679 (1967).

[16] A classical electrostatic calculation of the electric field penetration into electrodes was first given by H. Y. Ku and P. G. Ullman, J. Appl. Phys. 35, 265 (1964); also J. G. Simmons, Brit. J. Appl. Phys. 18, 269 (1967).

[17] See, for example, A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces* (North-Holland, Amsterdam, 1965), p. 132.

[18] D. C. Tsui, Bull. Am. Phys. Soc. 16, 418 (1971); Solid State Commun. 9, 1789 (1971).

[19] I. Giaever and K. Mergerle, Phys. Rev. 122, 1101 (1961).

[20] W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Chap. 11.

[21] D. E. Thomas and J. M. Rowell, Rev. Sci. Instr. 36, 1301 (1965).

[22] J. M. Rowell, W. L. McMillan, and W. L. Feldmann, Phys. Rev. 180, 658 (1969).

[23] F. S. L. Hsu and J. E. Kunzler, Rev. Sci. Instr. 34, 297 (1963).

[24] F. Matossi and F. Stern, Phys. Rev. 111, 472 (1958); C. R. Pidgeon, D. L. Mitchell, and R. N. Brown, *ibid.* 154, 737 (1967).

[25] D. C. Tsui, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass.*, 1970 (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1970), p. 468.

[26] The agreement is poor in the case of the least heavily doped samples, for which the effect of impurity banding is important.

[27] The number of atoms per unit area in the three major symmetry planes of an InAs crystal is $n_s(\{110\}) = 4/\sqrt{2}\,a^2$, $n_s(\{111\}) = 4/\sqrt{3}\,a^2$, and $n_s(\{100\}) = 2/a^2$. Here a is the InAs lattice constant.

[28] In Ref. 9, the electron screening length λ was incorrectly estimated. According to the Thomas-Fermi model, λ for the two samples is 100 and 180 Å.

[29] L. M. Roth and P. N. Argyres, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. I, Chap. 6.

[30] D. C. Tsui, Bull. Am. Phys. Soc. 16, 143 (1971).

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Donor-Electron Transitions between States Associated with the X_{1c} and X_{3c} Conduction-Band Minima in GaP

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Transitions from the ground states of Si, Te, and S donors associated with the lowest X conduction band have been observed to excited donor states associated with the next-higher X conduction band as well as transitions into the higher band. The X_{3c}-X_{1c} interband energy is found to be 355 ± 3 meV with the conductivity effective mass in the higher band being $(0.14 \pm 0.02) m_0$.

We report here the observation in GaP at 5.5 °K of transitions from the ground states of Si, Te, and S donors associated with the lowest X conduction band to excited states associated with the next-higher X conduction band. We believe this is the first direct observation of impurity levels within the conduction-band continuum, and certainly the first time they have been seen directly with optical excitation. Moreover, the experiment provides an excellent value for the X_{3c}-X_{1c} conduction-band crystal-field splitting as well as an estimate of the higher X conduction-band effective mass.

The first observation of impurity-related energy levels within the continuum of a band was by Zwerdling *et al.*[1] for B and Al acceptors in the valence band of silicon. The transitions observed were from the ground state (with s-like envelope function) associated with the $p_{3/2}$ valence band to p-like excited states associated with the spin-orbit split-off $p_{1/2}$ valence band. Kosicki and Paul[2] presented evidence for the existence of donor levels associated with higher-lying conduction bands in hydrostatic pressure measurements on GaSb.

Infrared-absorption measurements on GaP in the 300–600-meV photon energy range have been made previously by Spitzer *et al.*,[3] Zallen,[4] Zallen and Paul,[5] Remenyuk *et al.*,[6,7] and Shmartsev *et al.*[8] The observed absorption has been attributed to X_{1c}-X_{3c} band-to-band and donor-to-X_{3c} conduction-band transitions. The k-space symmetry of the final state has been shown to be consistent with hydrostatic pressure data[4,5] as well as extrapolation from data in $\mathrm{GaAs}_{1-x}\mathrm{P}_x$.[9]

The results of the present infrared-transmission measurements on GaP are shown in Fig. 1 for four samples doped with various donor species. Plotted is the absorptoin coefficient as a function of incident photon energy. The spectra are characterized by a relatively sharp principal absorption peak followed by a broader band at higher energy. A schematic representation of the energy levels involved in these transitions is shown in Fig. 2. We assign the principal peak to the $1s \rightarrow 2p'_{\pm}$ transition (i.e., from the ground state associated with the lower conduction band to the $m = \pm 1$ sublevel of the hydrogenic $2p$ state associated with the upper (primed) conduction band).[10] The higher-energy absorption band we assign to the $1s \rightarrow X_{3c}$ $[X_{1c}]$donor–to–higher-conduction-band transition. A discussion of these assignments follows.

