involved in transitions to these valleys were relatively small, it is possible that such states might go unnoticed in the FCA data. On the other hand, there is evidence from work on the $In_{1-x}Ga_xP$ alloys[1,16] that the lowest valleys in the Ga-rich alloys, the valleys at the point X in the Brillouin zone,[17,18] would have an energy in InP consistent with the value we have determined for ΔE. Unless some other set of valleys has moved to an even lower energy than the X point valleys as we go from GaP to InP, it seems reasonable to conclude that the valleys responsible for the interband FCA in InP are the lowest set of multiple conduction valleys.

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Valley-Orbit Interaction in Semiconductors*

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We consider the hypothesis that the valley-orbit interaction provides a sizable contribution to the observed splittings of the donor ground state in many-valley semiconductors. The effects of this interaction on the ground state of group-V donors in Si and Ge are estimated within the effective-mass theory and compared to central-cell corrections. It is shown that intervalley scattering effects are comparable in magnitude to central-cell corrections for donors in Si, whereas the latter are much more important for donors in Ge.

I. INTRODUCTION

It is well known[1] that the ground state of a donor impurity is split into two or more levels if the host semiconductor has many equivalent conduction-band minima at $\vec{k} \neq 0$. Spectroscopic investigations in Si,[2] Ge,[3] and AlSb[4] have provided accurate values of these splittings. The first successful theoretical investigation of impurity spectra in semiconductors was given by Luttinger and Kohn.[5] They developed the effective-mass theory and applied it to study the donor states in Si[6] taking into account the anisotropy of the conduction band near its six equivalent conduction-band minima. Recently Faulkner[7] has improved the variational solution of Kohn and Luttinger[6] and has shown that the effective-mass theory describes very well the excited states of the donor electron but predicts too low a binding energy for the ground state and does not explain the splittings between the ground states corresponding to different equivalent minima in the conduction band.

The effective-mass theory predicts a sixfold degenerate ground state for donors in Si and a fourfold degenerate ground state for donors in Ge. This prediction is in disagreement with the experimental results which have revealed that in Si[2] the ground state is split into three levels of degeneracies 1, 2, and 3 whose symmetries are A_1, E, and T_1, respectively, and that in Ge[3] it is split into two levels of symmetry A_1 and T_1. Many attempts have been made to explain the binding energy of the split levels since the early solution by Kohn and Luttinger.[6] They can be classified into two groups. The first[8–10] uses the effective-mass theory with an impurity potential different from that used by Kohn and Luttinger. They consider a more appropriate dielectric screening and the lattice distortion produced by the impurity donor. These corrections improve the binding energy of the ground state but do not explain its splitting. The second[11–13] goes beyond the effective-mass theory taking into account higher-order corrections. This approach also provides a splitting of the ground state which in some cases has been evaluated, and does not agree well with experiment.

Recently Phillips[14] has considered central-cell corrections to the ground-state binding energy of group-V donors in Si and Ge. He has shown that to obtain a satisfactory agreement with experiment three basic mechanisms have to be considered: valence bond mismatch, valence p-d hybridization, and core-core repulsive forces between the impurity and the surrounding host lattice. With three adjustable parameters he explains the impurity-dependent binding energy of the ground state A_1.

The corrections considered by Phillips depend on the probability of finding the donor electron in the central cell, and hence are of importance only for the ground state A_1. They cannot explain the splitting between the levels T_1 and E for donors in Si because the wave functions of these states are very small in the central cell due to symmetry reasons. A new mechanism has to account for this splitting. In the present paper we estimate within the effective-mass theory the effects of the scattering of the donor electron between equivalent conduction-band minima. We show that these effects are much more important in Si than in Ge and that the inclusion of this new mechanism leaves unaltered the interpretation of Phillips[14] except for reducing the importance of valence bond mismatch corrections for donors in Si.

II. THEORY OF INTERVALLEY SCATTERING

Let us consider the problem of donor states in a semiconductor whose conduction band has n equivalent minima at the points $\vec{k}_i$. The effective-mass equation in momentum space is[15]

$$E_i(\vec{k})C_i(\vec{k}) + \sum_{j=1}^{n}\int \tilde{U}(\vec{k}-\vec{k}')C_j(\vec{k}')d\vec{k}' = EC_i(\vec{k}), \qquad (i=1,\ldots,n) \tag{1}$$

where $E_i(\vec{k})$ is the second-order development in $(\vec{k}-\vec{k}_i)$ of the conduction-band energy near the point $\vec{k}_i$, $\tilde{U}(\vec{k})$ is the Fourier transform of the impurity potential $U(\vec{r}) = -e^2 r^{-1}$, and the $C_i(\vec{k})$ are the envelope functions which are strongly localized near $\vec{k}_i$ and are related to the impurity wave function ψ as follows:

