Electron-Core-Hole Interaction in GaAsP

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The electron–core-hole interaction is studied via energy derivative reflectance spectra of 20-eV transitions from Ga $3d$ core levels to lower conduction-band final states in $GaAs_{1-x}P_x$ alloys. A two-level anticrossing behavior of line shapes and threshold energies as the relative positions of the L and X minima invert yields a previously unanticipated L-X mixing energy $|V_{LX}| \sim 50$ meV.

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The nature of the electron-hole interaction in excitations from shallow core levels to the lower conduction band of semiconductors is a continuing source of controversy. This interaction is generally thought to be observable only through the differences between combinations of optical and photoemission threshold energies, i.e., the binding energies, E_B, of core excitons.[1] Effective-mass calculations[2,3] typically yield estimates of $E_B \sim 40$ meV, while estimates made by comparing experimentally determined optical and photoemission thresholds are systematically larger, of the order of 100–200 meV for transitions from Ga $3d$ core levels in GaAs and GaP.[4,5] Differences between measured and calculated reflectance spectra are interpreted[6] as being even larger, as much as 1 eV, and are also attributed mainly to the electron–core-hole interaction. These values vary sufficiently to allow qualitatively different interpretations of the excitations. If E_B is small, then an interpretation based on a single conduction-band minimum (or equivalent minima) is appropriate, while if E_B is large, then considerable interband mixing will occur.

In this Letter we show that the strength of the electron–core-hole interaction is intermediate to the above cases: final states corresponding to *different* (i.e., inequivalent) minima of the *same* conduction band are mixed by the core-hole potential. This mixing is revealed directly in the variation with composition x of the fine structure in reflectance spectra of $GaAs_{1-x}P_x$ pseudobinary alloys. The variations in peak position and intensity are described in detail by a two-level anticrossing model with an interaction energy of ~ 50 meV. This sets a scale for E_B nearer to but still larger than effective-mass values. However, the simple and natural explanation of our results in terms of final states having the symmetries of the the L and X lower conduction-band minima provides strong evidence for the single-band interpretation.

The analysis of these data also provides insight into the nature of the core-hole potential. First, it hybridizes the wave functions derived from the four L minima into singlet and triplet states. Second, the L-derived triplet states mix with their analogs at X to yield core excitons that are neither purely L- nor X-derived, but intermediate in character. Both effects suggest a strong central-cell component in the potential of the core hole. We note that the lattice remains essentially unrelaxed about the hole, due to the relatively short core-hole lifetime ($\Gamma \sim 100$ meV). Finally, we find that the ratio of transition probabilities from Ga $3d$ to L and X final states is ~ 0.1. Because the core hole is a model point defect, our results should also prove useful in understanding point defects in semiconductors, a problem of current interest.[7]

We investigated a number of single-crystal samples in the pseudobinary alloy series $GaAs_{1-x}P_x$. The GaAs sample was bulk material ($n = 1.5\times10^{16}$ cm^{-3}), while the other samples ($n \lesssim 1\times10^{17}$ cm^{-3}) were grown by vapor-phase epitaxy on GaAs or GaP substrates. The compositions x are accurate to approximately $\Delta x = \pm 0.02$. All samples were chemically stripped to remove overlayers just prior to measurement. Transitions from Ga $3d$ core levels to the lower conduction band were excited with synchrotron radiation with use of techniques that are described elsewhere.[8] Reflectance spectra were measured from 19.5 to 21.5 eV at 60° angle of incidence with 54 meV full width at half maximum resolution. Fine structure from transition thresholds was enhanced by numerically differentiating twice to yield second-energy-derivative reflectance (2EDR) spectra.

