

of Z_b against f_i does not establish conclusively that $Z_b=0$ for (metastable) tetrahedrally coordinated compounds with $f_i > 0.785$. The activity-composition measurements suggested here may provide further information on this basic question.

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Strain Fields and the Apparent Size of Donor Ions in GaP

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We report the first experimental determination of the microscopic strain fields surrounding substitutional impurities in a crystal. We have used pair spectra in GaP to reveal the splitting of Zn or C acceptor levels in the strain fields generated by O, S, Se, or Te donor ions. The anisotropic splitting, which agrees with a simple effective-mass theory, is the same for all four donors. We conclude that effects associated with the size of these impurities are distributed over a volume of the crystal extending more than 20 Å from the impurity.

Point imperfections in crystals generate local strain fields which can modify the properties of degenerate electronic states bound to them.¹ The experiment described in this Letter enables us not only to determine the magnitudes of the fields but also to measure their dependence on distance and direction from their sources. The method, which uses a careful analysis of the donor-acceptor pair lines from GaP which are split by these internal fields, generates a map of the strain field surrounding a donor through its effect on the energy levels of the nearby acceptors.

Sharp-line donor-acceptor pair spectra² provide a convenient indicator of interactions between donor and acceptor impurities at varying separations R . The major interaction term, the Coulomb energy of the bare ions, $e^2/\epsilon_0 R$, disperses the spectrum so that lines corresponding to different separations are resolved and can be identified and classified according to the interion separation vector \vec{R} . Once the pair lines have been classified by this gross structure, their properties can be correlated with the now known values of \vec{R} .³

We consider a donor ion which, because of its

intrinsic "size" relative to the atom it replaces or because of its (Coulomb) interaction with its neighbors, displaces its nearest neighbors from their normal radius R_0 by δR .⁴ This generates a strain field approximately equal to that produced in a homogeneous solid by a displacement (by δR) of a spherical shell of initial radius R_0 . It may be described by the displacement vector $\vec{u}(\vec{r})$ at a point \vec{r} measured from the donor site,⁵

$$\vec{u}(\vec{r}) = (A/r^3)\vec{r}, \quad (1)$$

where $A = R_0^2 \delta R$. In a cubic crystal the strain field may be anisotropic⁶—a complication which we discuss below. We seek the interaction of such a field with a hole bound to a nearby acceptor. In a cubic crystal this interaction depends upon two deformation-potential constants D_u and D_u' as expressed in the Kleiner and Roth Hamiltonian.⁷ The constants are those appropriate for the acceptor state and are in general different from those of the band edge.^{1,8} For holes in the strain field of Eq. (1) this Hamiltonian may be written [see Eqs. (2)–(4) of Ref. 1]

$$H_s(\vec{r}) = (2A/r^3)[D_u q(\vec{r}) + D_u' Q(\vec{r})], \quad (2)$$

where the operators $q(\vec{r})$ and $Q(\vec{r})$ reflect the

angular dependence of the components of this field. They may be written as 4×4 matrices whose components q_i and Q_i are the second-order spherical harmonics, $q_1 = (3z^2 - r^2)/2r^2$, $q_2 = \sqrt{3}(x^2 - y^2)/2r^2$, $Q_1 = \sqrt{3}yz/r^2$, $Q_2 = \sqrt{3}zx/r^2$, and $Q_3 = \sqrt{3}xy/r^2$. The terms in (2) simplify easily since in the effective-mass approximation the system has axial symmetry about the interion axis, and in this approximation that part of the hole wave function which lies outside of a sphere of radius R about the acceptor makes no contribution to the matrix elements. The remainder contributes a factor $P(R)/R^3$, where $P(R)$ equals the total hole probability density contained within the sphere of radius R ,

$$P(R) = 1 - (1 + \eta + \eta^2/2) \exp(-\eta). \quad (3)$$

Here $\eta = 2R/a_0$, and $a_0 = (\hbar^2/2m^*E_A)^{1/2}$ is the acceptor Bohr radius for a (perturbed) hydrogenic state of binding energy E_A .

