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k-LINEAR COUPLING AND THE E_1' TRANSITIONS IN GaAs

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The k-linear intravalence and intraconduction band coupling terms along the ⟨111⟩ directions are shown to explain the anomalously large strength of the E_1' structure relative to $E_1' + \Delta_1'$ and also the large energy separation between them. Quantitative agreement between theory and experiment is obtained using intraband coupling values calculated from $\mathbf{k} \cdot \mathbf{p}$ perturbation theory.

E_1' STRUCTURES observed in modulation spectra in materials with moderate spin-orbit splittings are characteristically doublets, with the E_1' structure much larger than that of $E_1' + \Delta_1'$, and the observed energy separation Δ_1' larger than the spin–orbit splittings Δ_1^v and Δ_1^c of the valence and second conduction bands at $k = 0$ [1–3]. Both features are surprising when viewed from the perspective of simple two- or three-band models [4] of the band structure along ⟨111⟩. Although the condition $\Delta_1' > \Delta_1^v$ has been interpreted as evidence that the E_1' and $E_1' + \Delta_1'$ critical points do not lie exactly on ⟨111⟩ [1, 3, 5] the reason for such a local distortion has not previously been understood.

Recent calculations for Si [6] showed that the intravalence band coupling [7] along ⟨111⟩ between the upper valence bands $\Lambda_{4,5}^v$ and Λ_6^v (k-linear term) significantly increases the transverse interband reduced mass, μ_T, of Λ_6^v with the lower conduction band, Λ_6^{cl}, and reduces it for $\Lambda_{4,5}^v$. The effect is large in Si because Δ_1^v is extremely small (~ 0.029 eV [8]). Because Δ_1^c is also small for most materials [9], with suggestive exceptions such as $\alpha - Sn$ [10] and InSb [11] where E_1' structural anomalies are not seen, it has been postulated [12] that the E_1' structural anomalies in small Δ_1^c materials are also caused by k-linear terms. The purpose of this note is to show that this hypothesis is supported quantitatively by theory.

1. BAND MODEL

To describe k-linear effects in E_1' transitions a minimum of five bands along ⟨111⟩ must be included explicitly: $\Lambda_{4,5}^v$, Λ_6^v, Λ_6^{cl}, and the second conduction bands $\Lambda_{4,5}^{cu}$, Λ_6^{cu}. Interactions with other bands are less significant and we include them by using momentum matrix elements previously calculated in a 15-band $\mathbf{k} \cdot \mathbf{p}$ expansion [13], or by fitting to experimental reduced masses [14].

Because Λ_6^{cl} couples primarily to $\Lambda_{4,5}^v$ and Λ_6^v we divide the full five-band ⟨111⟩ Hamiltonian into a three-band part containing $\Lambda_{4,5}^v$, Λ_6^v, and Λ_6^{cu}, and a two-band part containing $\Lambda_{4,5}^{cu}$ and Λ_6^{cu}. Interactions among Λ^v and Λ^{cu} are treated by second-order perturbation theory. Let k, θ express the magnitude and direction of $\mathbf{k}$ perpendicular to [111] as

$$k\, e^{i\theta} = k_{x'} + ik_{y'} \tag{1}$$

where $k_{x'}$ and $k_{y'}$ are the x' and y' components of $\mathbf{k}$ in a coordinate system $\hat{x}' = (\hat{x} - \hat{y})/\sqrt{2}$, $\hat{y}' = (\hat{x} + \hat{y} - 2\hat{z})/\sqrt{6}$, $\hat{z}' = (\hat{x} + \hat{y} + \hat{z})/\sqrt{3}$. Then using the standard orbital representations

$$\Lambda_6^v, \Lambda_6^{cu} \sim (x' + iy')/\sqrt{2}, \tag{2a}$$

$$\Lambda_{4,5}^v, \Lambda_{4,5}^{cu} \sim (x' - iy')/\sqrt{2}, \tag{2b}$$

$$\Lambda_6^{cl} \sim s, \tag{2c}$$

the three-band Hamiltonian matrix in atomic units ($\hbar = m_e = a_B = 1$) is

$$\begin{pmatrix} E_1 + \dfrac{k^2}{2} & \dfrac{kP}{\sqrt{2}}\, e^{i\theta} & \dfrac{kP}{\sqrt{2}}\, e^{-i\theta} \\ \dfrac{kP}{\sqrt{2}}\, e^{-i\theta} & \dfrac{k^2}{2}\left[1 - \dfrac{4Q^2}{3\Delta E_1'(k)}\right] & -ik\Pi_v\, e^{i\theta} \\ \dfrac{kP}{\sqrt{2}}\, e^{i\theta} & ik\Pi_v\, e^{-i\theta} & -\Delta_1 + \dfrac{k^2}{2}\left[1 - \dfrac{4Q^2}{3\Delta E_2'(k)}\right] \end{pmatrix} \tag{3}$$

