PHYSICAL REVIEW B VOLUME 41, NUMBER 8 15 MARCH 1990-I

Photoionization of deep impurity centers in semiconductors

V. Gonzalez Robles and G. Gonzalez de la Cruz
Departamento de Física, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional,
Apartado Postal 14-740, 07000 México, Distrito Federal, Mexico

(Received 17 July 1989)

The frequency dependence of the photoionization cross section for deep semiconductor impurity centers is calculated using a quantum-defect wave function with the correct normalization for the bound state. The effects of nonparabolicity of the conduction and valence bands are included by using an expression for the energy-dependent wave vector based on the **k**·**p** approximation. Comparison with experiment has been made for the photoionization of manganese and copper impurities in gallium arsenide.

I. INTRODUCTION

Since the advent of semiconductor physics, considerable effort has been devoted to calculating the cross section of transitions between bands and impurities, this problem presents a varying degree of complexity, depending on the type of impurity (effective mass or deep type) and the type of transition (involving an impurity state derived from the same or a different band) considered. In particular, a lack of knowledge of the proper impurity wave function often presents a major source of difficulty.

Pioneering work was performed by Bebb and Chapman,[1] who borrowed the phenomenological quantum-defect method (QDM) from atomic physics and applied it to the case of impurities having a mixture of Coulomb and short-range potentials. The δ-function model for very deep centers was developed by Lucovsky.[2] Very shallow centers are described in the framework of hydrogenic effective-mass theory. An up-to-date review on the validity of the effective-mass theory and on isocoric impurities has been given by Pantelides.[3] Bebb[4] used the QD wave function to calculate the optical-transition cross section involving an impurity. Ridley[5] derived an approximate analytical expression for the photoionization cross section and its temperature dependence. In contrast to earlier work, contributions of Bloch functions from both conduction and valence bands to the localized states were considered. In 1982, Chaudhuri[6] pointed out a number of important deficiencies of the earlier work. By eliminating unjustified approximations, correcting errors, and using a method to compare the overlap integrals of the cell periodic functions, Chaudhuri derived a rather general formalism to calculate the zero-temperature cross section for both types of transitions: band impurity transitions and photoionization or photodeionization. As an example and application of his method, he chose GaAs. Unfortunately, the complexity which arises due to the degeneracy of the valence band in zinc-blende-structure semiconductors was not taken into account. Recently, the frequency dependence of the photoionization cross section of deep centers was described by Perep and Yassievich[7] using a zero-range potential applicable to semiconductor crystals whose band structure can be described by the Kane approximation.[8] The wave functions were also constructed for deep centers (acceptors)[9] with an arbitrary relation between the band-gap-width, energy level, and spin-orbit splitting of the valence band. More recently, Coon and Karunasiri[10] derived an analytical expression for the photoionization cross section of impurity atoms using the quantum-defect wave function for the impurity ground state and the Green-function formalism within the parabolic approximation for the energy of the photoexcited carrier. They obtained that the peak position of the photoionization cross section for donor impurities in Si and Ge is given at the ionization energy of the impurity center. However, it is well known from experimental evidence that for acceptor impurities the peak of the cross section is shifted to higher photon energy.

In this work, our aim is to further develop the phenomenological approach used by Chaudhuri in order to provide a description of electron transitions involving an impurity center, with the inclusion of first-order nonparabolicity corrections to the energy-band structure for diamonds- and zinc-blende-structure semiconductors. The influence of this effect has been considered important in the calculation of high-field transport equations for electronic devices.[11] By way of application, we shall calculate the photoionization cross section for manganese and cooper deep acceptors in gallium arsenide.

II. PHOTOIONIZATION CROSS SECTION OF THE IMPURITY CENTER

The wave function of the electron in the presence of the impurity potential may be represented by the sum of Bloch functions:

$$\psi_v(r)=\sum_{n,k} F_{nk}\psi_{nk} \ , \tag{1}$$

where n is the band number, k is the wave vector, and the F_{nk} are slowly varying envelope functions satisfying the well-known effective-mass equation

$$\sum_m [D_{nm}^{\alpha\beta}k_\alpha k_\beta + U(r)\delta_{nm}]F_m(r)=E_I F_n(r) \ . \tag{2}$$