$$\psi(\vec{r}) = \sum_{i=1}^{n}\int C_i(\vec{k})\psi(\vec{k},\vec{r})d\vec{k} \quad , \tag{2}$$

where $\psi(\vec{k},\vec{r})$ are the Bloch wave functions of the conduction band. Luttinger and Kohn[5] estimate that the coupling terms [i.e., terms for $j \neq i$ in Eq. (1)] are negligible with respect to terms for $j=i$. Neglecting the coupling terms, Eq. (1) reduces to the following set of n equivalent Schrödinger equations:

$$E_i(\vec{k})C_i(\vec{k}) + \int \tilde{U}(\vec{k}-\vec{k}')C_i(\vec{k}')d\vec{k}' = EC_i(\vec{k}) , \qquad (i=1,\ldots,n) \tag{3}$$

each one corresponding to a different valley. Under this condition the donor electron will have an n-fold degenerate ground state and we can choose the corresponding wave functions in such a way that they are characterized by the index of the valley in which the electron spends all its time. As we have already noted, this prediction of the effective-mass theory is in disagreement with experiment.

The assumption made by Luttinger and Kohn that the coupling terms are negligible is true only if the dielectric screening is neglected. In fact, from the computed values of the wave-number–dependent dielectric function of Si and Ge[16–18] we see that the screening for $\Delta\vec{k} = \vec{0}$ is ten times greater than that corresponding to $\Delta\vec{k}$ equal to the separation in $\vec{k}$ space between two equivalent minima in Si and Ge. Taking into account the properly screened impurity potential Eq. (1) becomes

$$E_i(\vec{k})C_i(\vec{k}) + \sum_{j=1}^{n}\int \frac{\tilde{U}(\vec{k}-\vec{k}')}{\epsilon(\vec{k}-\vec{k}')}C_j(\vec{k}')d\vec{k}' = EC_i(\vec{k}) , \qquad (i=1,\ldots,n) \tag{4}$$

where the coupling terms are no longer negligible because of the low screening. Equation (4) can be simplified if we take into account the fact that the $C_i(\vec{k})$ are strongly localized around $\vec{k}_i$. This enables us to assume that the proper dielectric constant for the term which couples the minima at $\vec{k}_i$ and $\vec{k}_j$ is

$$\epsilon_{ij} = \epsilon(\vec{k}_i - \vec{k}_j) \quad . \tag{5}$$

In the case $i=j$, condition (5) reduces to the usual assumption that for small values of $\vec{k}$, $\epsilon(\vec{k})$ is well approximated by its value $\epsilon(0)$. Condition (5) allows us to take the dielectric screening outside the integral in Eq (4), and going back to coordinate space we obtain

$$\sum_{\nu=1}^{3} \frac{(p_\nu - \hbar k_{i\nu})^2}{2m^*_{i\nu}} f_i(\vec{r}) - \sum_{j=1}^{n} \frac{e^2}{|r|\epsilon_{ij}} f_j(\vec{r}) = E f_i(\vec{r}) , \qquad (i=1,\ldots,n) \qquad (6)$$

where $\nu = 1$, 2, and 3 means x, y, and z, respectively, and the $m^*_{i\nu}$ is the $\nu\nu$ component of the diagonal effective-mass tensor of the ith minimum.

Equation (6) has the symmetry of the point group of the host semiconductor which is lower than the symmetry of Eq. (3) obtained neglecting the coupling terms. The degeneracies of the effective-mass theory will be removed and the resulting splittings will be a function of the position of the minima in the conduction band. In fact, Eq. (6) depends on $\vec{k}_i$ through the ϵ_{ij} and the kinetic-energy term.

III. RESULTS

A convenient way to solve (6) is to treat the coupling terms as a perturbation. We use as unperturbed wave function relative to a single valley the variational function

$$\Phi(x, y, z) = A \exp\left[-\left(\frac{x^2+y^2}{a^2} + \frac{z^2}{b^2}\right)^{1/2}\right], \qquad (7)$$

proposed by Kohn and Luttinger[6] to describe the ground state in the case of anisotropic mass tensor. While (7) is a very good approximation to the true effective-mass solution, as shown by Faulkner,[7] it is well known[1,19,20] that it describes accurately the behavior of the donor electron only at distances from the impurity large compared to the lattice constant. In effect the donor electron is much more localized near the impurity than predicted by the effective-mass theory. To get an estimate of intervalley scattering effects in Si and Ge we use the wave function (7) and later we discuss the consequences of deviations from (7). Furthermore, we make use of the wave-number-dependent dielectric functions of Si and Ge as computed by Nara[16,17] who takes into account anistropy effects at $\vec{k} \neq 0$. We note that Nara's results agree quite well with a more recent isotropic calculation by Srinivasan.[18]

