wavelength-modulated reflectivity

In order to establish the correspondence between the structures seen in the photovoltaic spectra and the pertinent transition energies, a comparison was made between the photovoltaic derivative spectrum and the modulated-reflectivity spectrum. On Fig. 1, the wavelength-modulated reflectivity $\Delta R/R$ near the 1S exciton line at 1.4183 eV is presented together with the wavelength-modulated photovoltaic spectrum ΔV_{pv}. The reflectivity curve

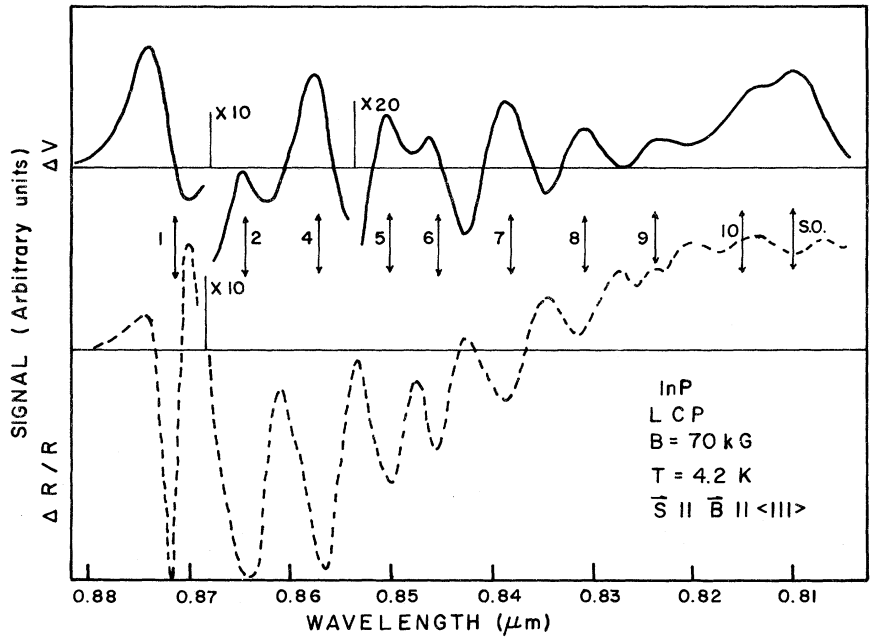

FIG. 2. Spectral distribution of the modulated photovoltaic (ΔV) signal and its corresponding modulated reflectivity ($\Delta R/R$) signal at a magnetic field of 70 kG for left-circularly-polarized (LCP) light. The transitions are labelled as in Table II.

was fitted to the form[15]

$$\frac{\Delta R}{R} \propto \left(- \mathrm{Re}\, \frac{\delta \epsilon}{\delta E} + 2A\ \mathrm{Im}\, \frac{\delta \epsilon}{\delta E} \right), \tag{7}$$

where A is an exciton asymmetry-broadening parameter and ϵ is the complex dielectric constant, which includes excitonic participation, as given by Senechal *et al.*[16] The parameter A was found to be $A = 0.6$ and the Lorentzian broadening parameter Γ, which is included in the theory, was found to be $\Gamma = 1$ meV.

It is to be noted that the exciton energy which corresponds to the minimum in the $\Delta R/R$ curve is associated with the zero crossover of the ΔV_{pv} curve, a point which experimentally can be measured with some accuracy.