Here, U and E_I are the potential and energy of the impurity center, and the quantities $D_{nm}^{\alpha\beta}$ are a set of numbers defined by[12]

$$D_{nm}^{\alpha\beta}=\frac{\hbar^2}{2m_0}\delta_{nm}\delta_{\alpha\beta}+\frac{\hbar^2}{m_0^2}\sum_i\frac{P_{ni}^{\alpha}P_{im}^{\beta}}{E_0-E_i}\ , \tag{3}$$

where the summation over i is over all those states on the unperturbed problem not belonging to the degenerate set n (valence-band wave function in GaAs), E_0 is the energy of the degenerate state, E_i is the energy of the unperturbed state, P_{ni}^{α} are the momentum matrix elements between the different bands evaluated at the degeneracy point, and m_0 is the free-electron mass. We see that the numbers $D_{nm}^{\alpha\beta}$ in the theory of degenerate bands have the same significance as the inverse effective mass in the theory of simple bands, which may be determined, for instance, from cyclotron resonance experiments. Since most of the work has been reported in cubic or zinc-blende materials, we use the $\mathbf{k}\cdot\mathbf{p}$ method as a basis for calculation.

For those materials in which the Γ_6-Γ_7-Γ_8 separations (Fig. 1) are small as compared to the energy difference between these states and higher valence and conduction bands, the most useful formulation of $\mathbf{k}\cdot\mathbf{p}$ perturbation theory has been given by Kane.[8] The states at the band edges are put into two groups: group A includes the closely bunched states of interest, i.e., Γ_6, Γ_7, and Γ_8; and group B includes the remainder. $\mathbf{k}\cdot\mathbf{p}$ interactions between A and B are removed to lowest order, giving a "renormalized" interaction matrix between the states in A which is then diagonalized exactly. When the spin-orbit interaction is included, the sixfold-degenerate (with spin) valence-band states split up into the doubly degenerate light- (E_{lh}) and heavy- (E_{hh}) hole band state, Γ_8, and the split-off (E_s) band state Γ_7. For $\mathbf{k}$ in the direction of z corresponding to one of the crystal symmetry axes, the doubly degenerate cell periodic wave functions which result from the diagonalization of the Hamiltonian $D_{nm}=D_{nm}^{\alpha\beta}k_\alpha k_\beta$ may be written as

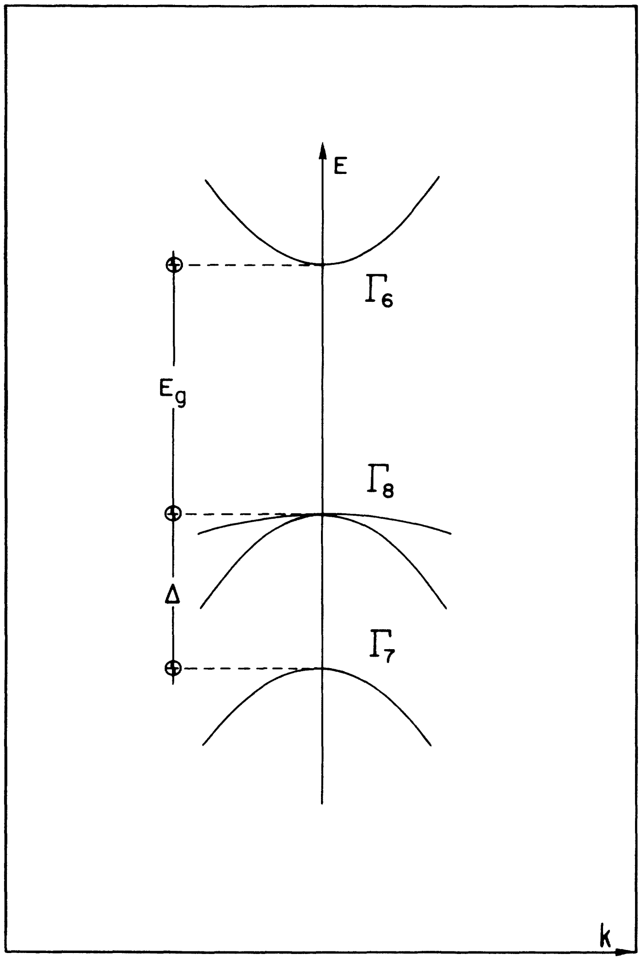

FIG. 1. Conduction and valence bands of GaAs in the vicinity of the center of the Brillouin zone. E_I is the energy level of the impurity center.