In Si there are six conduction-band minima along the (1, 0, 0) and equivalent directions. A study of the phonons which assist the optical indirect transitions at the absorption edge in Si has lead Dumke[21] to localize the minima at $2\pi/a$ (0.82, 0, 0) and equivalent points, a being the lattice constant. We suppose that the minima are located at $\vec{k} \equiv 2\pi/a$ $(x, 0, 0)$ and compute the intervalley scattering effects as x varies between 0.5 and 1. For a single value of x two different dielectric function values have to be considered: the value at $\vec{k} \equiv 2\pi/a(2x, 0, 0)$ for minima which lie on opposite symmetry directions, and the value at $\vec{k} \equiv 2\pi/a(x, x, 0)$ for minima which lie on orthogonal symmetry directions. For every value of x the ground state splits into the three levels A_1, T_1, and E in order of decreasing binding energy, in agreement with the experimental results. In Fig. 1 we give the value of the splittings $\Delta_1 = E(T_1) - E(A_1)$ and $\Delta_2 = E(E) - E(T_1)$ as functions of x. The maximum of Δ_2 and the irregularity in Δ_1 near $x = 0.7$ are due to a competition between the dielectric screening and the unscreened interaction between different minima, which, respectively, enhance and reduce the intervalley scattering effects as x increases. Assuming $x = 0.82$, we find $\Delta_1 = 10.6$ meV and $\Delta_2 = 1.1$ meV. These results can be compared with the experimental values $\Delta_1 = 11.85$, 9.94, and 21.15 meV and $\Delta_2 = 1.35$, 2.50, and 1.42 meV for phosphorus, antimony, and arsenic impurities, respectively.

In Ge there are four conduction-band minima located at the zone edge along the (1, 1, 1) and equivalent directions. In this case we use the dielectric

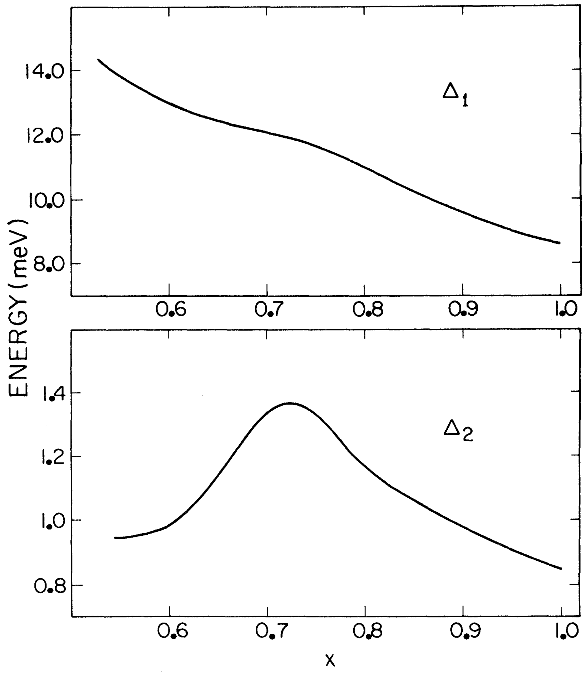

FIG. 1. Splittings between the levels A_1, T_1, and E which originate from the sixfold degenerate donor ground state in Si when valley-orbit interaction is considered. In abscissa the position of the minima of the conduction band of Si along the (1, 0, 0) and equivalent directions. $\Delta_1 = E(T_1) - E(A_1)$ and $\Delta_2 = E(E) - E(T_1)$.

function value $\epsilon = 1.872$ as given by Nara[17] for a wave vector equal to the separation in $\vec{k}$ space between every pair of minima. The ground state splits into the levels A_1 and T_1, the latter having a lower binding energy. The computed splitting between these two levels $\Delta_1 = E(T_1) - E(A_1)$ is 0.6 meV which is to be compared to the experimental values 2.83, 4.23, and 0.32 meV for phosphorus, arsenic, and antimony impurities, respectively.

IV. DISCUSSION

As already noted the central-cell corrections considered by Phillips are expected to affect only the ground state A_1 and hence only the splitting Δ_1. We see in fact that our value of the splitting Δ_2 for donors in Si is in quite good agreement with experiment. The deviations from the predicted value of Δ_2 can be understood if we consider that we have taken as unperturbed wave function the solution of the effective-mass theory. As is well known, electron-spin resonance experiments[20] have demonstrated that the probability for the donor electron to be in the central cell is higher than predicted by the effective-mass theory. Kohn and Luttinger[19] were able to show theoretically the plausibility of this result. As a consequence of the fact that the wave function is more localized near the donor site, intervalley scattering effects are enhanced in agreement with the fact that our estimate of Δ_2 is a lower bound to the experimental values.