The symmetries of the band and donor levels in Fig. 2 with respect to whether the donor impurity is on a group-III (Si in GaP) or group-V (Te and S in GaP) site have been discussed by Morgan.[11] Here the notation appropriate for the Si donor has been placed in square brackets. At the temperature of the measurement, 5.5 °K, the electrons are in the $1s$ ground states of the donors.[12] Transitions from the $1s$ ground state to excited states associated with the same $X_{1c}[X_{3c}]$ conduction band have been reported earlier.[10,13] In those measurements it was clear that by far the dominant excitation process is the $1s \rightarrow 2p_{\pm}$ transition. Since all the parameters for the $2p'_{\pm}$ level, including its irreducible representation $T_1 + T_2$, are similar to those of the $2p_{\pm}$ level, we expect the $1s \rightarrow 2p'_{\pm}$ transition to dominate in its spectral range.

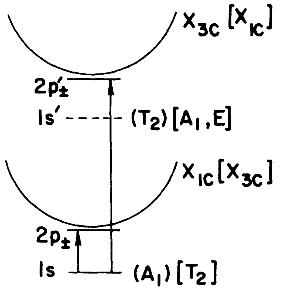

FIG. 2. Inter-conduction-band donor-electron transitions. The notation appropriate for Si donors in GaP is in square brackets, the others apply to Te and S donors.

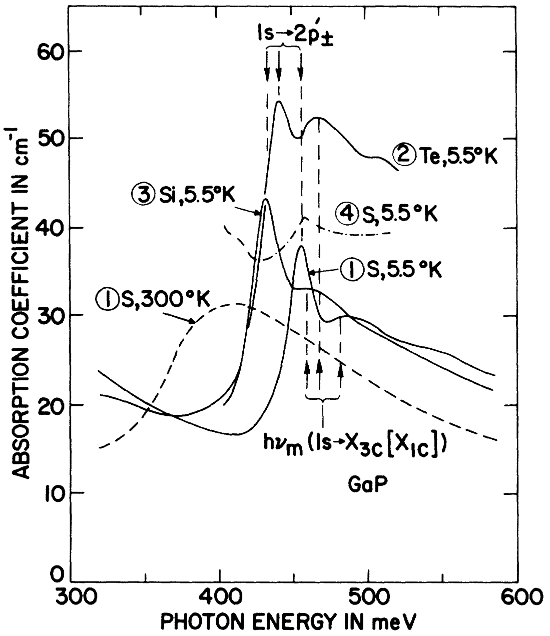

FIG. 1. Absorption coefficient vs photon energy for four n-type GaP samples in the X_{3c}-X_{1c} interband energy region. The room temperature carrier concentrations were 1: S, 3.2×10^{17}; 2: Te, 1.4×10^{17}; 3: Si, 2×10^{17}; and 4: S, 3×10^{16}. The spectrum for sample 2 has been shifted downward by 100 cm^{-1}. The strength of the $1s \rightarrow 2p'_{\pm}$ transition should be judged relative to the minimum in absorption near the low-energy threshold of the $1s \rightarrow 2p'_{\pm}$ transition. This minimum in absorption represents the best available estimate of the background absorption due to other processes.