$$U_n(k)=\begin{Bmatrix} a_n(is\beta)+b_n\left[(x-iy)\frac{\alpha}{\sqrt{2}}\right]+c_n(z\beta) \\ a_n(is\alpha)+b_n\left[-(x+iy)\frac{\beta}{\sqrt{2}}\right]+c_n(z\alpha)\ , \end{Bmatrix}$$

$$U_h(k)=\begin{Bmatrix} \left[(x+iy)\frac{\alpha}{\sqrt{2}}\right] \\ \left[(x-iy)\frac{\beta}{\sqrt{2}}\right]\ , \end{Bmatrix} \tag{4}$$

where α and β are spin functions, and a_n,b_n,c_n are real coefficients; the index n refers to the bands E_c (conduction-band energy) E_l,E_s. The general expressions for a_n, b_n, and c_n may be written[8] as

$$\begin{aligned} a_n&=kP(E_n+E_g+\tfrac{1}{2}\Delta)/N\ ,\\ b_n&=\frac{\sqrt{2}\Delta}{3N}E_n\ ,\\ c_n&=E_n(E_n+E_g+\tfrac{2}{3}\Delta)/N\ , \end{aligned} \tag{5}$$

where N is a normalizing factor and the E_n are the solutions of the following cubic equation:

$$E'(E'+E_g)(E'+E_g+\Delta)-k^2P^2(E'+E_g+\tfrac{2}{3}\Delta)=0 \tag{6}$$

with P the momentum matrix element between the valence and conduction bands, E_g is the band gap at $k=0$, and Δ is the energy of the valence-band spin-orbit coupling. Note that the zero of the energy scale has been taken at the top of the valence band. The energy variable in Eq. (6) is

$$E'=E-E_g-\hbar^2k^2/2m_0\ . \tag{7}$$

Therefore, when diagonalized, D_{nm} yields the energy bands at each $\mathbf{k}$ in the vicinity of $\mathbf{k}=0$. The coefficients of the various terms in D_{nm} are parameters similar to effective masses and can be expressed in terms of the second derivatives of the energy bands in particular directions. In this approximation, the envelope function $F_m(r)$ [Eq. (2)] satisfies the following effective-mass equation:

$$[E_n(-i\hbar\nabla)+U(r)]F_n(r)=E_I F_n(r) \; . \qquad (8)$$

The impurity wave function will be given by Eq. (1) with the Bloch functions given by Eqs. (4). It is possible to derive a more accurate version of the **k**·**p** model by including additional perturbative interactions caused by other lower and higher bands.[13] However, we confine ourselves to the three-level Kane model because, despite its obvious limitations, it appears to describe features of the zone-center extrema with reasonable accuracy. One notable advantage of the Kane model is that it also serves well for compounds such as GaAs, InP, etc.

In this paper, we shall consider only acceptor impurity states, where the main contributions to the coefficients $F_n(r)$ comes from the top of the valence band (fourfold degenerate) and the top of the spin-orbit–split-off band (doubly degenerate), and the only nonzero ones are $F_h(r), F_l(r), F_s(r)$, which take into account the contribution to the state of the center from the heavy-hole band (hh), the light-hole band (lh), and the spin-orbit–split-off band(s). Because of the different symmetry of the conduction band, the coefficients $F_c(r)$ are negligible, see Ref. 9. This contribution decreases with increasing distance to the band from the impurity level.

In order to get an analytic expression for the photoionization cross section of the impurity center, it is necessary to know the envelope function near the center zone. Assuming a Coulomb potential Eq. (8) reads

$$\left[-\frac{\hbar^2}{2m_n}\nabla^2-\frac{e^2}{Kr}\right]F_n(r)=E_I F_n(r) \qquad (9)$$

with m_n the effective mass corresponding to the appropriate band at the center of the Brillouin zone and K the dielectric constant of the crystal. At this point, we borrow the well-known phenomenological QDM from atomic physics by replacing the ionization energy of the impurity by

$$E_I=\frac{m_n e^4}{K^2\hbar^2}\frac{1}{2\nu_n^2}=\frac{E_I^0}{\nu_n^2} \; , \qquad (10)$$

where ν_n is, in general, a nonintegral defect quantum number corresponding to the appropriate band. In this approximation, Chaudhuri[6] obtained an envelope function which is irregular at the origin, but normalizable. With the exact normalization, the QD function F may be written as

$$F_n(r)=\frac{2^{2\nu_n}}{\sqrt{4\pi}(\nu_n a_n^*)^{\nu_n+1/2}}\frac{1}{\Gamma(\nu_n+1)} \times |D(\nu_n)| r^{\nu_n-1}\exp(-r/\nu_n a_n^*) \; , \qquad (11)$$

where

$$|D(\nu)|^2=\frac{\pi}{|\sin(\nu\pi)|}\left[\frac{1}{2}\sum_{m=0}^{\infty}\frac{1}{(\nu-m-1)^2(\nu-m)^2}\right]^{-1/2} . \qquad (12)$$