The previous argument is valid also for the splitting Δ_1 in Si and Ge. However in this case central-cell corrections to the ground state A_1 are more relevant and the experimental values of Δ_1 have to be explained as a combined result of intervalley scattering and central-cell corrections. A comparison of the percentage contribution of these two effects to the experimental values of Δ_1 immediately reveals that intervalley scattering effects are very important in Si and nearly negligible in Ge. This result can be attributed to two different reasons. The first is that the mean radius of a donor electron in its ground state in Ge is about three times as large as in Si.[1] This means that the wave function in momentum space for donors in Si is much more spread out than it is for donors in Ge giving rise to larger intervalley scattering effects. The second reason was pointed out by Phillips[14] and is that the minimum at L_1 in Ge is about five times more sensitive to pressure and to chemical shifts than is the minimum at X_1 in Si.[22]

As a result of the inclusion of intervalley scattering effects, the interpretation by Phillips of the binding energy of group-V donors in Si and Ge is not appreciably changed especially for donors in Ge where the effects considered in this paper are practically negligible. For donors in Si, the value of the parameters introduced by Phillips to describe central-cell corrections to the binding energy of the state A_1 is reduced if intervalley scattering is included. This reduction in value is particularly large for the parameter which describes the valence bond mismatch correction. This parameter (a_{Si} in the notation of Ref. 14) is reduced to less than half of its value due to the fact that intervalley scattering provides a large contribution to the binding energy of the ground state of phosphorus impurities in Si. This reduction in valence bond mismatch correction for donors in Si is particularly important for nitrogen impurities. While Phillips predicts a correction of 116 meV for N in Si, 85% of which is due to valence bond mismatch, we obtain that the correction is 60 meV with the inclusion of the intervalley scattering contribution.

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Sharp-Line Photoluminescence in $ZnSiP_2$

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We have studied the photoluminescence spectra of $ZnSiP_2$. Time-resolved spectra, time decays of different spectral components, and excitation-intensity dependence studies were performed at various temperatures between 1.8 and 250 °K. We observe a series of sharp emission lines (half-width ~ 1 meV) which we attribute to phonon-assisted processes of an unidentified transition involving impurities or defects. Superimposed on this series is a featureless broad emission band. At energies above this series of lines, several other independent sharp lines are observed. Some of the latter are strongly enhanced as the temperature increases from 1.8 to 35 °K. These results are discussed and compared with somewhat similar spectra of GaP.

I. INTRODUCTION

Interest has risen recently in ternary semiconducting compounds of the group II-IV-V. Although these compounds are expected to have properties analogous to III-V compounds, they are clearly a step towards more complexity. The possibility of interesting physics and the potential of these compounds for devices make them attractive materials for intensive studies.

We report here the photoluminescence studies of $ZnSiP_2$ crystals. At 1.8 °K, we observe many sharp lines (half-width ~ 1 meV) at wavelengths greater than 6000 Å. These sharp lines merge into a rather broad band peaking at 6400 Å. Another broad emission band is also observed at ~ 7100 Å. We have studied these spectra in detail, including investigation of the temperature dependence between 1.8 and 250 °K, time-resolved spectra (TRS) at various temperatures, as well as the time decay of several spectral components. We describe and analyze these results in this paper.

General discussions of II-IV-V compounds have been published by several authors.[1-3] For $ZnSiP_2$ in particular, band-edge absorption has been studied by Goryunova *et al.*[4] for temperatures greater than 77 °K. These authors reported a steep absorption edge at ~ 6300 Å (~ 2.0 eV) where the absorption coefficient rose to values greater than 10^3 cm^{-1}. However, preliminary absorption measurements by Shaklee[5] on our samples, which have high resistivity, show an absorption edge at wavelengths less than ≈ 5400 Å (> 2.3 eV). Cathodoluminescence spectra for $T > 77$ °K were reported by Alekperova *et al.*[6] for samples of different dopings. These spectra all showed rather broad bands at wavelengths longer than 7000 Å. Some of the bands contained weak secondary maxima separated from each other in energy by ≈ 0.03 eV. This was attributed to participation of phonons of energy 0.03 eV. The present work, to the best of our knowledge, is the first study of photoluminescence in $ZnSiP_2$.[7,8] We have observed the first sharp-line emission spectrum in this material. Sharp lines were not obtained by previous authors,[6] who worked with electron beam excitation and samples at temperatures above 77 °K. However, Shay *et al.*[9] in this laboratory have obtained spectra similar to ours using electron beam excitation with samples at temperatures between 10 and 50 °K.

II. CRYSTAL DATA

The samples were grown with no intentional doping by a vapor transport technique using $ZnCl_2$. They were irregular in shape but showed several facets about 2×3 mm in size, which were used for the photoluminescence studies. The x-ray measurements indicated that the crystals have chalcopyrite structure. No measurements on Hall