TABLE I. Experimental values of the Reststrahlen frequencies and elastic constants of CuI; values in parentheses are relative to 90°K measurements. The uncertainty in the elastic constants is ±10%

C_{44}	C_{12} (10^{12} dyn/cm^2)	C_{11}	ν_{LO}' (cm^{-1})		ν_{TO}' (cm^{-1})		Source
...	...	...	(224)[a]	211[a]	(132)	124.2	Ref. (4)
0.158	0.305	0.405	(168)	160	(134)	126	This work

[a]Deduced by the Lyddane-Sachs-Teller relation and dielectric constants given in Ref. (4).

be noted that these displacements are just indicative, because they are only slightly greater than the uncertainty of the measurements at these points.

In conclusion, and before any fitting with a more complete model, we may consider our hypothesis concerning the influence of the overlap and hybridization of the $3d$ electron wave functions in cuprous halides as likely to be true; considering the ionic radii of chlorine, bromine and iodine, CuBr should present an intermediate behavior.

The authors are thankful to Professor D. Cribier and Professor M. Sieskind for fruitful discussions.

TABLE II. Rigid-ion–model parameters for CuI; force constants are in e^2/v (v is the volume of a unit cell). $Z_{Cu}^* = 0.69$.

1	s		s'	α	β	$\Phi_{\alpha\beta}(0_s; 1_{s'})$
(0, 0, 0)	1		2	1	1	2.812
		or				
	2		1	1	2	3.734
				1	1	0.562
	1		1	1	2	0.393
$\frac{1}{4}a(2, 2, 0)$		or				
	2		2	1	3	−0.253
				3	3	−0.6

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Direct Optical Observation of the Subsidiary X_{1c} Conduction Band and Its Donor Levels in InP

A. Onton, Y. Yacoby,* and R. J. Chicotka
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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Zero-phonon and phonon-assisted optical transitions from the Γ_{1c} conduction band to the subsidiary X_{1c} conduction band and its donor levels have been observed in InP at 8°K. The X_{1c}-Γ_{1c} interband energy is measured at 960 ± 5 meV, and the binding energies of donors associated with the subsidiary X_{1c} band are found to be 106 and 175 meV (±5 meV) for Te and Si, respectively.

We report here on a measurement of the $\Gamma_{1c} \rightarrow X_{1c}$ inter-conduction-band energy in InP by means of optical absorption, utilizing the wavelength-derivative technique. The interband free-carrier absorption in InP has been measured by Dumke, Lorenz, and Pettit.[1] With the present measurement technique we have observed for the first time phonon structure associated with the $\Gamma_{1c} \rightarrow X_{1c}$ indirect transition in degenerately doped InP, as well as transitions from the Γ_{1c} conduction band to donor levels associated with the subsidiary X_{1c} conduction-band minima.

Optical band structure measurements of the relative energies of band minima or maxima at different points in the Brillouin zone are usually not as accurate as measurements of direct transitions (the exception being the measurement of an indirect energy gap). Here we report on the first measurement of an indirect interband energy in a direct–band-gap material with high accuracy.

A schematic diagram illustrating the transitions and energy levels involved in the present measurements is given on the top of Fig. 1. Transitions originate from the partially filled Γ_{1c} conduction band and terminate on the donor level associated with the X_{1c} conduction band A or in the X_{1c} conduction-band continuum B. The lower part of Fig. 1 is a schematic plot of the density of pairs of initial filled states and final empty states, $j(E)$, in this interband energy range.

The theory of inter-conduction-band free-carrier absorption has been discussed by Haga and Kimura[2] for III-V semiconductors, and an analysis of it in InP has been performed previously by Dumke, Lorenz, and Pettit.[1] The analytical form for the inter-conduction-band absorption becomes very involved, especially if phonon interactions and impurity scattering are accounted for. Basically, however, the strength of the free-carrier absorption process can be described as follows:

$$F(h\nu)=\sum_i g_i^{\pm}(h\nu)p_i^{\pm}j(h\nu\pm\hbar\omega_i), \qquad (1)$$

where $g_i^{\pm}(h\nu)$ includes the relatively slowly and smoothly varying dependence of transition probability on photon energy. The summation on the density of pairs is performed to include phonon emission and absorption processes which occur with a probability $p_i^{\pm}$ at energies $\hbar\omega_i$. It is immediately evident from Eq. (1) and Fig. 1 that any sharp spectral structure in a wavelength-derivative spectrum will have its origin in the relatively discontinuous density-of-pairs function $j(E)$.