Here $a_n^*=K\hbar^2/m_n e^2$. Equations (1), (11), and (12) give the wave function of an electron or hole at the impurity center, and may be used to calculate the various transition probabilities involving impurity states. Specifically, the differential cross section for photoionization of an impurity center, i.e., the effective cross section of the center for absorption of light accompanied by the release of carriers, in the well-known dipole approximation, is

$$\sigma_n(\hbar\omega)=\frac{4\pi^2\alpha_0\hbar\omega}{g\sqrt{K}}\left[\frac{E_{\text{eff}}}{E_a}\right]^2\left[\frac{m_n}{m_0}\right]^2 \times |\langle\psi_{nk}|z|\psi_v\rangle|^2\rho(E_n) \; , \qquad (13)$$

where α_0 $(=e^2/\hbar c)$ is the fine-structure constant, $\hbar\omega$ is the photon energy, $\rho(E_n)$ is the density of the continuum states at the band energy E_n at which the transition takes place, and g is the degree of degeneracy of the state on the center.[7] Here the direction of the z axis is chosen along the photon polarization direction. The factor E_{eff}/E_a is the so-called effective-field ratio, which takes into account the fact that the electric field E_{eff}, which is effective in inducing a transition, is different from the average field E_a in the medium. Using the wave functions given by Eq. (4), the matrix elements in Eq. (13) can be written explicitly as

$$\langle\psi_{nk}|z|\psi_v\rangle=\int e^{-i\mathbf{k}\cdot\mathbf{r}} z F_n(r)\mu_{n0} d^3r \qquad (14)$$

with the overlap integrals of the cell periodic functions at **k** for the band n defined as $\mu_{n0}=\langle U_{nk}|U_{n0}\rangle$. For the valence band, they are given by

$$\begin{aligned}\mu_{h0}&=1 \; ,\\ \mu_{l0}&=\sqrt{1/3}b_l+\sqrt{2/3}c_l \; ,\\ \mu_{s0}&=\sqrt{2/3}b_s-\sqrt{1/3}c_s \; .\end{aligned} \qquad (15)$$

In order to reduce Eq. (14) to a one-dimensional integration, $\exp(-i\mathbf{k}\cdot\mathbf{r})$ is expanded in the well-known spherical Bessel functions, averaging over all directions of the unit vector $\hat{\mathbf{k}}$, the general formula for the transitions cross section may be written as

$$\sigma_n(\hbar\omega)=\frac{8\pi^3\alpha_0\hbar\omega}{3g\sqrt{K}}\left[\frac{E_{\text{eff}}}{E_a}\right]^2\left[\frac{m_n}{m_0}\right]^2 \times\frac{2^{2\nu_n}(\nu_n a_n^*)^5|D(\nu_n)|^2 f(y_n)|\mu_{n0}|^2}{y_n(1+y_n)^{\nu_n+1}}\rho(E_n) \; , \qquad (16)$$

where

$$f(y)=\cos^2\theta\left[\frac{\sin[(\nu+1)\theta]}{\sin\theta}-(\nu+1)\cos[(\nu+2)\theta]\right]^2 , \qquad (17a)$$

in which

$$\theta=\arctan(\sqrt{y}) \qquad (17b)$$

and

$$y=(k\nu a^*)^2 \; . \qquad (17c)$$

The effect of nonparabolicity of the conduction and valence bands on the energy levels of our system is taken into account in the density of states $\rho(E)$ as a function of the energy, and in Eq. (17c) in the following manner: Equation (6) for electrons in the light-hole valence band may be rewritten as

$$(E-\hbar^2k^2/2m_0-E_g)(E-\hbar^2k^2/2m_0)(E-\hbar^2k^2/2m_0+\Delta) - k^2P^2(E-\hbar^2k^2/2m_0+2\Delta/3)=0\ . \tag{18}$$

In the neighborhood of the light-hole valence-band edge where the energy tends to zero when k tends to zero, Eq. (18) may be simplified to

$$k^2P^2=\frac{[E(1+b_l)-E_g]E(1+b_l)[E(1+b_l)+\Delta]}{E(1+b_l)+2\Delta/3} \cong \tfrac{3}{2}E_g\left[\frac{\hbar^2k^2}{2m_l}\right](1+b_l)\ , \tag{19}$$

where $b_l=m_l/m_0$ and m_l is the effective mass of holes in the light-hole valence-band edge. Equation (19) is in agreement with the expression obtained by Blakemore.[14] In particular, for semiconductors such as GaAs, the effective mass of an electron or hole is much lower than its free-electron mass m_0. So we may neglect $(m_l/m_0)^n$ for $n\geq 2$; then Eq. (18) reduces to the form

$$E(E-E_g)(E+\Delta)-\frac{\hbar^2k^2}{2m_0}\left[E(E+\Delta)+(E-E_g)(E+\Delta)+E(E-E_g)-\frac{E(E-E_g)(E+\Delta)}{E+2\Delta/3}\right]-k^2P^2(E+2\Delta/3)=0\ . \tag{20}$$

