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[28] If required, a vector component could equally well represent the concentration in a collection of sites, e.g., the sites in a shell about the radius. In this case the P_{ji} reflect the transitions for the whole shell. Care must be taken, however, since simple enumeration of the sites associated with a shell can lead to spurious results in the recovery.

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[34] The size of the correlated region is chosen such that this asymptote is essentially independent of the size.

SYMMETRY OF ELECTRON STATES IN GaP

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We show that the symmetry of bound electron states in GaP depends upon the choice of origin for the group operations and hence upon the location of impurity in the crystal lattice. This provides an explanation of the discrepancy between the high radiative efficiency associated with group VI donors and group V isoelectronic centers and the low efficiency of group IV donors (Si) in GaP.

Shallow donor states may be introduced into GaP by S, Se, or Te impurities substituting for a P atom or by Si and (possibly) C substituting for Ga.[1] Both types of impurities contribute extrinsic electrons.[1] However, high radiative efficiencies—from donor-acceptor pairs[2] and donor-to-valence band transitions[3]—have been reported only for donors located on P sites. Strong emission has been observed from donors on Ga sites only when a deep impurity state is involved.[4,5] In addition, numerous neutral centers occur on P sites and produce strong emission and absorption,[6] while no such centers on Ga sites have been identified. It is the purpose of this Letter to point out that the selection rules which govern these radiative transitions can be predicted on the basis of the band symmetry alone.

We show that for valleys at the zone edges the representation X_1 or X_3 to which the conduction band minima belong depends upon the choice of the origin of the coordinate system. This is chosen for convenience at the impurity site. If the impurity occurs on the more attractive (P) site, the lower band has X_1 symmetry about that site and is coupled to the Γ_1 band at $\vec{k}=0$ by an attractive (but not by a repulsive) short-range potential. Hence for the former, direct, zero-phonon, optical transitions to the Γ_{15} ($\vec{k}=0$) valence band are allowed. If the impurity occurs on the more repulsive (Ga) site, the symmetry is X_3 which cannot couple to Γ_1 but can to the higher Γ_{15} conduction band. In this case the transition probability is small and the matrix elements are those appropriate to a $\Gamma_{15}\rightarrow\Gamma_{15}$ optical transition. For six valleys these rules would be somewhat relaxed.

Band states. – GaP is an example of a III-V semiconductor which has $\langle 100\rangle$ conduction-band minima. We follow Cohen and Bergstresser's assignment of the conduction-band minima to the X points (three valleys).[7] Their calculated band structure is shown in Fig. 1. We neglect spin-orbit coupling.

The Bloch wave function for an electron of wave vector $\vec{k}$ in a band may be written

$$\psi_{\vec{k}}(\vec{r}) = Au_{\vec{k}}(\vec{r})\exp(i\vec{k}\cdot\vec{r}), \tag{1}$$

where $u_{\vec{k}}(\vec{r})$ is normalized in a unit cell and possesses the lattice periodicity. This function is a solution of the one-particle Schrödinger equation,

$$(H-E)\psi_{\vec{k}}(\vec{r}) = \{-(\hbar^2/2m)\nabla^2 + V(\vec{r})-E\}\psi_{\vec{k}}(\vec{r}) = 0, \tag{2}$$

where $V(\vec{r})$ is a periodic pseudopotential. When $\vec{k}$ occurs at the edge of the Brillouin zone, say $\vec{k}=\vec{k}_0$ in the z direction, $\psi_{\vec{k}_0}(\vec{r})$ mixes with the equivalent function $\psi_{-\vec{k}_0}(\vec{r})$, and the proper eigenstates are the even and odd combinations of these two functions. They may be considered to be derived from a single X_1 band (as in silicon) by the introduction of a potential which differs in the P and Ga sites. The eigenstates are thus

$$\psi_{\vec{k}_0}{}^{+}(\vec{r}) = Au_{\vec{k}_0}(\vec{r})\cos k_0 z \quad (X_1), \tag{3a}$$

and

$$\psi_{\vec{k}_0}{}^{-}(\vec{r}) = Au_{\vec{k}_0}(\vec{r})\sin k_0 z \quad (X_3), \tag{3b}$$

where the $u_{\vec{k}_0}(\vec{r})$ are equal to lowest order in the X_1-X_3 splitting.