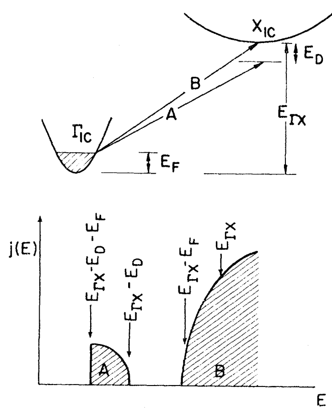

FIG. 1. Schematic representation of the conduction-band structure of degenerately doped InP, where ϵ_F designates the position of the Fermi level with respect to the bottom of Γ_{1c}, and ϵ_D is a donor binding energy relative to X_{1c}. $j(E)$ represents the corresponding density of initial filled states in Γ_{1c} and final empty states at X.

The optical measurements were made in a single beam mode (sample-in, sample-out technique) with a double modulation applied to the beam. A 10% amplitude modulation at 23 Hz was applied before the monochromator entrance slit; wavelength modulation at 2.2 kHz was achieved in the littrow-mount grating monochromator by oscillation of a plane mirror about a vertical axis. The signals at the two frequencies were recorded simultaneously in digital form, and the spectral derivative of the absorption coefficient as a function of photon energy $h\nu$ was calculated from the equation

$$\delta F(h\nu)=I_s'/I_s-I_0'/I_0, \qquad (2)$$

where I_s and I_0 are the photon energy-dependent 23-Hz signals with the sample in and out of the beam, respectively, and the primed quantities are the corresponding spectral derivatives measured at 2.2 kHz. It was found to be extremely important to adjust the spectrometer and sample so that the derivative signal read zero at a true zero slope position in the transmitted beam intensity-versus-wavelength characteristic. To a large extent this adjustment could be made by restricting the f number of the system in the source optics. A tungsten-halogen lamp was used as the source; a wide area lead-sulfide cell as detector.

The InP was grown by a modified two-zone Bridgman drop technique.[3] The ingots were polycrystalline and had grain sizes in the range 1 to 5 mm. Electrical characterization was done by the Van der Pauw technique. Optical samples varied between 0.7 and 2.0 cm in thickness.

The experimental results are shown in Fig. 2. Plotted there are the absorption coefficient and its first derivative as a function of photon energy for one Te-doped sample and one Si-doped sample. Detailed data on the electrical properties of these and other samples and quantitative data from derivative spectra are given in Table I. The spectra obtained with the three Te-doped samples in Table I are similar except for some broadening of the spectral features and a shift of the

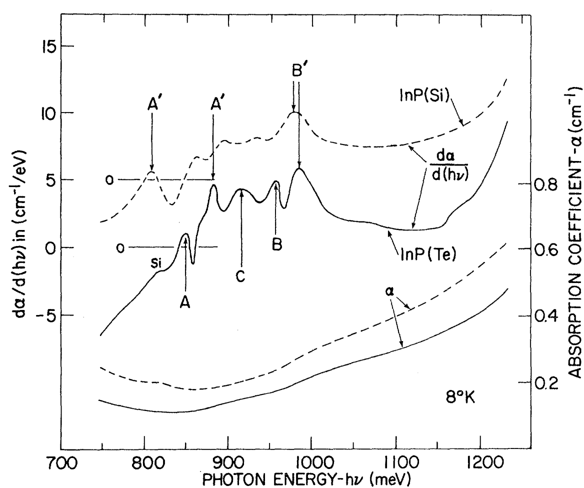

FIG. 2. Absorption coefficient and its first derivative as a function of photon energy for InP samples Te 1 and Si at 8°K. The transitions A and B designate zero-phonon processes and the primed letters their phonon-assisted replicas.

spectrum to lower energy with increasing donor concentration. As shown in Table I, the donor-concentration–dependent spectral shift is consistent with the Burstein shift measured in InP by Dumke, Lorenz, and Petti.[1] Thus it is clear that the initial state for the transitions we observe in the derivative spectrum is from near the Fermi level in the Γ_{1c} conduction band. As expected, the structure in the derivative spectrum disappears in undoped samples. The extreme sensitivity of the derivative measurement to spectral structure is clear from a comparison of the absorption coefficient spectrum and its derivative.

The transitions observed in the derivative spectrum span an energy range of almost 200 meV. Given the momentum-conserving phonons expected [TA(X) = 9.3,[4] LA(X) = 28.6, TO(X) = 34.3, and LO(X) = 29.3 meV],[5] no possible interpretation of the spectrum in terms of only band-to-band, Γ_{1c}-to-X_{1c}, transitions with the cooperation of phonons seems reasonable. Instead, since some of the structure (B') is common to the Si- and Te-doped samples and some of it is not (A'), and since all the transitions have a common origin near the Fermi level in Γ_{1c}, the only possible explanation of the spectra appears to be that the transitions labeled A have X_{1c} donor levels as final states, and that the transitions labeled B terminate in the X_{1c} conduction band.