Using the same value of k^2P^2 from Eq. (19) in Eq. (20) we obtain

$$\frac{2E(E-E_g)(E+\Delta)}{3E_g(1+b_l)(E+2\Delta/3)}-\frac{\hbar^2k^2}{2m_l}-\frac{2(\hbar^2k^2/2m_0)}{3E_g(1+b_l)(E+2\Delta/3)} \times\left[E(E+\Delta)+(E-E_g)(E+\Delta)+E(E-E_g)-\frac{E(E-E_g)(E+\Delta)}{E+2\Delta/3}\right]=0\ . \tag{21}$$

Usually, near the center of the Brillouin zone, E is less than both E_g and Δ. Expanding various quantities in Eq. (21) and retaining up to the third-order terms of the expansion we get

$$-\frac{\hbar^2k^2}{2m_l}=E(1-\alpha_lE+\beta_lE^2-\gamma_lE^3+\delta_lE^4)\ , \tag{22}$$

where the nonparabolicity factors are given by

$$\alpha_l=\frac{1+2b_l}{1+b_l}\left[\frac{1}{E_g}+\frac{1}{2\Delta}\right]\ , \tag{23a}$$

$$\beta_l=\frac{1+3b_l}{1+b_l}\left[\frac{3}{2\Delta}\right]\left[\frac{1}{3E_g}+\frac{1}{2\Delta}\right]\ , \tag{23b}$$

$$\gamma_l=\frac{1+4b_l}{1+b_l}\left[\frac{3}{2\Delta}\right]^2\left[\frac{1}{3E_g}+\frac{1}{2\Delta}\right]\ , \tag{23c}$$

and

$$\delta_l=\frac{1+5b_l}{1+b_l}\left[\frac{3}{2\Delta}\right]^3\left[\frac{1}{3E_g}+\frac{1}{2\Delta}\right]\ . \tag{23d}$$

A similar solution to Eq. (22) may be derivated for the split-off valence band and conduction band within the same approximation. Then, we only write the results for the conduction band,

$$\frac{\hbar^2k^2}{2m_c}=E(1+\alpha_cE+\beta_cE^2+\gamma_cE^3) \tag{24}$$

with

$$\alpha_c=\frac{1-2b_c}{1-b_c}\left[\frac{1}{E_g}+\frac{1}{\Delta+E_g}-\frac{1}{E_g+2\Delta/3}\right]\ , \tag{25a}$$

$$\beta_c=\frac{1-3b_c}{1-b_c}\left[\frac{1}{E_g(E_g+\Delta)}-\frac{1}{E_g+2\Delta/3}\left[\frac{1}{E_g}+\frac{1}{\Delta+E_g}\right]+\frac{1}{(E_g+2\Delta/3)^2}\right]\ , \tag{25b}$$

$$\gamma_c=\frac{-\beta_c}{E_g+2\Delta/3}\ . \tag{25c}$$

From the dependence of crystal moment on energy E as given by Eqs. (22) and (23), we get an expression for the density of states, including the spin degeneracy, as

$$\rho_l(E)=\left[\frac{k}{\pi}\right]^2\left|\frac{dk}{dE}\right|=\frac{2^{1/2}m_l^{3/2}}{\pi^2 h^3}|E|^{1/2}(1-\alpha_l E+\beta_l E^2-\gamma_l E^3+\delta_l E^4)^{1/2}|1-2\alpha_l E+3\beta_l E^2-4\gamma_l E^3+5\delta E^4| \tag{26}$$

for the light-hole valence band. In this approximation the quantity y_l in Eq. (17c) is related to the binding energy by the relation

$$y_l=-\frac{E}{E_I}(1-\alpha_l E+\beta_l E^2-\gamma_l E^3+\delta_l E^4)\ . \tag{27}$$