The initial state in the observed transitions is clearly the $1s$ ground state since the same donor species shifts are observed for the $1s \rightarrow 2p'_{\pm}$ transition as have been observed for the $1s \rightarrow 2p_{\pm}$ transition[14] (see Table I). Also, the strength of the transition is proportional to the donor concentration (cf. sample 1 with 3×10^{17} cm^{-3} and sample 4 with 3×10^{16} cm^{-3} room-temperature carrier concentrations derived from S donors). The final state $2p'_{\pm}$ is clearly lifetime broadened by the possibility of a spontaneous decay into states of the lower $X_{1c}[X_{3c}]$ conduction band. The half-width of the $1s \rightarrow 2p'_{\pm}$ transition is ~ 20 meV compared to 0.6 meV for the $1s \rightarrow 2p_{\pm}$ transition.[10] The total linewidth observed, however, undoubtedly includes some broadening (small relative to 20 meV) associated with the large donor concentrating used to observe the $1s \rightarrow 2p'_{\pm}$ transitions clearly. The decrease of the intensity of the $1s \rightarrow 2p'_{\pm}$ peak with temperature is characteristic of donor excitation spectra.[10] At 80 °K the transition is still clearly distinguishable, not broadened significantly relative to its half-width at 5.5 °K, but reduced in intensity. At 300 °K the transition is no longer distinguishable. The fact that the $1s \rightarrow 2p'_{\pm}$ transition was not observed previously[3,8] must thus be related to excessively large intentional and/or unintentional impurity concentrations. Qualitatively the spectra in Fig. 1 are similar to photoexcitation spectra of acceptors and donors in other materials.[15]

The following expression for the conductivity effective masses m_1^* and m_3^* of the conduction bands $X_{1c}[X_{3c}]$ and $X_{3c}[X_{1c}]$, respectively, can be derived from prior studies of such transitions by Dumke[16]

TABLE I. Donor-electron transition energies in GaP (meV).

Donor	$1s \rightarrow 2p_{\pm}$ [a] (±0.05) E (ΔE)	ϵ_I [b] (±0.3)	$1s \rightarrow 2p'_{\pm}$ (±1) E(ΔE)	$h\nu'_m$ (peak of $1s \rightarrow X_{3c}[X_{1c}]$)	$2p'_{\pm} - 2p_{\pm}$ (±1)
Si	74.9	82.1	432	460 ± 5	357
Te	82.6 (7.7)	89.8	441 (9)	468 ± 3	358
S	96.9 (14.3)	104.1	457 (16)	483 ± 3	360

[a] References 10 and 13.

[b] Reference 13.

and Shmartsev *et al.*[8]:

$$\frac{m_1^*}{m_3^*} = \frac{4}{1/2y - \epsilon_I/h\nu'_m} - y \quad , \tag{1}$$

where

$$y = (h\nu'_m - \epsilon'_I)/\epsilon_I \quad , \tag{2}$$

ϵ_I and ϵ'_I are, respectively, the thresholds of the $1s \to X_{1c}[X_{3c}]$ and $1s \to X_{3c}[X_{1c}]$ transitions, and $h\nu'_m$ is the photon energy at the maximum absorption point on the $1s \to X_{3c}[X_{1c}]$ band. As a first approximation Eq. (1) gives $(m_1^*/m_3^*) = 1.55$ on the basis of the Te and S donor data (for Si, $h\nu'_m$ is not well defined experimentally) when the value of ϵ'_I used in Eq. (2) is derived by adding the $2p'_\pm$-$2p_\pm$ interband energy (Table I) to ϵ'_I. In this approximation the binding energy of the $2p'_\pm$ level is obtained by subtracting the energy of the $1s \to 2p'_\pm$ transition from ϵ'_I. It is found to be 7.1, 6.8, and 7.1 meV (± 1 meV), respectively, for Si, Te, and S donors. Neglecting effects of effective mass anisotropy, which we shall assume are the same for both conduction bands, we can estimate the theoretical effective-mass binding energy[17] of the $2p'_\pm$ level $(E_B)_{2p'_\pm}$ by

$$(E_B)_{2p'_\pm} = (m_3^*/m_1^*)\,(E_B)_{2p_\pm} \quad . \tag{3}$$

This gives $(E_B)_{2p'_\pm} = (4.6 \pm 0.5)$ meV in the effective-mass approximation.[13,17] Thus we find as a first correction that the X_{3c}-X_{1c} interband energy difference is about 2.4 ± 0.5 meV smaller than the $2p'_\pm - 2p_\pm$ energy difference. A further iterative calculation of (m_1^*/m_3^*) and $(E_B)_{2p'_\pm}$ approaches $(m_1^*/m_3^*) = 1.85 \pm 0.3$ and $(E_B)_{2p_\pm} = 4$ meV, with (355 ± 3) meV for the average X_{3c}-X_{1c} interband energy.

