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FINAL-STATE INTERACTIONS IN CORE EXCITATIONS OF III-V SEMICONDUCTORS

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Composition and uniaxial stress dependence of structures in Ga3d core-conduction band spectra of $GaAs_{1-x}P_x$ are described by one-electron band theory with local minima hybridized and mixed by the core-hole (defect) potential. The measured L-X mixing potential allows the central-cell range to be estimated.

The use of tunable synchrotron radiation to selectively excite electrons from shallow core levels of semiconductors provides a unique opportunity to study in an otherwise perfect crystal prototypical substitutional point defects whose identity and unit-cell location are unambiguous. We wish to use core-level spectroscopy to determine information about the nature of the core-hole potential and its effect on the one-electron final states from the dependence of structure on composition in $GaAs_{1-x}P_x$ and on uniaxial stress in GaAs.

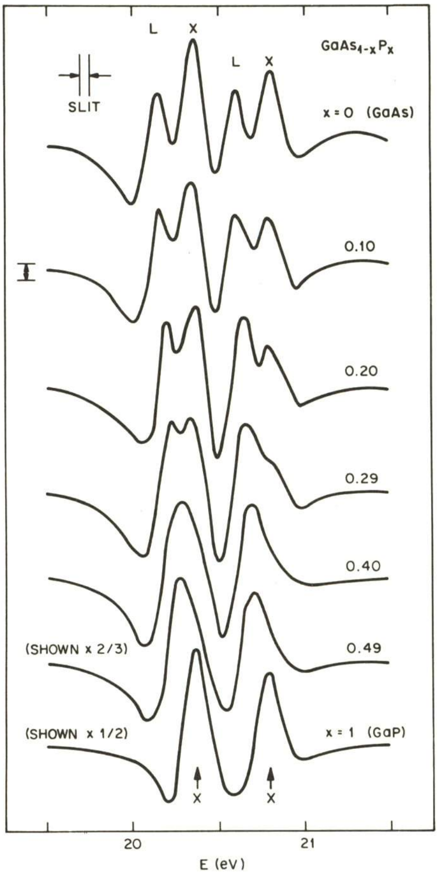

FIGURE 1

Figure (1) shows second energy derivative reflectance spectra between 19.5 and 21.5 eV for several $GaAs_{1-x}P_x$ compositions x which show fine structure due to core-level transitions. For x=0 (GaAs), four structures are seen which are assigned in accordance with previous work [1] to thresholds for transitions to local minima of the lower conduction band at L and X from Ga $3d_{5/2}$ (lower-energy doublet) and $3d_{3/2}$ (higher-energy doublet) initial states. As the P fraction x increases, the structure labeled L in GaAs gradually increases in amplitude and evolves into the structure identified with X in GaP (x=1), while that labeled X in GaAs gradually disappears. The cause of this behavior can be understood qualitatively from the variation of peak energies with composition as shown in Fig. (2) [2]. A classic two-level anticrossing behavior is observed as the local lower conduction band minima at L cross those at X, due to an

L-X interaction potential $|V_{LX}|$ that mixes the appropriate one-electron wavefunctions and prevents an actual crossing of the unperturbed levels. The disappearance of the higher-lying structures in Fig. (1) (and indeed the ability to see the L structure at all in GaAs) can be understood in this model as a transfer of oscillator strength by the same mixing potential from the higher- to lower-energy transition of an L-X pair, if the Ga3d-X transitions (including both matrix element and density of states) are inherently stronger than Ga3d-L.