On substitution of this expression for $\rho_l(E)$, the total cross section for photoionization in the approximation $E<\Delta$, is given by

$$\sigma(\hbar\omega)=\sigma_h(\hbar\omega)+\sigma_l(\hbar\omega)\ , \tag{28}$$

where $\sigma_n(\hbar\omega)$ is the cross section for the transition between the nth valence band and the impurity center which can be written in the form

$$\sigma_h(\hbar\omega)=\frac{4\pi\alpha_0}{3g\sqrt{K}}\left[\frac{E_{\text{eff}}}{E_a}\right]^2\left[\frac{m_h}{m_0}\right]^2 \times\frac{2^{2\nu_h}(\nu_h a_h^*)^2|D(\nu_h)|^2 f(y_h)}{y_h^{1/2}(1+y_h)^{1+\nu_h}} \tag{29}$$

with

$$y_h=-E/E_I$$

and

$$\sigma_l(\hbar\omega)=\frac{4\pi\alpha_0}{3g\sqrt{K}}\left[\frac{E_{\text{eff}}}{E_a}\right]^2\left[\frac{m_l}{m_0}\right]^2 \times\frac{2^{2\nu_l}(\nu_l a_l^*)^2|D(\nu_l)|^2 f(y_l)}{y_l^{1/2}(1+y_l)^{1+\nu}}G(E)|\mu_{l0}|^2\ , \tag{30}$$

where

$$G(E)=\frac{1-2\alpha_l E+3\beta_l E^2-4\gamma_l E^3+5\delta_l E^4}{1-E(-\alpha_l E+\beta_l E^2-\gamma_l E^3+\delta_l E^4)/\hbar\omega}\ . \tag{31}$$

Equations (28)–(31) define the magnitudes and frequency dependences of the photoionization cross sections. Although these expressions are quite lengthy, there is no fundamental difficulty in using them for calculations, as they contain, apart from the impurity center ionization energy E_I, only the known parameters of the valence band, such as the spin-orbit splitting energy Δ and the effective masses m_h and m_l, which describe the band spectrum of the small wave vector **k**.

In order to analyze the frequency dependence given by these equations, we did a specific calculation for two values of the ionization energy E_I in gallium arsenide ($E_g=1.519$ eV, $\Delta=0.34$ eV): $E_I=0.11$ and 0.37 eV corresponding to manganese[15] and copper[16] impurities in this material. The results are shown in Fig. 2, which also gives the experimental values for these impurities. As we can see the theory is in agreement with the experiment in predicting the peak position, in contrast to either the hydrogenic or the δ-function model. From this fit we have obtained the effective-field ratio (E_{eff}/E_a) to be about 2. When the impurity level ionization energy E_I exceeds the spin-orbit splitting Δ (curve 2) the feature of the frequency dependence of the photoionization cross section is smoothed out in comparison with the cross section corresponding to the impurity level energy of manganese (curve 1). Recently, Lowney and Kahn[17] have calculated the density-of-states effective masses for the valence band of GaAs using the full **k**·**p** theory finding important effects of nonparabolicity in the effective masses. When the perturbing effects of other bands on the valence bands are included, the heavy-hole valence band can no longer be parabolic and the nonparabolicity factors of the light-hole valence and are slightly different of those given by Eqs. (23). We have included these interaction effects on the valence bands through the density of states and the parameter y given by Eq. (17c) in the photoionization cross section, however, these effects on the dependence of the photoionization are shown to be relatively unimportant.

Up to now we have only considered the process in which a neutral impurity atom becomes ionized when a photon is absorbed (photoionization), the process in which an ionized impurity becomes neutral with the absorption of a photon (band impurity absorption) has not yet been investigated. In this case both the conduction and the valence bands are involved. Let us specifically consider transitions between an acceptor state and a

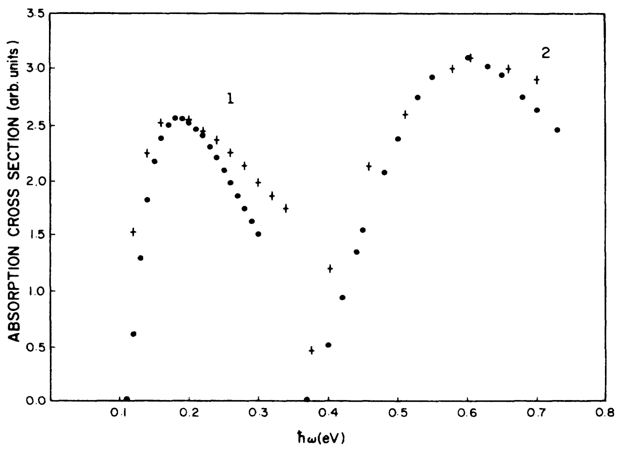

FIG. 2. Frequency dependence of the photoionization cross section for two levels in gallium arsenide: 1, $E_I=0.11$ eV (Mn); 2, $E_I=0.37$ eV (Cu). The levels are measured from the top of the valence band. Crossed curve, experiment; dotted curve, theory.