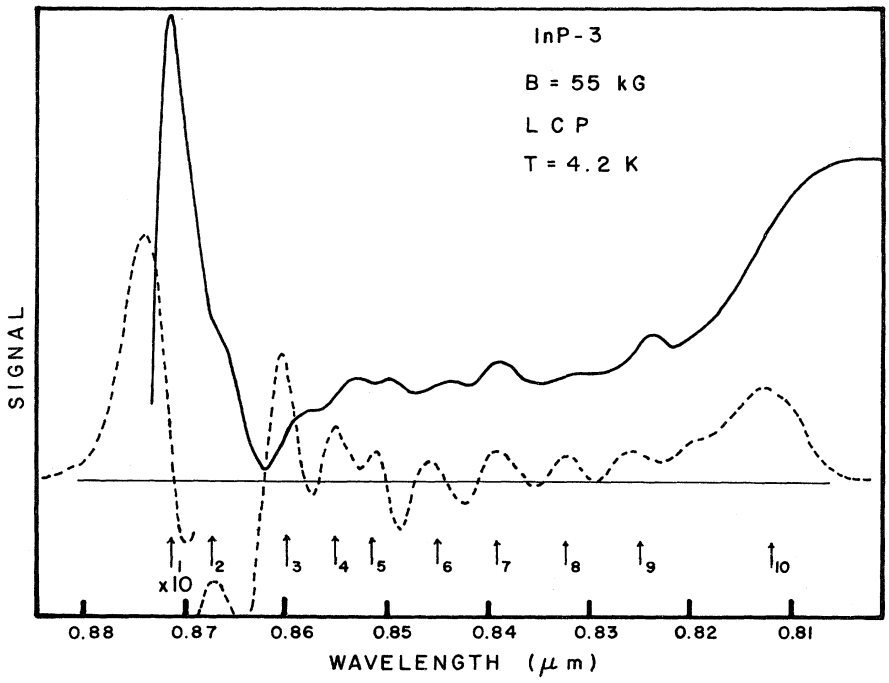

FIG. 3. Spectral distribution of the direct-photovoltage (solid line, V_{pv}) signal and its associated wavelength-modulated photovoltaic (dashed line, ΔV_{pv}) signal at 55 kG for left-circularly-polarized light. The transitions are labeled as in Table II.