The nature of the electron–core-hole interaction was investigated by modifying the relative positions of the L and X minima by alloying. In $GaAs_{1-x}P_x$, L lies below X for $x = 0$ (GaAs)[9,10] and above X for $x = 1$ (GaP).[11] If the positions of the minima are assumed to vary quadratically with

composition with similar bowing parameters for L and X, then the L-X crossover is expected to occur near $x_c = 0.33$. Several 2EDR spectra are shown in Fig. 1 for compositions x spanning crossover. The structures in the GaAs spectrum are identified, as in previous electroreflectance[9,10] and 2EDR[5] spectra, with transitions from the $j = \frac{5}{2}$ and $\frac{3}{2}$ spin-orbit–split Ga $3d$ core levels to final states at L and X. The X structures gradually weaken and disappear with increasing P content, while the L structures evolve into those associated[5,12] with X in GaP.

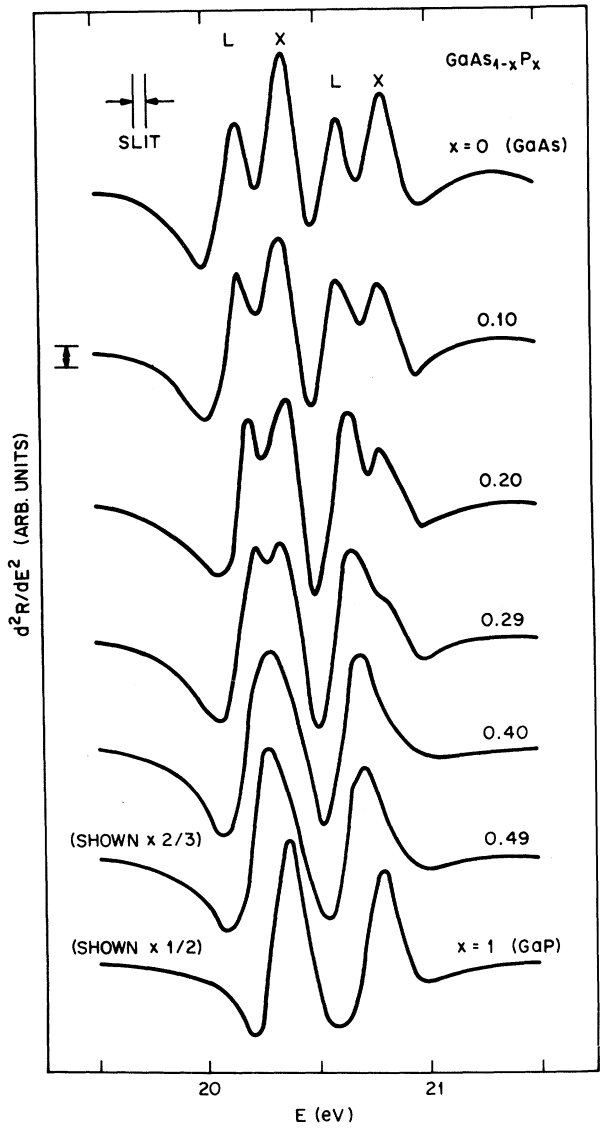

FIG. 1. 2EDR spectra for several samples in the pseudobinary-alloy series $GaAs_{1-x}P_x$. Transitions are identified from the $j = \frac{5}{2}$ and $\frac{3}{2}$ spin-orbit–split Ga $3d$ core levels to L-like and X-like conduction-band final states. Monochromator slit resolution (full width at half maximum) was 54 meV. Maximum noise is indicated on the second curve.

Quantitative information is obtained from the variation of these structures with composition. The energies of the peaks of the 2EDR spectra are shown as a function of x in Fig. 2. Although a line-shape analysis is necessary to obtain absolute critical-point energies, *relative* energy positions may be obtained from the peaks alone because the Fresnel-reflection coefficients do not vary rapidly over the ~1 eV energy range of these transitions.[13] The peak energy positions in Fig. 2 show a classic two-level anticrossing behavior. This naturally suggests a two-level model, in which the wave functions corresponding to the unperturbed L and X minima are mixed according to

$$\begin{pmatrix} E_X - W & V_{LX} \\ V_{LX} & E_L - W \end{pmatrix} \begin{pmatrix} a_X \\ a_L \end{pmatrix} = 0. \quad (1)$$