In conclusion, we have observed excited states of donors associated with the next-higher-lying X conduction band. An analysis of the results gives (355 ± 3) meV for the X_{3c}-X_{1c} interband energy and a conductivity effective-mass ratio of $(m_1^*/m_3^*) = 1.85 \pm 0.3$ for carriers in the two bands. Thus $m_3^* = (0.14 \pm 0.02)m_0$, where m_0 is the free electron mass.[13] The present measurement is unique in its accuracy and falls approximately in the middle of the range of X_{3c}-X_{1c} interband energies reported previously. The extremes seem to be the values of 290 ± 10 meV reported by Dean *et al.*[18] on the basis of intrinsic absorption measurements and 470 meV reported by Cardona *et al.*[19] on the basis of electroreflectance measurements. Our result is in good agreement with the interband energy of 350 meV reported by Shmartsev *et al.*[8] on the basis of extrinsic infrared-absorption measurements and 340 meV reported by Dumke *et al.*[20] from an analysis of intrinsic absorption.

We wish to acknowledge the helpful cooperation of Dr. T. S. Plaskett and Dr. R. C. Taylor in making available the samples used in these measurements.[21] We wish to thank Dr. T. N. Morgan and Dr. W. P. Dumke for discussions on the results, and R. E. Fern for performing the experimental work.

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[1] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters 4, 173 (1960).

[2] B. B. Kosicki and W. Paul, Phys. Rev. Letters 17, 246 (1966). See also discussion by A. G. Foyt, R. E. Halsted, and W. Paul, Phys. Rev. Letters 16, 55 (1966).

[3] W. G. Spitzer, M. Gershenzon, C. J. Frosch, and D. F. Gibbs, J. Phys. Chem. Solids 11, 339 (1959).

[4] R. Zallen, Ph.D. thesis (Harvard University, 1964) (unpublished).

[5] R. Zallen and W. Paul, Phys. Rev. 134, A1628 (1964).

[6] A. D. Remenyuk, L. G. Zabelina, Yu. I. Ukhanov, and Yu. V. Simartsev, Fiz. Tekh. Poluprov. 2, 666 (1968); 2, 671 (1968) [Sov. Phys. Semicond. 2, 557 (1968); 2, 561 (1968)].

[7] A. D. Remenyuk, L. G. Zabelina, Yu. I. Ukhanov, V. M. Tuchkevich, and Yu. V. Shmartsev, *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow*, 1968 (Nauka, Moscow, 1968), p. 222.

[8] Yu. V. Shmartsev, A. D. Remenyuk, and E. M. Kistova, Fiz. Tekh. Poluprov. 4, 195 (1970) [Sov. Phys. Semicond. 4, 155 (1970)].

[9] J. W. Allen and J. W. Hodby, Proc. Phys. Soc. (London) 82, 315 (1963).

[10] A. Onton, Phys. Rev. 186, 786 (1969). This article contains more extensive references to prior studies of electronic impurities in semiconductors.

[11] T. N. Morgan, Phys. Rev. Letters 21, 819 (1968).

[12] There is no possibility of population of the higher $1s(E)$ levels of Te and S donors since they have been observed, respectively, 40.5 and 53.4 meV above the $1s(A_1)$ level [D. D. Manchon, Jr., and P. J. Dean, *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass.*, 1970 (U. S. Atomic Energy Commission, Oak Ridge, Tenn., 1970), p. 760]. The spin-orbit splitting of the $1s(T_2)$ ground state of the Si donor has been estimated at 0.35 meV [F. Mehran and co-workers (private communication)]. Such a small splitting is of no consequence in the present measurement.

[13] A. Onton and R. C. Taylor, Phys. Rev. B 1, 2587 (1970).

[14] The actual agreement in Table I is slightly outside estimated experimental error. This may arise from the relatively large concentrations of donors used in the present samples together with the relatively large half-width of the $1s \to 2p'_\pm$ transition.