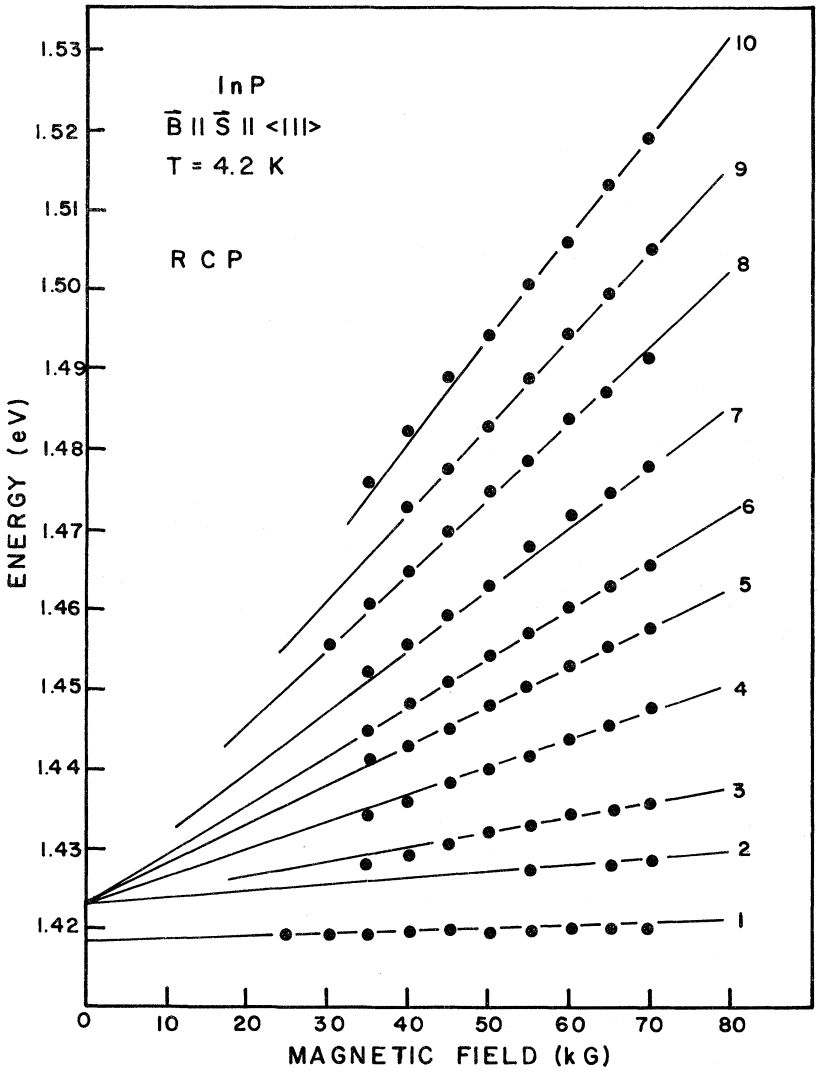

FIG. 4. Energy positions of the spectral oscillations as functions of the magnetic field for right-circularly-polarized (RCP) light. The lines represent theoretical transitions labeled as in Table II. Only the points of line 7–10 were used in the fit.

The complete spectra of $\Delta R/R$ and ΔV_{pv} at 70 kG are presented for comparison in Fig. 2. The transition-energy positions (labeled as in Table II below) which were taken as data, are indicated on the figure. It is noted that in the case of the Landau-like oscillations having a large broadening parameter, the maxima of the ΔV_{pv} curves corresponded with the minima for the $\Delta R/R$ curves to within 0.5 meV, which is as good as the resolution of the apparatus. A major difficulty in using only the $\Delta R/R$ data is that the reflectivity signal was very weak and noisy, in contrast to that of the photovoltage. This is clearly demonstrated on Fig. 2 by the high visibility of the S.O. transition in the ΔV_{pv} spectrum in comparison with that of the $\Delta R/R$ spectrum. Thus, for each magnetic-field value and polarization, the accumulated data consisted of the data from the $\Delta R/R$ spectra, from the ΔV_{pv} spectra as well as from the direct photovoltaic (V_{pv}) spectra.

Figure 3 presents a comparison of the direct photovoltaic spectrum and its associated wavelength-modulated ΔV_{pv} spectrum at 55 kG for left-circularly-polarized light. The transitions are seen in the direct spectrum as very small oscillations, even when the signal is amplified and offset; these oscillations, however, are quite evident in the modulated spectrum.

B. Landau-level analysis

The energies of the oscillations seen in the spectra are plotted as functions of the magnetic field in Figs. 4 and 5 for right- and left-circularly-polarized light, respectively. Following Vrehen,[8] it was assumed that the binding energy of the excitons associated with Landau levels of higher quantum numbers (e.g., $n = 4$, 5, 6) is negligible when compared to the experimental resolution (~0.5