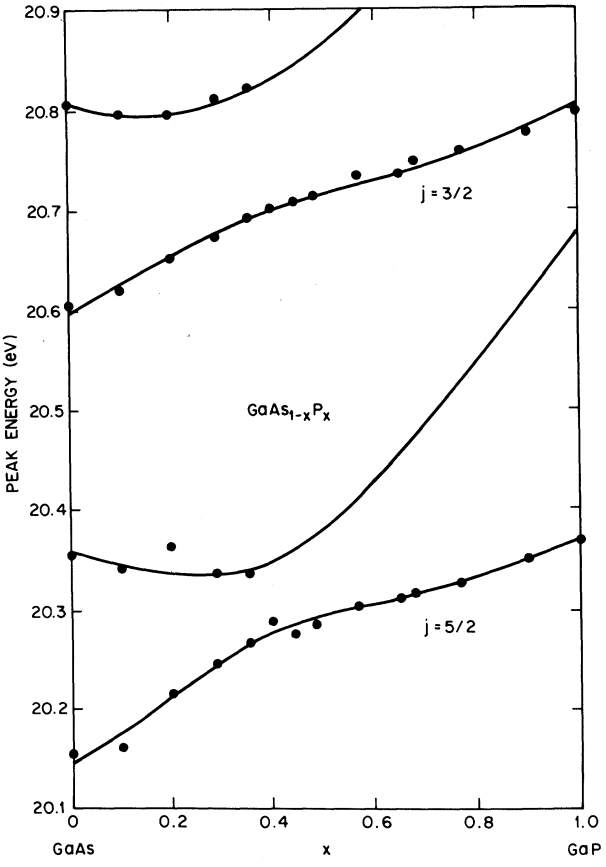

FIG. 2. Energy positions of peaks in 2EDR spectra for $GaAs_{1-x}P_x$ samples. The curves represent fits to the data and are discussed in the text.

Here a_L and a_X are the coefficients of the unperturbed final-state wave functions $|L\rangle$ and $|X\rangle$, and the dressed energies E_L and E_X include self-energy terms V_{LL} and V_{XX} as corrections to the bare energies. The term V_{LX} represents L-X mixing.

The curves in Fig. 2 represent fits of Eq. (1) to the experimental points, in which the energies E_L and E_X are assumed to vary quadratically with composition with bowing parameters of the unperturbed bands.[14,15] The data for $j=\frac{5}{2}$ and $j=\frac{3}{2}$ were fitted independently, with each set yielding dressed values for E_L and E_X for both GaAs and GaP and a value for the mixing energy V_{LX}. We find $|V_{LX}|$ to be 37 ± 9 and 63 ± 4 meV for the $j=\frac{5}{2}$ and $j=\frac{3}{2}$ cores, respectively. These values are just half the observed splittings at crossover. We find that crossover occurs at $x_c=0.41$ ($j=\frac{5}{2}$) and $x_c=0.34$ ($j=\frac{3}{2}$); the shift of these values toward P-rich compositions indicates that the self-energy $|V_{LL}|$ is slightly larger than $|V_{XX}|$ for this series. If $V_{LL}=V_{XX}$, then the fitting procedure yields a bare L-X separation of 310 ± 60 meV for GaP, in good agreement with the results of Kyser and Rehn.[11]

We expect that V_{LX} arises mainly from the central-cell part of the core potential, because the Bloch functions corresponding to different minima would remain essentially orthogonal in a slowly varying perturbation potential.[16] On the other hand, the self-energies V_{LL} and V_{XX} contain significant contributions from intraminima (dynamic of effective-mass-like) effects in addition to a central-cell term and thus may be expected to *exceed* V_{LX} in magnitude. This puts a lower limit on core-exciton binding energies that is larger than effective-mass estimates which treat equivalent minima independently.[2,3] Therefore, an approach similar to that of Resca and Resta[7] to calculate these energies appears promising. We note that as a result of the L-X interaction, core excitons have mixed character, even for the GaAs and GaP endpoints. For example, the X-like wave function in GaAs has $a_L/a_X=0.18$ for $j=\frac{5}{2}$ and 0.34 for $j=\frac{3}{2}$. Thus the X exciton has significant L character.