The matrix $\langle H_s(\vec{r}) \rangle$ of (2) is now easily diagonalized to yield the strain contribution to the energy, $\pm E_s$, and the splitting of the acceptor levels $\delta E_s = 2E_s$. This energy depends on the direction of the vector \vec{R} through two angular factors—one for the $\langle 100 \rangle$ or E part of the strain field (q_i) and one for the $\langle 111 \rangle$ or T_2 part (Q_i). Writing

$$Q^2(\vec{R}) = \sum_{i=1}^3 Q_i^2(\vec{R}) = 1 - \sum_{i=1}^2 q_i^2(\vec{R}), \quad (4)$$

we find for the strain energy the expression

$$E_s = K_\tau [P(R)/R^3][\epsilon^2 + (1 - \epsilon^2)Q^2(R)]^{1/2}, \quad (5)$$

where R is in units of $(a/4) = 1.36 \text{ \AA}$ and the parameters are

$$K_\tau = 2D_u'R_0^2\delta R/(a/4)^3 \text{ and } \epsilon = D_u/D_u'. \quad (6)$$

Emission from the upper level appears only when $kT \gtrsim \delta E_s$.

In a cubic crystal Eq. (1) gives the correct radial dependence of the strain field at a large distance from a point defect but predicts the correct angular dependence only if the elastic constants satisfy the condition of isotropy,⁶ $K = 2c_{44}/(c_{11} - c_{12}) = 1$. In GaP this ratio is 1.8,⁹ and the fields are more complex than Eq. (1) predicts. Thus, the observed anisotropy is due in part to the strain field itself and not entirely to the ratio ϵ of the deformation potentials, as we indicate. However, the isotropic solution (1) is found to be adequate for our work at this stage.

In Ref. 1 perturbations of the valence band by the Stark and strain fields of the impurity ions were found to be of comparable importance for

the acceptor binding energies. In the present system, we expect dielectric screening and the shielding of the Coulomb field of the donor by the bound electron to make the direct Coulomb interaction negligible at the important ion separations for all donors, though *most certainly* for the deep donor O which is bound by 900 meV. Hence, the consistency of the results we present below for all four donors (*including* oxygen) indicates strongly that only the strain field is important.

Before discussing the experimental results we estimate the magnitudes of splitting expected from two possible sources. First we assume that the radial misfit equals that computed from the tetrahedral radii¹⁰ of the donors (R_D) relative to that of P (R_P) according to $\delta R \approx 0.5(R_D - R_P)$ (cf. footnote 8 of Ref. 1). Thus, the group-VI donors O, S, Se, and Te give values of δR ranging from ~ -0.22 to $+0.11 \text{ \AA}$ relative to the GaP nearest-neighbor distance of $R_0 = 2.36 \text{ \AA}$ and predict values of $K_{\tau 1}$ ranging from -3.8 to 1.9 eV . In this estimate we use the Pauling-Huggens tetrahedral radii¹⁰ and assume for the deformation potential the band-edge value of Balslev, $D_u' = 4 \text{ eV}$.¹¹ In our second example the positive charge on the donor displaces the nearest-neighbor Ga ions with a force which is opposed by the elastic restoring forces of the lattice. The charge on the Ga is about $0.6e$ (presumably negative) and the effective dielectric constant between nearest neighbors (only) is approximately unity, so that in equilibrium this displacement is $\delta R \approx -0.11(a/4)$ and the corresponding contribution to K_τ is $K_{\tau 2} \approx -2.7 \text{ eV}$. Here we have assumed that the restoring force is proportional to $c_{11} + 2c_{12}$.