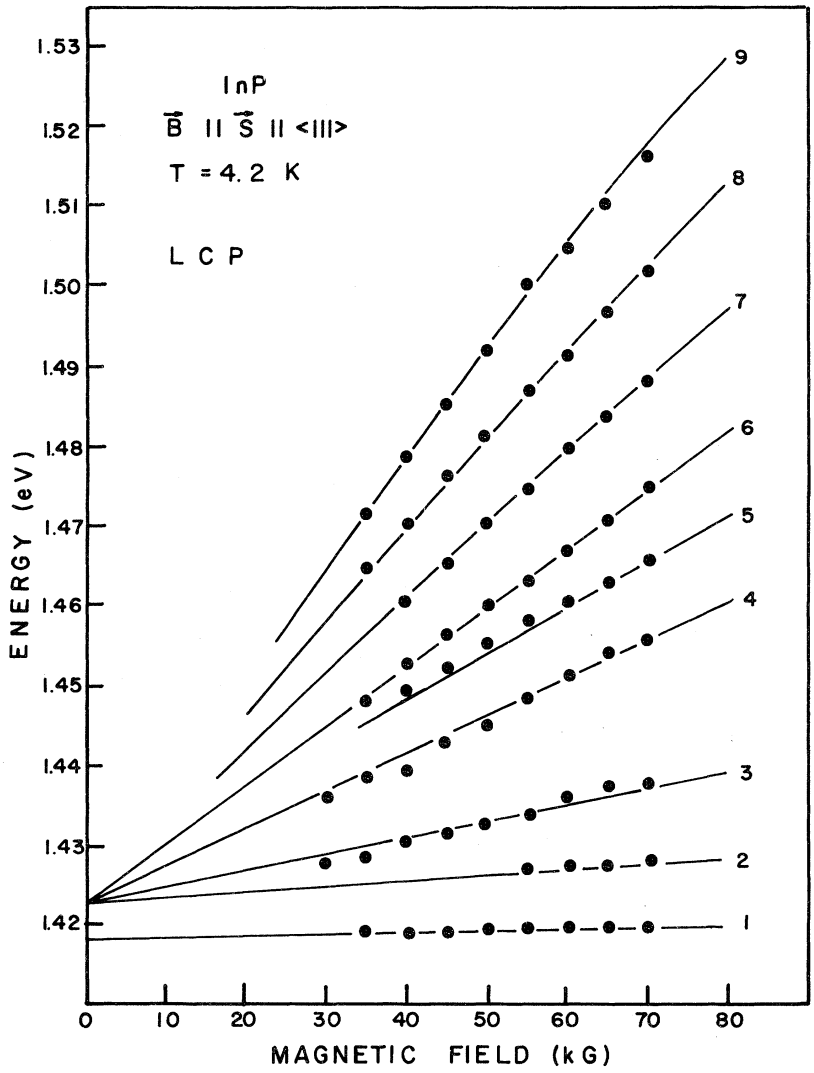

FIG. 5. Energy positions of the spectral oscillations as functions of the magnetic field for left-circularly-polarized light. The lines represent theoretical transitions labeled as in Table II. Only the points of lines 7–9 were used in the fit.

meV). Thus these three levels for both polarizations were simultaneously fitted to the Pidgeon-Brown theory for Landau-level transitions. The fit was done by a convergence program which iterates with respect to the conduction-band effective mass and the Luttinger parameters γ_1^L and γ_2^L. Other parameters necessary to the fit were obtained as follows:

(a) The band-gap value $E_g = 1.423$ eV was obtained from the zero-field convergence point of the three upper curves of both polarizations.

(b) The spin-orbit-splitting energy $\Delta = 0.108$ eV was obtained directly from the spectra at $B = 0$.

(c) The higher-band interaction parameter $f = 0.0$ was obtained by minimizing the rms error of the fit with respect to this parameter.

(d) The anisotropy factor $(\gamma_3^L - \gamma_2^L)$ was taken from Lawaetz.[17]

(e) The value of K^L is approximately[3] given by

$$K^L = \gamma_3^L + \tfrac{2}{3}\gamma_2^L - \tfrac{1}{3}\gamma_1^L - \tfrac{2}{3}\,.$$

The fit produced the band parameters presented in Table I, where parameters such as g_c, g_{so}, m_{so}, and E_p are calculated using the approximate equations of Aggarwal.[22] The parameters obtained differ somewhat from theoretical values; however, they are in agreement with the latest experimental values obtained by cyclotron resonance; for example, $m_{lh}/m_0 = 0.12$ of Leotin *et al.*[19] and $m_c/m_0 = 0.0803$ of Chamberlain *et al.*[21]

The theoretical lines produced in Figs. 4 and 5 are derived from the parameters obtained in the fit and are identified in Table II. The lines are labeled according to the Pidgeon-Brown notation in the case of Landau levels; in the case of exciton levels, the lines are labeled as the corresponding Landau level [which is $R(H)/(2n+1)$ eV above the exciton level]. For example, in the right-circu-

TABLE I. Comparison of the band parameters determined in the present experiment with the theoretical values and other experimental values.