According to the idealized $j(E)$ in Fig. 1, the strongest peaks in the derivative spectrum should correspond to the energies $E_{\Gamma X} - E_D - E_F$ and $E_{\Gamma X} - E_F$ as defined in the figure, and those energies plus momentum-conserving phonon energies. Then according to the data on the sample Te 1, which involve the smallest correction for the position of the Fermi level, $E_{\Gamma X} = 960 \pm 5$ meV and $E_D(\mathrm{Te}) = 106 \pm 5$ meV; and from the Si sample, $E_D(\mathrm{Si}) = 175 \pm 5$ meV (see the discussion that follows).[6] The estimated errors include approximately equal uncertainties in interpretation of the derivative spectra and precise knowledge of the location of the Fermi level with respect to the bottom of the Γ_{1c} conduction band in nondegenerate InP.

The $\Gamma_{1c} \rightarrow X_{1c}$ inter-conduction-band energy of 960 meV measured here is to be compared with 900 ± 20 meV measured by Dumke, Lorenz, and Pettit,[1] and 700 ± 70 meV measured by Pitt.[7] The difference with the former is primarily that we have resolved transitions to X_{1c} donor levels from the band-to-band transitions. This points up the necessity of accounting for impurity-state involvement in all interband transitions in heavily

TABLE I. Interband transitions in InP (8°K). The light path was in the direction of the donor concentration gradient whose extreme values are given in the table. ϵ_F is the position of the Fermi level relative to the bottom of the conduction band in intrinsic material.

Sample No.	78°K carrier concentration (10^{17} cm^{-3})	ϵ_F^{av} [a] (meV)	Transition energies (meV) A	A'	C	B	B'	$\epsilon_F^{\mathrm{meas}}$ (meV)
i	0.18–0.18	...	...	...	...	...	...	...
Te 1	4.6–5.8	4	850	882	915	956	984	4[b]
Te 2	6.0–12.9	15	845	879	910	949	980	8
Te 3	13.8–23.7	30	...	869	902	940	965	23
Si	10.1–11.9	18	...	809	...	...	979	9

[a]See Ref. 1.

[b]This number has been set at 4 meV. The remaining numbers in this column are calculated relative to it from B'.

doped semiconductors. The present investigation covered the photon energy range from 450 to 1230 meV. Transitions to L_{1c} would be expected near 610 meV and to X_{3c} near 1700 meV.[8] There was no evidence of L_{1c} or X_{3c} conduction-band involvement in this energy range with the sample thicknesses used.

The peaks in the spectra of the Te-doped InP related by momentum-conserving phonons are separated by about 30 meV. From their energies these are LA(X_1), LO(X_3), or TO(X_5) phonons (the origin of coordinates being the group-V element P).[9] In addition, it appears that the A-A' separation of 33 meV is consistently larger than the B-B' separation of 28 meV. This suggests that the TO phonon is the one primarily involved in transitions to the donor level, whereas LA or LO phonons participate in transitions to the X_{1c} band. The same phonon selection rules have been assumed to apply in the case of the Si-doped sample in the calculation of the Si donor binding energy. The zero-phonon transition to the X_1 band is observed presumably because of donor-impurity scattering.[10] Zero-phonon transitions are allowed to the $1s(A_1)$ lowest ground-state sublevel of the Te donor through the Γ_{1c} intermediate state, and to the $1s(T_2)$ ground state of the Si donor via the Γ_{15c} intermediate state.[11] As expected, experimentally the zero-phonon transitions involving Te are much stronger than with Si for which no clear zero-phonon transitions are observed.[12] The transition marked C in the Te spectrum is either a two-phonon replica of the $\Gamma_{1c} \rightarrow 1s(A_1)$ donor level transition or a phonon-assisted transition to the $1s(E)$ donor level. It is not possible at present to distinguish between these alternatives. The additional structure observed with the Si sample between 850 and 950 meV has not been established to be related to Si in InP. The shoulder marked "Si" in the InP(Te) spectrum suggests Si is an unintentional impurity in our InP.

In conclusion, we have observed optical transitions of electrons from the Γ_{1c} conduction band to the X_{1c} conduction band and its donor levels, with and without phonon cooperation. The derivative technique employed should be useful in determining the relative energies of band-structure critical points at different points in the Brillouin zone for a number of other materials.

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*Permanent address: Graduate School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, Israel.

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