conduction-band state. Because of the degeneracy of the valence band, the matrix element for transition between the impurity center and the conduction band is given by

$$\langle \psi_{ck}|z|\psi_v\rangle = \mu_{cv}(k)\sum_n \int e^{-i\mathbf{k}\cdot\mathbf{r}} zF_n(r)d^3r , \quad n=h,l,s \tag{32}$$

where an analytical result of the overlap integrals $\mu_{nm}(k)$ can be obtained by the $\mathbf{k}\cdot\mathbf{p}$ perturbation method,[18]

$$\mu_{nm}(k)=\delta_{nm}+\frac{\hbar}{m_0}\frac{\mathbf{k}\cdot\mathbf{P}_{nm}}{E_n(0)-E_m(0)}(1-\delta_{nm}) . \tag{33}$$

Assuming that $\mathbf{P}_{nm}$ is isotropic and using the sum rule for momentum matrix elements between states n and m,[19] we finally obtain

$$|\mu_{cv}(\mathbf{k})|^2=\frac{1}{6}\frac{m_c}{m_0}\left[\frac{m_0}{m_c}-1\right]\frac{E_g+\Delta}{E_g+2\Delta/3} \times\frac{E}{E_g}(1+\alpha_c E+\beta_c E^2+\gamma_c E^3) . \tag{34}$$

The quantity $|\mu_{cv}(\mathbf{k})|^2$ is equal to zero at $\mathbf{k}=\mathbf{0}$, since the electron energy in the conduction band $E_c=0$. This can also be shown to be an exact result from the orthogonality of the Bloch wave functions. Thus, we write the cross-section formula which should be valid for small energies of the conduction band,

$$\sigma(\hbar\omega)=A[\sigma_h(\hbar\omega)+\sigma_l(\hbar\omega)+\sigma_s(\hbar\omega)]^2\frac{\hbar\omega}{E_g}G_c(E) , \tag{35}$$

where

$$A=\frac{4\pi\alpha_0}{3\sqrt{K}}\left[\frac{E_{\text{eff}}}{E_a}\right]^2\left[\frac{m_c}{m_0}\right]^2\frac{1}{6}\frac{m_c}{m_0}\left[\frac{m_0}{m_c}-1\right] \times\frac{E_g+\Delta}{E_g+2\Delta/3} , \tag{36}$$

$$G_c(E)=\left[\frac{E}{E_I}\right]^{3/2}(1+\alpha_c E+\beta_c E^2+\gamma_c E^3)^{3/2} \times(1+2\alpha_c E+3\beta_c E^2+4\gamma_c E^3) , \tag{37}$$

$$\sigma_n(\hbar\omega)=\frac{2^{\nu_n}|D(\nu_n)|f^{1/2}(y_n)}{[y_n(1+y_n)^{1+\nu_n}]^{1/2}}\left[\frac{m_c}{m_n}\right]^{3/4}\nu_n a_n^* , \quad n=h,l \tag{38}$$

and

$$\sigma_s(\hbar\omega)=\frac{2^{\nu_s}|D(\nu_s)|f^{1/2}(y_s)}{[y_s(1+y_s)^{1+\nu_s}]^{1/2}}\left[\frac{m_c}{m_s}\right]^{3/4} \times\frac{(\nu_s a_s^*)}{(1+\Delta/E_I)^{3/4}} . \tag{39}$$

In Fig. 3 we display the variation of the absorption cross section as a function of the energy $x=E_c/E_I$ corresponding to binding energies $E_I=0.05$ and 0.1 eV, respectively, including the effects of nonparabolicity of the conduction band (dotted curve). For comparison we also plot the variation of $\sigma(x)$ as a function of x, assuming a simple parabolic band model (crossed curve). We find, as expected, that the peak position of σ is shifted to lower energies when the ionization energy of the impurity center decreases (hydrogenic limit); while, on the other hand, the photoionization cross section is approximated to the δ-function limit (Lucovsky's results) when the ionization energy increases. The effect of the nonparabolicity on σ is significant at the peak position; however, this contribution is negligible for large x.