These states transform according to the representations X_1 and X_3 as noted and can be identified with the X-point conduction-band states as we discuss below.[8]

GaP has the zinc-blende structure and contains a Ga and a P sublattice displaced from each other by $\frac{1}{4}(1,1,1)a$. The wave vectors at the X points are (see Fig. 1)

$$k_0 = 2\pi/a$$

in the x, y, and z directions. Hence if we fix the origin of our coordinate system on a Ga site, Eqs. (3a) and (3b) describe electron states whose probability densities reach their maxima on the Ga and P atoms, respectively. If our origin had been at a P site, these roles would have been interchanged. The difference δE between the energies of these two states depends upon $V^A(r)$, the antisymmetric part of the pseudopotential, which measures the difference between the core potentials for Ga and P (taken in that order).[7] If $V^A(r)$ were zero, as in silicon, the $u(r)$ would be equal on all sites and δE would vanish. When $V^A(r)$ is negative (attractive for electrons) on one sublattice, the states localized on those sites lie lowest and belong to the conduction-band minima. With our sign convention a positive $V^A(r)$ makes P the attractive site. From the pseudopotential form factors of Animalu and Heine[9] and of Phillips[10] we find that $V^A(r)$ is positive.[8] Hence, an electron in the lower band is concentrated on P sites and in the upper on Ga sites – an assignment which is confirmed by the selection rules found experimentally. The observed splitting is $\delta E \approx 0.3$ eV.[11]

Symmetry about impurities. – The importance of the nature of the conduction-band minima lies in its effect on the symmetries and selection

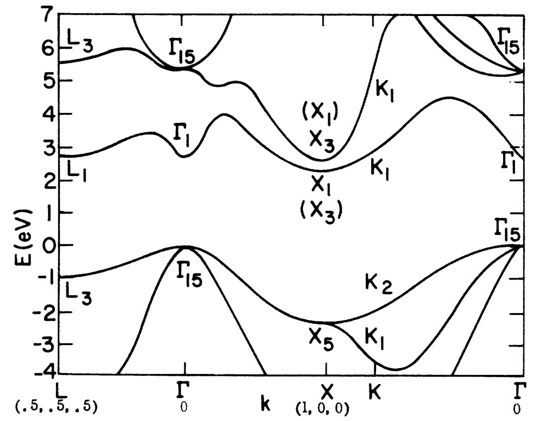

FIG. 1. Band structure of GaP from Cohen and Bergstresser, Ref. 7. The values of k are in units of $2\pi/a$.

rules associated with bound states in the crystal. The substitution of a single impurity for Ga or P atom automatically fixes the origin appropriate for discussion of the symmetry of an electron state which interacts with that defect. Thus, for an impurity on the attractive (P) sublattice the electron basis function at $\vec{k}_0$ in the lower band is Eq. (3a), which belongs to an X_1 representation. For an impurity on the repulsive (Ga) sublattice the proper wave function is Eq. (3b), which belongs to X_3. This same symmetry assignment can be applied to interstitial impurities if they occupy cubic sites, since these coincide with $\langle 100\rangle$ group III (Ga) or group V (P) planes. These assignments are collected in Table I and identified with the common impurities. Note that excitons may also be bound to neutral forms of the donors and acceptors listed.[6]

The selection rules for optical transitions between holes and bound electrons depend on the symmetry properties of the lowest conduction band. Since there are three equivalent X valleys, the band states are threefold degenerate. The degeneracy which remains in the bound state can be determined from the irreducible representations (in group T_d) to which the state belongs.[12] If the band symmetry is X_1, the bound states become a nondegenerate, totally symmetric (A_1) state and a doubly degenerate (E) state.[13] If the band symmetry is X_3, the degeneracy is not lifted and the state transforms as T_2. The E state vanishes at the impurity site and does not couple to any states in the lowest (Λ_1) conduction band in the $\langle 111\rangle$ directions, including Γ_1 and L_1. The A_1 state is nonvanishing at the origin and couples to the lowest band in all regions of the Brillouin zone, including Γ_1 and Λ_1. It is shifted relative to the E state by the core potential of the impurity. For these reasons, if the core potential is attractive, the low-lying state from an X_1 band is an A_1 state which can recombine with a band-edge hole in a $\Gamma_1 \rightarrow \Gamma_{15}$ radiative transition without phonon assistance. If the core is repulsive, a zero-phonon transition will occur only through (higher energy) electron and hole states which avoid the region of Λ. The T_2 state, which transforms like the $\Gamma_{15}(\equiv T_2)$ zone-center conduction band, can mix with the latter and with T_2 combinations of other states (such as Λ_1). Thus no-phonon recombination is possible, but its strength is reduced because of the higher energies of the admixed states. It is expected to be important only if the matrix elements which mix the states are large, as for a deep donor (e.g., Ge). Although overlap with the core is small, distortions affecting the surrounding P atoms may shift the binding energy of the electron state. The matrix elements are those of a $\Gamma_{15} \rightarrow \Gamma_{15}$ transition.