The simple two-level model is applicable if and only if the wave functions for the four L minima hybridize into a singlet and a triplet by means of a valley-orbit interaction involving the core-hole potential. This can be shown quite elegantly by group theory[13] and also by the following simple arguments. The wave functions corresponding to the lowest X minima have X_3 symmetry with respect to the origin on a Ga site[17] and to first order are totally p-like about Ga. These wave functions thus form a triplet with Γ_{15} symmetry, and they cannot be mixed by the core-hole potential. However, the wave function of each of the four L minima is p- and s-like about Ga. The core-hole potential has full cubic symmetry and thus hybridizes the quartet into an s-like singlet (Γ_1) and a p-like triplet (Γ_{15}). (Note that this valley-orbit splitting also gives a small contribution to V_{LL}.) The core-hole potential then mixes L- and X-derived Γ_{15} states of like symmetry, so that the full 7×7 Hamiltonian matrix for the four L and three X minima reduces to a 1×1 and three identical 2×2 matrices. The latter matrices describe the L-X mixing.

The two-level model also gives information about the relative intensities of the structures. Because the initial state is atomic d-like, transitions to Γ and to the singlet L are forbidden to first order and are not observed. The intensity of a given structure corresponding to a p-like final state depends on the intrinsic relative strengths of transitions to L and to X and on the degree of L-X mixing by the attractive core-hole potential. The resulting interference between the unperturbed L and X wave functions causes a (partial) transfer of oscillator strength to the lower-energy structure.[13] Thus, when L is below X, as in GaAs, the L structure gains oscillator strength from X but when L is above X, as in GaP, L loses oscillator strength to X. By a quantitative analysis we find that in the absence of L-X mixing the ratio of transition probabilities from the Ga $3d$ core to L and to X is 0.10 for $j=\frac{5}{2}$ and 0.15 for $j=\frac{3}{2}$. These values are in good agreement with simple model estimates[12] but disagree with more extended calculations.[6] Thus the L-X mixing model both explains the previously puzzling electroreflectance line-shape difference between GaAs and GaP and explains why transitions to L have been observed[5] in other III-V materials only when L lies below X in the unperturbed band structure.

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Coherence and Disorder in Arrays of Point Contacts

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By measuring the penetration depth and the critical current of three-dimensional assemblies of weakly coupled superconducting grains as a function of temperature, two critical exponents, β and ν', were determined characterizing the transition to coherence of the system. As in calculations on disordered systems, strict universality does not hold, but the exponents are shown to be compatible with the hypothesis of weak universality.

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Since the early work of London[1] supercurrents and the penetration depth of superconductors appear as manifestations of phase coherence, or order in momentum space, among the superconducting electrons. Similarly Josephson currents and penetration depth result from phase correlations between superconductors separated by a barrier. By the same token, one may expect intuitively that an array of a great number of junctions (such as a granular superconductor) will display supercurrents and static screening of external fields provided long-range correlations exist between superconducting phases in different electrodes. We report here on measurements of critical current and penetration depth of three-dimensional (3D) assemblies of bulk grains (diameter $a \lesssim 50$ μm) weakly coupled through Josephson point contacts.

Our samples are made by simply pressing together in an epoxy resin slightly oxidized superconducting Nb grains. We thus obtain arrays of about 10^6 point contacts which can be molded to the desired shape, in this case cylinders 3 mm in diameter and 13 mm long. Resistivities ρ_n in the range 0.1–1 Ω cm are easily obtained by controlling the pressure on the system during hardening of the resin. On the basis of resistive measurements we have pointed out[2,3] that a phase transition from a high-temperature "paracoherent" state to a low-temperature coherent one takes place at a temperature $T_0 < T_c$. This is due to the fact that superconducting phases in indi-