Figure 1 shows the resolvable region of the recombination spectrum of sulfur-carbon pairs (type I) in GaP recorded photoelectronically at four temperatures. In the low-temperature spectrum the shell number of each pair is indicated. With increasing temperature, subsidiary lines appear with activation energies which can be determined from the temperature dependence of their intensities. These activation energies allow us to assign each new line to its parent line (as shown by the number in the upper spectrum of Fig. 1) and hence to determine the splitting energy δE_s with an accuracy limited only by the linewidth. Excited states with larger splittings, $\delta E_s > 2 \text{ meV}$, are difficult to observe both because of their lower thermal population and because they are usually obscured by other

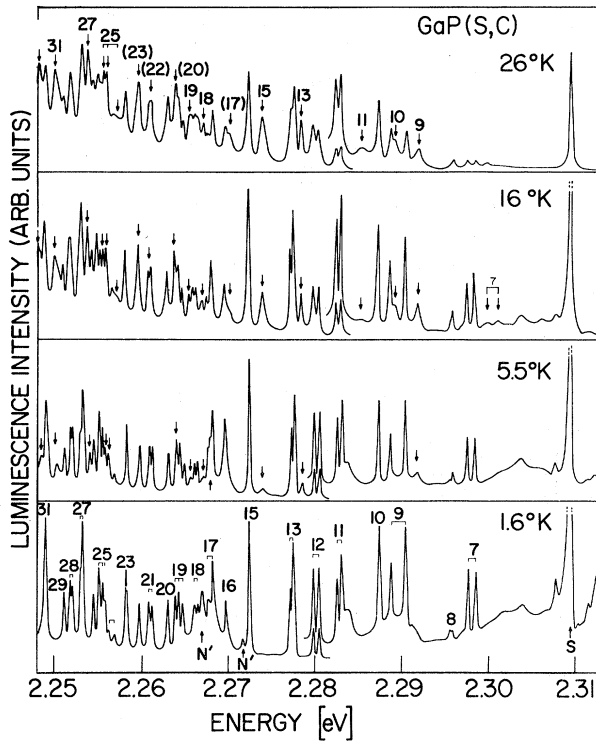


FIG. 1. Luminescence spectra of GaP(S,C) under 4880-Å excitation at various temperatures. The numbers in the lowest spectrum correspond to the shell numbers of the (S,C) pairs. The arrows indicate temperature-dependent lines due to the strain-split acceptor states. These are identified by shell numbers in the uppermost spectrum.

low-temperature lines. However, lower and upper limits can frequently be established from the lack of temperature-dependent structure between the original lines (see lines 22 and 23 in Fig. 1 whose excited states overlap lines 21 and 22, respectively). The splitting energies $\frac{1}{2}\delta E_s$ as well as the radial factor $P(R)/R^3$ are shown in Fig. 2. Where the temperature-dependent lines could be measured and assigned to a specific shell, a solid bar indicates the experimental uncertainty in energy. Where only limits could be established because of interfering lines, the range of probable energy values is shown by dashed lines.

Using the energy values of Fig. 2 weighted by their accuracy, we have determined the parameters in Eq. (6), $|K_\tau| = 3.95 \pm 0.3$ eV and $\epsilon = 0.22 \pm 0.05$. In this way five GaP pair spectra involving the acceptors C (type I) or Zn (type II) and the donors O, S, Se, or Te have been studied, although the resolution attained for the donors O and Se was somewhat lower.

The two fitting parameters K_τ and $K_\epsilon \equiv \epsilon K_\tau$

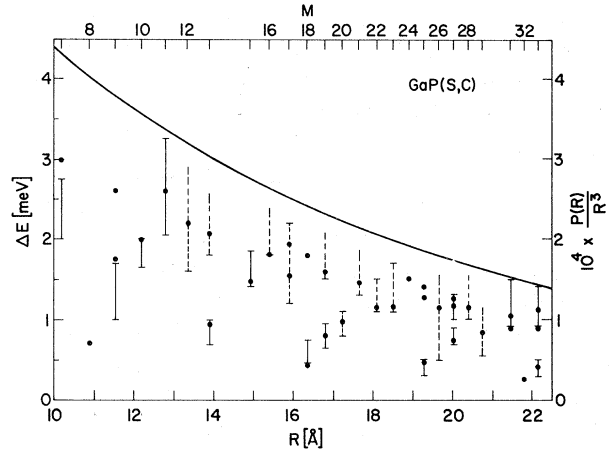


FIG. 2. Theoretical (circles) and experimental (bars, see text) splitting energies $|E_s|$ of the acceptor ground state in GaP(S,C) and the radial function $P(R)/R^3$ (solid curve) versus R for a Bohr radius $a_0 = 10.25$ Å.