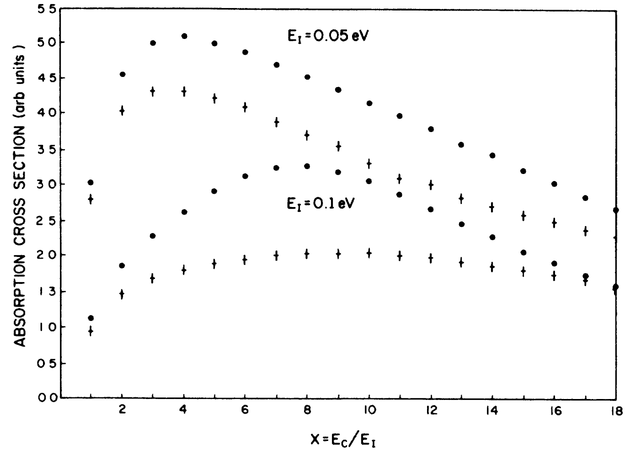

FIG. 3. Band impurity transition of the photoionization cross section for GaAs as a function of the normalized band energy $x=E_c/E_I$ for the center binding energy $E_I=0.05$ and 0.1, using a nonparabolic conduction band (crossed curve) and a parabolic conduction band (dotted curve).

III. CONCLUSIONS

In summary, we have calculated cross sections for both photoionization and band impurity tranasitions in the quantum-defect model scheme including the effects of nonparabolicity of the conduction and the valence bands. The effect of the band nonparabolicity on the energy levels is taken into account by using an expression for the energy-dependence wave vector based on the $\mathbf{k}\cdot\mathbf{p}$ approximation. The frequency dependence of the photoionization cross section for manganese and copper impurities in gallium arsenside are calculated and these results are compared with the experimental results obtained in Ref. 15. Finally, it is worth mentioning that our method, such as Lucovsky's method, does not yield any information on the internal structure of the center on the energy of the deep level, but does make it possible to obtain, with good accuracy, the frequency dependence of the photoionization cross section in a vital frequency interval. In addition, it makes it possible to take into account details that are essential for this interval, such as the influence of the spin-orbit interaction and the difference between the carrier masses. This explains a number of qualitative features of the behavior of the photoionization cross sections.

We are aware that, in contrast with the hydrogenic impurities, the defects dominated by short-range interaction may exhibit strong dynamic coupling to the lattice due to the high degree of localization of the bound particles, act as a nonradiative recombination center with large probability of multiphonon emission, etc., and that a truly quantitative understanding of any particular deep-level problem requires that a self-consistent calculation be performed of the electronic spectrum in which the minimum of the total energy of the many-electron system can be established. Ridley[20] has shown that at low temperature the effect of the phonon coupling is to rise the apparent threshold, and it is very small.

---

[1] H. Bebb and R. A. Chapman, J. Phys. Chem. Solids **28**, 2087 (1967).

[2] G. Lucovsky, Solid State Commun. **3**, 299 (1965).

[3] S. T. Pantelides, Rev. Mod. Phys. **50**, 797 (1978).

[4] H. Bebb, Phys. Rev. **185**, 1116 (1969).

[5] B. K. Ridley, J. Phys. C **13**, 2015 (1980).

[6] S. Chaudhuri, Phys. Rev. B **26**, 6593 (1982).

[7] V. I. Perel and I. N. Yassievich, Zh. Eksp. Teor. Fiz. **87**, 237 (1982) [Sov. Phys.—JETP **55**, 143 (1982)].

[8] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).

[9] N. M. Kolchanova, I. D. Loginova, and I. N. Yassevich, Fiz. Tverd. Tela (Leningrad) **25**, 1650 (1983) [Sov. Phys.—Solid State **25**, 952 (1983)].

[10] D. D. Coon and R. P. G. Karunasiri, Phys. Rev B **33**, 8228 (1986).

[11] E. M. Azoff, J. Appl. Phys. **64**, 2439 (1988).

[12] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

[13] G. Ambrazevicius, M. Cardona, and R. Merlin, Phys. Rev. Lett. **59**, 700 (1987).

[14] J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).

[15] R. A. Chapman and W. G. Hutchinson, Phys. Rev. Lett. **18**, 443 (1967).

[16] A. Chantre and D. Bois, J. Phys. Soc. Jpn. Suppl. A **49**, 247 (1980).

[17] Jeremiah R. Lowney and Arnold H. Kahn, J. Appl. Phys. **64**, 447 (1988).

[18] J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1967).

[19] M. J. Adams and P. T. Landsberg, in *Gallium Arsenide Lasers*, edited by C. H. Gooch (Wiley-Interscience, New York, 1969).

[20] B. K. Ridley, J. Phys. C **14**, 1255 (1981).