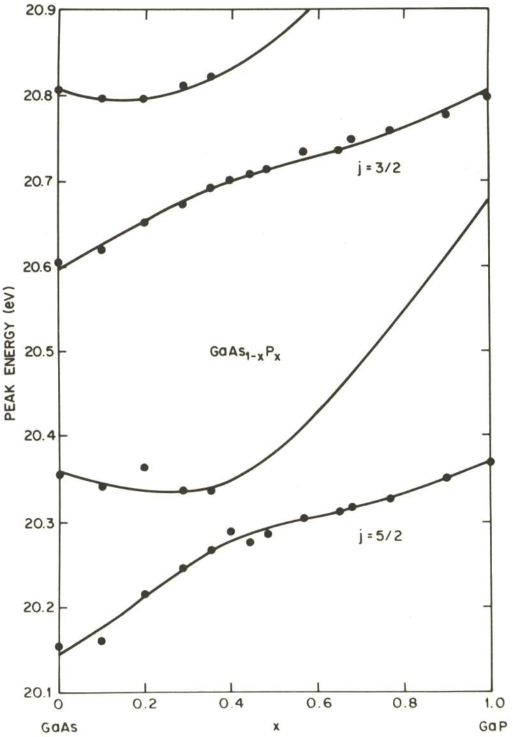

FIGURE 2

A quantitative treatment can be given [2] if we suppose that the effective-mass approximation has at least approximate validity. That is, we assume that the core hole (defect) potential is sufficiently weak that the part of the final state wavefunction associated with any single local conduction band minimum centered about $\vec{k}=\vec{K}$ is constructed of Bloch functions $\Phi_c(\vec{k},\vec{r})$ whose wave vectors are localized near the minimum [3]:

$$\psi_{\vec{K}}(\vec{r}) \cong \sum_{\vec{k}\cong\vec{K}} A_{\vec{k}}\Phi_c(\vec{k},\vec{r}) \cong \{\sum_{\vec{k}\cong\vec{K}} A_{\vec{k}} e^{i(\vec{k}-\vec{K})\cdot\vec{r}}\}\Phi_c(\vec{K},\vec{r}). \qquad (1)$$

In this case the wavefunctions for the four L minima hybridize via the valley-orbit interaction to form a Γ_1 singlet and a Γ_{15} triplet. The wavefunctions for the three X minima also form a Γ_{15} triplet. The L triplet states then mix with their equivalents at X to yield levels described by three identical 2×2 matrices with eigenvalues given as follows:

$$W_{1,2} = \frac{1}{2}(E_X+E_L) \pm \sqrt{\frac{1}{4}(E_X-E_L)^2 + |V_{LX}|^2}. \qquad (2)$$

Here, E_X and E_L contain self-energy corrections V_{LL} and V_{XX} as well as the "bare" one-electron variation of the minima. Assuming V_{LL}, V_{XX}, and V_{LX} to be independent of x, and assuming E_L and E_X to vary quadratically with composition with bowing parameters of the unperturbed bands, we obtain fitted curves for peak energies as indicated in Fig. (2) [2]. We find $|V_{LX}|$ = 37±9 meV for j=5/2 and 63±4 meV for j=3/2. We also find dressed (self-energy included) L-X crossover compositions of x_c=0.41 and 0.34 for j=5/2 and j=3/2, respectively, compared to x_c=0.33 for the unperturbed bands. The higher crossover composition for j=5/2 is evident in Fig. (1) and suggests that $|V_{LL}|$ is slightly larger than $|V_{XX}|$ for the j=5/2 core. If we assume $V_{LL}=V_{XX}$, then the least-squares fit parameters show a bare L-X separation of 310±60 meV for GaP, in good agreement with other

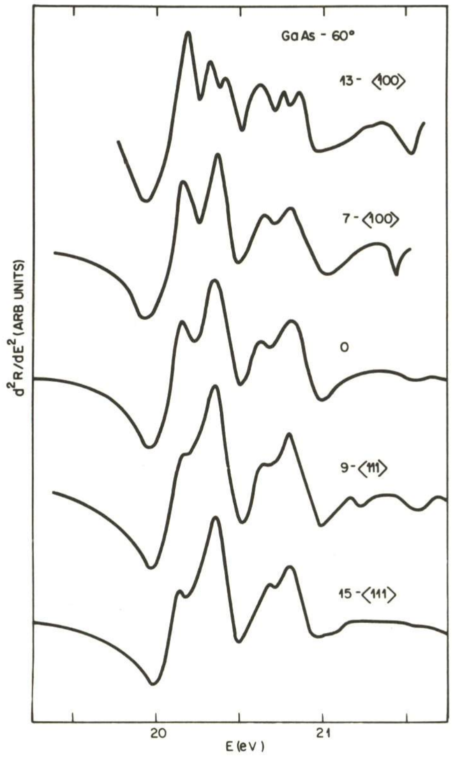

FIGURE 3

measurements [4].