Phonons.—The selection rules for phonon-assisted processes between impurity states can be deduced most simply by treating the phonons as quasilocalized about the impurity. The maximum coupling will occur through phonon wave packets of extent comparable with that of the electron-hole overlap. Each of the sixfold-degenerate transverse phonon states at X decomposes into two representations of T_1 and T_2 symmetries. The longitudinal phonons at X are analogous to the electron states in that the lower energy LA phonons involve out-of-phase motion of adjacent planes of the heavier Ga atoms while the P atoms remain at rest. The LO modes involve motion of only the P atoms and occur at a higher frequency as determined by the mass ratio,

$$\omega(\mathrm{LO})/\omega(\mathrm{LA}) = \{M(\mathrm{Ga})/M(\mathrm{P})\}^{1/2} = 1.50.$$

Thus their symmetries depend on the choice of origin. For an impurity on a P site, an LO phonon belongs to X_3 and transforms as T_2, while an LA phonon belongs to X_1 and decomposes into A_1+E. For an impurity on a Ga site the roles of the LA and LO phonons are interchanged (see Table I). For a material like AlSb composed of heavier group V atoms, the labels LA and LO must be interchanged. Note that since A_1 phonon

Table I. The dependence of electron and phonon symmetries on impurity site. The columns of the periodic table are listed on the right for the common impurities. The decompositions into localized states (for electrons or phonons) are shown at the bottom.

Site	First band	Second band	LA	LO	TA TO	Donors	Acceptors	Neutral
V (P)	X_1	X_3	X_1	X_3	X_5	VI	IV	V
III (Ga)	X_3	X_1	X_3	X_1	X_5	IV	II	III

$X_1 \rightarrow A_1+E$, $X_3 \rightarrow T_2$, $X_5 \rightarrow T_1+T_2$

Table II. Allowed transitions through four of the possible intermediate states in the conduction and valence bands (superscript c or v). The energies in eV of the intermediate electron and hole states above their respective band edges are shown (in that order) in parentheses. For Λ we give the energies at L. Allowed phonons are labeled according to the symmetry of their localized modes and 0 denotes a no-phonon transition.

Site	State	$\Gamma_1^c(0.5,0)$	$\Gamma_{15}^c(2.6,0)$	$X_5^v(0,3)$	$\Lambda^{c+v}(0.5,0.8)$
P	A_1	0 + LA(A_1)	LO + TA + TO(T_2)	0 + all	0 + all (at L)
Ga	E	LA(E)	LO + TA + TO(T_2)	0 + all	weak
Ga	T_2	LA(T_2)	0 + all	0 + all	0 + all (at L)
	(A_1 in 2nd band)	0 + LO(A_1)	(See text)		

packets involve hydrostatic deformation about the impurity, their energies may be perturbed by changes in size or elastic constant at the impurity.

The one-phonon selection rules are easily derived from the symmetries of the localized states and are summarized in Table II. We have listed the intermediate states along Λ. These are expected to be important because of the large densities of states at nearly constant (and small) energies along these directions in k space. If V^A were negative, the roles of the LA and LO phonons would be interchanged as would those of the Ga and P sites. The energies of the intermediate states, given in Table II, favor coupling to the LA phonons, though this factor is compensated by the higher densities of states near X_5, Λ_{15}, and L_1. The final entry in Table II deserves an explanation. When the impurity occurs on a Ga site, the second conduction band belongs to X_1 and possesses an (in-band) A_1 bound state which is strongly mixed with the Γ_1 minimum lying only ~0.2 eV above it. Thus, T_2 combinations of near zone-center phonons (Λ_1, Λ_3, Δ_3, etc.) can contribute to electron-hole recombination through this higher X_1 band.