Parameter	Present work	Theory	Experiment
E_g	1.423 ± 0.0005 eV	1.42 eV[a]	1.424 ± 0.001[b]
Δ	0.108 ± 0.002 eV	0.13 eV[a]	0.11[b]
E_p	17 ± 1	20.4 eV[a]	16[c]
f	0.0 ± 0.2	−2.0[a]	
m_c/m_0	0.079 ± 0.001	0.080,[a] 0.072[d]	0.0803[e]
γ_1^L	5.15 ± 0.05	6.28[a]	
γ_2^L	0.94 ± 0.03	2.08[a]	
γ_3^L	1.62 ± 0.03	2.76[a]	
m_{lh}/m_0	0.12 ± 0.01	0.089,[a] 0.086[d]	0.12[c]
m_{hh}/m_0	0.45 ± 0.05	0.85,[a] 0.50[d]	0.60[c]
m_{so}/m_0	0.21 ± 0.01	0.17,[a] 0.18[d]	
K^L	0.12 ± 0.03	1.47[a]	
g_c	1.48 ± 0.05	1.20[a]	
g_{so}	−1.90 ± 0.05		
D_{rms}	0.5 meV		

[a]Reference 17.
[b]Reference 18.
[c]Reference 19.
[d]Reference 20.
[e]Reference 21.

larly-polarized data both the Landau transition $a^+(1)\alpha^c(0)$ (line 3) and its associated exciton level (line 1) are seen. The higher-quantum-number lines (4, 5, 6) are an unresolved mixture of Landau and associated exciton levels. At low quantum numbers, due to the admixture of a number of possible Landau transitions and associated exciton levels, the exact identity of data was difficult to establish. Thus, among the possible overlapping theoretical lines, the line which best described the data was chosen as the label.

C. Exciton parameters

In zero magnetic field, the exciton position is found to be $E_x = 1.4183 \pm 0.0002$ eV, which agrees with the values of Evangelisti *et al.*[23] (1.4185) and White *et al.*[24] (1.4182).

Using the expression developed by Baldereschi and Lipari[25] for the exciton-reduced effective mass together with the band parameters of Table I we obtain

$$\mu_0/m_0 = (m_0/m_c + \gamma_1^L)^{-1} = 0.056 \ .$$

In turn using

$$R_{ex}^0 = \mu_0 e^4/2\hbar^2\epsilon_s^2$$

gives $R_{ex}^0 = 5.2 \pm 0.1$ meV, a value which compares favorably with that of Evangilisti *et al.*[23] (4.8 meV) and White *et al.*[24] (4.9 meV).

The binding energy of the exciton and its position at zero field thus give the band-gap value of E_g = 1.4237 eV, essentially the value deducted from the extrapolated Landau levels.

TABLE II. Identification of the quantum oscillations. The notation used is as in the Pidgeon and Brown (Ref. 4) scheme. In the table the transitions are identified as Landau levels (L) or as exciton states (Ex) associated with the pertinent Landau level. For $n > 4$ the experimental resolution does not allow the differentiation between a Landau level and its associated exciton.