Uniaxial stress measurements can be used to further investigate symmetry assignments and the approximate validity of the one-electron band picture. The results for GaAs are shown in Fig. (3). For <100> stress, the L minima remain equivalent and the only effect is to split the (already independent) minima at X. The proper X splitting of ∿150 meV is observed at 13 kbar. For <111> stress, two of the 2×2 matrices remain unaffected but the third is mixed with the singlet state, forming a 3×3 matrix. This mixing simply reflects the fact that in the limit of extremely large <111> stress the valley-orbit interaction is overridden and the singlet becomes pure <111>. The invariance of the X structure and the weakening of the L structure at 15 kbar are consistent with the redistribution of oscillator strength as the singlet changes character. Thus both original assignments and the band nature of the final states are confirmed. No effect is observed for either <100> or <111> stress until the shear splitting reaches values comparable to the linewidth.

We comment finally on the implications of these results upon the nature of the defect potential V(r) and the magnitude of core-exciton binding energies in these materials. For the sake of obtaining an explicit, though considerably oversimplified, expression, we suppose V(r) has the screened Coulomb form $e^2/r\varepsilon(r)$, where [5]

$$\varepsilon(r)^{-1} = \varepsilon_\infty^{-1} + (1-\varepsilon_\infty^{-1})e^{-Q_D r}, \qquad (3)$$

where Q_D^{-1} is a screening length. We suppose further that the envelope functions in an effective-mass solution are hydrogenic s-like with radius a_b similar for both L and X minima, and in the spirit of the pseudopotential approximation replace the actual Bloch functions with single plane waves. Then we find that

$$\langle V\rangle = \frac{e^2}{\varepsilon_\infty a_b}\left(\frac{1}{1+(\frac{1}{2}a_b\Delta K)^2} + \frac{\varepsilon_\infty-1}{(1+\frac{1}{2}Q_D a_b)^2+(\frac{1}{2}a_b\Delta K)^2}\right). \qquad (4)$$

Here, <V> is an expectation value if ΔK=0 and a matrix element if $\Delta K = |\vec{K}_L - \vec{K}_X| = \pi\sqrt{3}/a_0$, where a_0 is a lattice constant.

Equation (4) is easily evaluated if we use as estimates $a_b=2a_0$ and $Q_D^{-1} = a_0\sqrt{3}/4$, the interatomic spacing, and use values for ε_∞ and a_0 appropriate for GaAs. Then Eq. (4) predicts a self-energy (∿2x binding energy) of ∿200 meV and a mixing energy of ∿30 meV. These energies are in basic agreement with experiment; further, the value used for Q_D^{-1} is probably not unreasonable considering that the defect potential arises from a relatively extended d orbital and thus should be expected to be larger than the point-charge screening value $Q_D^{-1} \cong 1.2\ a_B$ for Ge [5]. We note that the contribution of the non-central-cell part of V(r), i.e., the first term of Eq. (4), is ∿100 meV to the self-energy and only ∿3 meV to the mixing energy. The main points with Eq. (4) are to indicate that V_{LX} arises principally from the central-cell part of V(r), i.e., the second term of Eq. (4), and that V_{LX} is always substantially less than V_{LL} or V_{XX}, even with microscopic overlap reductions neglected. Thus our measured value of $|V_{LX}|$ places a lower limit on the binding energy that is already larger than effective-mass estimates, which are ∿40 meV [6]. In further support, our measurements on mixed-cation crystals such as $In_{0.53}Ga_{0.47}As$ with different core levels excited to the same final state show changes in L-X energy differences of 150 meV between Ga3d and In4d cores, indicating that at least one binding energy is larger than 150 meV [7]. Finally, the connection to the properties of point defects is completed by noting that binding energies with respect to L and X of the substitutional donor Sn in $Al_xGa_{1-x}As$ are 150 meV (possibly L singlet) and 101 meV, respectively [8].

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