found for each of the four donors used are shown with their experimental uncertainties in Fig. 3. The dashed line shows the values predicted for K_τ from the estimates described above. The conclusions drawn from these results are unambiguous and in part unexpected: (1) Strain fields *are* present which produce splittings whose radial and angular dependences are in excellent agreement with theory. (2) However, these fields are *independent*, within the experimental uncer-

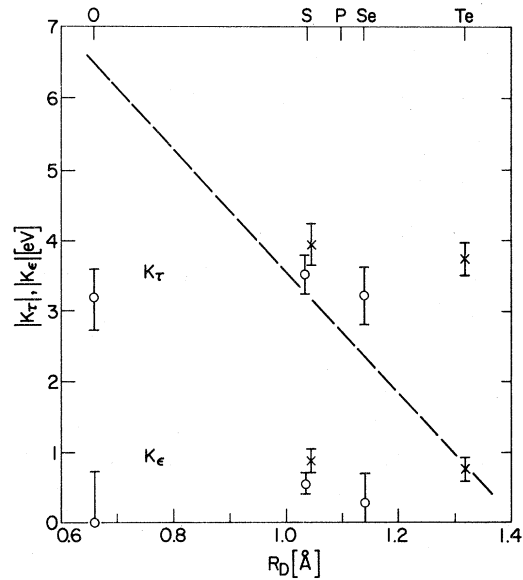


FIG. 3. Parameters K_τ and $K_\epsilon (= \epsilon K_\tau)$ for various pairs in GaP versus the covalent radius of the donors. The acceptors are Zn (circles) and C (crosses). The dashed curve shows the values of K_τ predicted from the two effects (misfit plus Coulomb strain) estimated in the text. The Bohr radii used for $P(R)$ were 8.88 and 10.25 Å for Zn and C, respectively.

tainties, of the "size" of the group VI impurities. We conclude, therefore, that the misfit volume associated with any of these substitutional impurities is either very small ($<0.2 \text{ \AA}^3$) or is distributed over a macroscopic region of the crystal which extends more than $\sim 20 \text{ \AA}$ from the donor. This latter assumption seems to be required to correlate our results with published changes of lattice constant observed by x-ray diffraction in heavily doped crystals of Si.¹² We note that the average value $|K_\tau| \sim 3.6 \text{ eV}$ ($\delta R \approx 0.2 \text{ \AA}$) agrees with the value $|K_{\tau_2}| \approx 3 \text{ eV}$ within the accuracy of the estimate and that the splitting factors are about 20% larger for C acceptors than for Zn.

There is space in this Letter for only a brief comment on the consequences of the absence of a "size" effect for substitutional donors in GaP. In a covalently bonded crystal the inter-atom spacing is determined (self-consistently) by the wave functions of the bonding electrons and not by any intrinsic size of the atom cores, since the latter are negligibly small for ions such as P^{+V} , Ga^{+III} , or even Zn^{+II} . When an impurity replaces one of these atoms, the local distortion of the crystal depends on the degree of localization of the bonding electrons. If the bonds are very local, as in an ionic crystal, the lowest energy of the system is attained when the electrons bonding the impurity are nearly characteristic of the impurity. Consequently, an impurity tends to retain its size when it enters the crystal. If, however, the bonds extend throughout a large volume of the crystal then the perturbing effect of the impurity is distributed over a corresponding region of the crystal and little or no local distortion is apparent, even though the total disturbing effect may be appreciable. The results of our experiment support this latter intuitive interpretation of valence bonding and, indeed, *might have been anticipated*. The existence of the expected total volume changes with doping are indicated by other experiments (such as the x-ray determination of lattice constants)¹² which measure bulk properties of doped crystals, while the absence of local fluctuations seems essential to an understanding of both the physical and band properties of III-V ternary alloys, which interpolate smoothly between the properties of the pure binary compounds. These latter systems may provide the experimental

data needed to test quantitatively the correctness of this interpretation.

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