	RCP			LCP	
No.	Notation	Type	Number	Notation	Type
1	$a^+(1)\ \alpha^c(0)$	Ex	1	$b^+(0)\ \beta^c(1)$	Ex
2	$a^-(1)\ \alpha^c(0)$	L	2	$b^-(0)\ \beta^c(1)$	L
3	$a^+(1)\ \alpha^c(0)$	L?	3	$b^+(0)\ \beta^c(1)$	L?
4	$a^+(2)\ \alpha^c(1)$	Ex?	4	$a^+(1)\ \alpha^c(2)$	L?
5	$b^+(2)\ \beta^c(1)$	L?	5	$a^+(2)\ \alpha^c(3)$	L?
6	$a^+(3)\ \alpha^c(2)$	L?	6	$b^+(2)\ \beta^c(3)$	Ex?
7	$a^+(4)\ \alpha^c(3)$	L, Ex	7	$b^+(3)\ \beta^c(4)$	L, Ex
8	$a^+(5)\ \alpha^c(4)$	L, Ex	8	$b^+(4)\ \beta^c(5)$	L, Ex
9	$a^+(6)\ \alpha^c(5)$	L, Ex	9	$b^+(5)\ \beta^c(6)$	L, Ex
10	$a^+(7)\ \alpha^c(6)$	L, Ex			

D. Spin-orbit transition-energy shift

Because of the observed spectral width of the S. O. transition, the exact energy positions of such transitions were limited to a resolution of approximately 1 meV. It was thus difficult to observe dif-

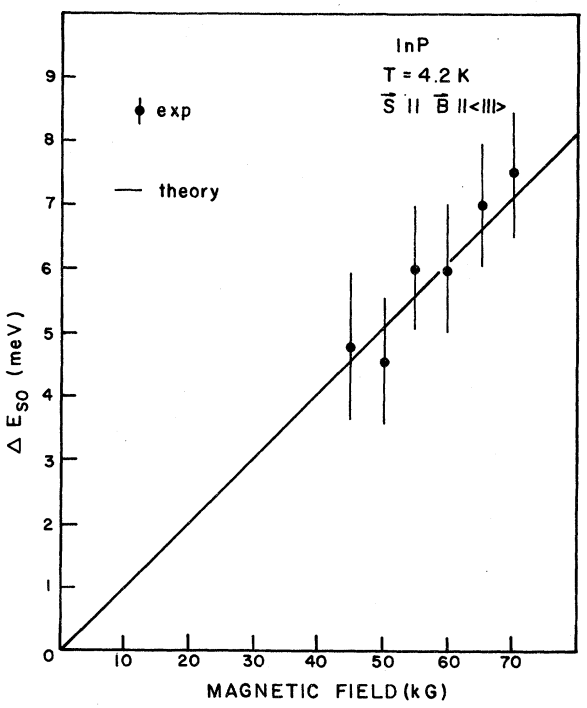

FIG. 6. Energy shift of the split-off to conduction-band transition as a function of the magnetic field. The points represent the averages of both polarizations; the line is a theoretical fit using the parameters of Table I (present work).

ferences between the left- and right-circularly-polarized spectral positions of the transition at a given magnetic field. A general energy shift as a function of magnetic field was, however, observed and is presented in Fig. 6. The points here represent the average shifts in energy of both polarizations. The theoretical line shown in Fig. 6 is given by[22]

$$\Delta E = \tfrac{1}{2}\,(m_0/m_c - m_0/m_{so})S(B)\,, \qquad (8)$$

which is a first-order approximation for the shift in the S. O. transition. In this equation the values $m_c/m_0 = 0.079$ and $m_{so}/m_0 = 0.21$ (from Table I, present work) were used. The function $S(B)$ is given by

$$S(B) = e\hbar B/m_0 c\,.$$

The agreement of the data to the fit again increases our confidence in the parameter derived from the Landau-level analysis, specifically the values of m_c, γ_1^L, and thus m_{so}.

V. CONCLUSION

The above study of the interband magneto-optical properties of InP has shown that the photovoltaic effect and its wavelength derivative can be powerful methods for observing very small changes in the optical properties of semiconductors. These methods can be especially useful in the infrared where the usual reflectivity and absorption measurements are sometimes difficult due to the lack of suitable detectors.

In the case of InP, further investigation at low and intermediate fields should prove useful in determining more precisely the effects of exciton participation. It may then be possible to study the exciton's behavior in the light of the recent theoretical developments of Altarelli and Lipari[6,7] and of Cho[26] *et al.*

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