[15] See, for example, E. Burstein, G. Picus, B. Henvis, and R. Wallis, J. Phys. Chem. Solids 1, 65 (1956); G. Picus, E. Burstein, and B. Henvis, *ibid.* 1, 75 (1956).

[16] W. P. Dumke, Phys. Rev. 132, 1998 (1963).

[17] R. A. Faulkner, Phys. Rev. 184, 713 (1969).

[18] P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. 38, 3551 (1967).

[19] M. Cardona, K. L. Shaklee, and F. H. Pollack, Phys. Rev. 154, 696 (1967).

[20] W. P. Dumke, M. R. Lorenz, and G. D. Pettit (private communication).

[21] The preparation of the Si-doped sample of GaP has been described by T. S. Plaskett, S. E. Blum, and L. M. Foster [J. Electrochem. Soc. 114, 1303 (1967)], with the GaP synthesized according to T. S. Plaskett [*ibid.* 116, 1722 (1969)]. The other samples were prepared by the vapor transport method described by R. C. Taylor, J. F. Woods, and M. R. Lorenz [J. Appl. Phys. 39, 5404 (1968)].

PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Electron Shielding in Doped Semiconductors*

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The binding energy of an electron bound to two ionized impurity atoms is calculated as a function of the screening parameter δ, which occurs in the screened Coulomb potential. The binding energy is found to diminish with increase in δ, ultimately becoming zero at $\delta \approx 1.254$. The role played by such a system in the Mott transition is discussed.

I. INTRODUCTION

The binding energy of an electron, bound to a donor atom in a doped semiconductor, relative to the conduction-band minima is usually calculated[1,2] for a single impurity atom in the crystal. On the experimental side, it is known[3,4] that the binding energy of the electron decreases as the number of donors increases until at some critical impurity concentration there is practically no activation energy.

The theoretical problems associated with this phenomena can be conveniently discussed in terms of the potential of the singly charged donor screened by the conduction electrons[5,6]:

$$V(r) = -(e^2/\kappa r)e^{-qr} , \tag{1}$$

where κ is the static dielectric constant and q is the Mott screening parameter defined by $q^2 = 4m^* e^2 n^{1/3}/(\kappa\hbar^2)$, n being the free-electron density.

The approximation that the electron is bound to a single ionized impurity is, however, no longer justified if there is considerable overlap between the wave functions of electrons bound to two neighboring impurity atoms. The occurrence of such a situation is governed by three factors: the static dielectric constant κ, the effective mass m^*, and the free-electron density n. The effect of κ and of m^* can be seen from the expression of the Bohr radius, $a_0 = \hbar^2\kappa/m^*e^2$; since in semiconductors, $\kappa > 1$ and $m^* < m$, this means a greater radius than that in the free space. An increase in the doping concentration acts in two ways: First, it decreases the average distance between impurities, and second, it increases the value of q, which in its turn leads to an increase in the average distance $\langle r\rangle$ between the electron and nucleus of the impurity atom.[7] An appropriate combination of these factors can lead to the situation such that $\langle r\rangle \simeq \frac{1}{2}d$, where d is the average distance between impurities. We may note here that such a condition can sometimes exist at fairly low impurity concentrations, e.g., for InSb it occurs at an impurity concentration of $\sim 10^{14}/\mathrm{cm}^3$. As this limit is approached, there will be an increasing concentration of systems in which two or more impurity atoms are participating. In the present paper we investigate the stability of the simplest of these systems, consisting of two ionized impurity atoms and an electron. We shall represent this system by Im_2^+ in analogy with H_2^+.

II. CALCULATION AND RESULTS

As shown in Fig. 1, r_a and r_b represent the distances between the electron and the nuclei a and b, and R is the distance between the nuclei. We shall carry out the calculation in the following units: unit of energy $= m^*e^4/\hbar^2\kappa^2$, unit of length $a_0 = \hbar^2\kappa/m^*e^2$. Also $\delta = qa_0$.

The Hamiltonian of the system may be written

$$H = -\tfrac{1}{2}\,\nabla^2 - e^{-\delta r_a}/r_a - e^{-\delta r_b}/r_b + e^{-\delta R}/R . \tag{2}$$

At this point, the reader may well raise the question whether it is justified to represent the poten-