The above restrictions (with or without phonons) apply strictly to systems of high (T_d) symmetry. Such a system would be a bound exciton where both electron and hole states are perturbed by a single-impurity potential. In systems of symmetry lower than T_d the selection rules are relaxed. In particular, pair spectra are generally (at least weakly) allowed. For distant pairs the relaxation of the selection rules is small and depends upon the distortion of the electron wave function in the region where it overlaps the hole. Thus, in Si-Si pair recombination the overlap occurs near the deep acceptor on a P site and the efficiency is observed to be high.[4] In the case of pair spectra involving Si donors and shallow acceptors, the no-phonon distant pair peak is expected (and found) to be weak relative to its phonon replicas, although transitions from close-spaced pairs are visible without phonon cooperation. Replicas of the distant-pair peak are expected from phonons near Γ_1, X_1, and L with the first (from Λ_1 near Γ) appearing a few meV below the no-phonon energy. These predictions are found to be in agreement with unpublished photoluminescent spectra observed in Si-doped crystals.[14] In the light of this theory it is not surprising that although Si is a common accidental donor in GaP, its participation with shallow acceptors in radiative processes has until recently remained unrecognized.

Thus, in conclusion, we find that the location of an impurity in the GaP lattice determines the optical selection rules for electron-hole recombination through its bound states. The experimental consequences of this analysis are in detailed agreement with the previously unexplained experimental results. Other indirect gap III-V semiconductors with ⟨100⟩ minima (such as AlSb) can be analyzed similarly.

The author would like to acknowledge many helpful discussions with Dr. Frank Stern.

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[14] A detailed account of the spectra produced by group IV dopants in GaP has been prepared by P. J. Dean, C. J. Frosh, and C. H. Henry, to be published. Their results are also in complete accord with the conclusions of this analysis. The author wishes to thank Dr. Dean for providing a preprint.

REBUTTAL TO THE ALTERNATIVE SCHROEER-TRIFTSHÄUSER INTERPRETATION OF RECENT MEASUREMENTS ON COBALTOUS OXIDE*

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In a recent Letter Schroeer and Triftshäuser offered a reinterpretation to the extensive data on cobaltous oxide by the present authors. We show herein that a careful examination of the microcrystal model proposed by Schroeer and Triftshäuser does not, in fact, account for the main observation on cobaltous oxide.

Recently much interest has been shown in the origin of the multiple charge states found in Mössbauer spectra of Fe^{57} in CoO.[1-4] After a period, during which much work was done with samples showing both Fe^{2+} and Fe^{3+} lines, we succeeded in isolating two materials showing only Fe^{2+}, or Fe^{3+}, in their respective Mössbauer spectra, with each having the nominal composition CoO. Extensive experimental data on CoO(I), CoO(II), and CoO(I, II), a mixture of forms I and II, were analyzed and explained on the basis of a two-phase model.[2] In this model we postulated that CoO(I) had ideal stoichiometry and translational symmetry, while CoO(II) was a highly vacated lattice with the number of Schottky defects equal to the number of CoO molecules contained in this material. The main reasons for assuming the vacated structure, CoO(II), was the observation that the relative density ρ_{II}/ρ_I was of order 0.5, the relative Debye temperature, θ_{II}/θ_I, was 0.61, and CoO(II) was observed to absorb more than 60% excess oxygen at room temperature. Also, thermal cycling and quenching experiments supported this view. Furthermore, this Schottky defect model for CoO(I, II) could explain the reversible increase[2-4] of Fe^{3+} with increasing temperature on the basis of anion vacancy dissociation.[2]

Recently, however, Schroeer and Triftshäuser (ST) reinterpreted our data for CoO(II) on the basis of a microcrystal model, using vague arguments supplemented by rough numerical estimates. The purpose of this Letter is to point out some weaknesses in the ST arguments, which indicate that their model is not consistent with our observations.

ST propose that CoO(II) is merely microcrystals of CoO, with an average diameter of about 50 Å. As evidence for their microcrystal model they point out that our preparation technique, involving a liquid reaction, can lead to microcrystals, quoting a similar preparation for CuO. The fact that such reactions do not necessarily lead to microcrystals, however, has been strikingly shown by Ikornikova,[6] who has grown large single crystals of $CoCO_3$ in aqueous solutions at 100-500°C.

To explain our observed low density of CoO(II), ST assume a simple cubic packing of spherical microcrystals to show that the density of CoO(II) can be about half of that of CoO(I). There is, however, no reason why spherical microcrystals should be packed in a simple cubic arrangement. A close-packed structure, such as fcc or hcp,