where E_1 is the Λ_6^v–Λ_6^{cl} separation at $k = 0$, and

$$P = \langle x^v | p_x | s \rangle, \tag{4a}$$

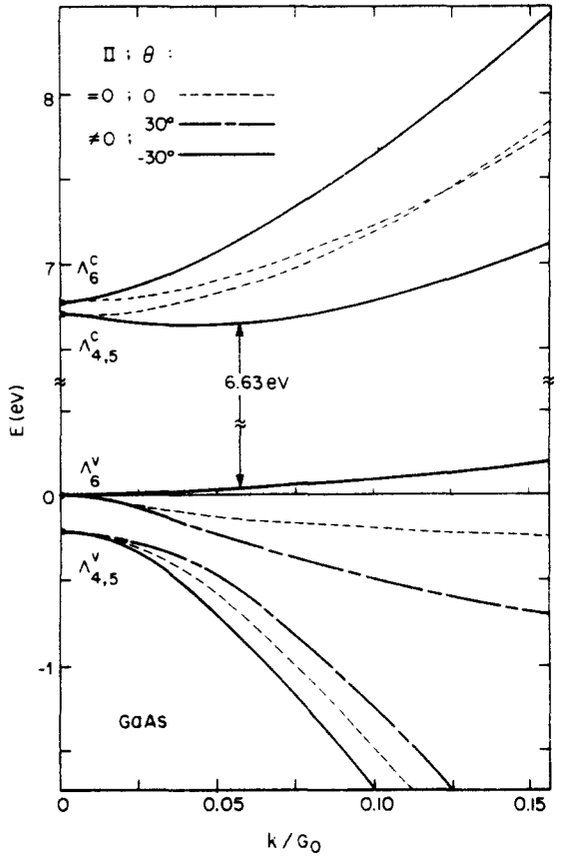

Fig. 1. Calculated band structure perpendicular to the [111] symmetry axis without (----) and with (——) k-linear coupling effects included. Values of parameters are given in the text. The absolute minimum of the interband energy, which occurs at 0.057 G_0 in a direction toward a nearest cube edge, is shown.

$$Q = \langle x^v | p_y | z^{cu} \rangle, \tag{4b}$$

$$\Pi_v = \langle x'^v | p_{x'} | y'^v \rangle, \tag{4c}$$

$$\Delta E_1'(k) = E_{4,5}^{cu}(k) - E_6^v(k), \tag{4d}$$

$$\Delta E_2'(k) = E_6^{cu}(k) - E_{4,5}^v(k). \tag{4e}$$

The two-band Hamiltonian matrix for Λ^{cu} is

$$\begin{pmatrix} E_1' + \Delta_1' + \dfrac{k^2}{2}\left[1 + \dfrac{4Q^2}{3\Delta E_2'(k)}\right] & ik\Pi_c\, e^{i\theta} \\ -ik\Pi_c\, e^{-i\theta} & E_1' + \dfrac{k^2}{2}\left[1 + \dfrac{4Q^2}{3\Delta E_1'(k)}\right] \end{pmatrix} \tag{5}$$

where E_1' is the Λ_6^v–$\Lambda_{4,5}^{cu}$ separation at $k = 0$ and Π_c is defined as Π_v but using conduction band states.

The solutions of equations (3) and (5) are shown in Fig. 1 for $\Pi_v = \Pi_c = 0$, and for $\Pi_v = 0.16\hbar G_0$, $\Pi_c = -0.23\hbar G_0$ for the two extremal directions normal to the ⟨111⟩ axes: $\theta = -30° \pm n \cdot 120°$, toward a nearest cube edge, and $\theta = +30° \pm n \cdot 120°$, away from a nearest cube edge. The nonzero values of Π_v and Π_c

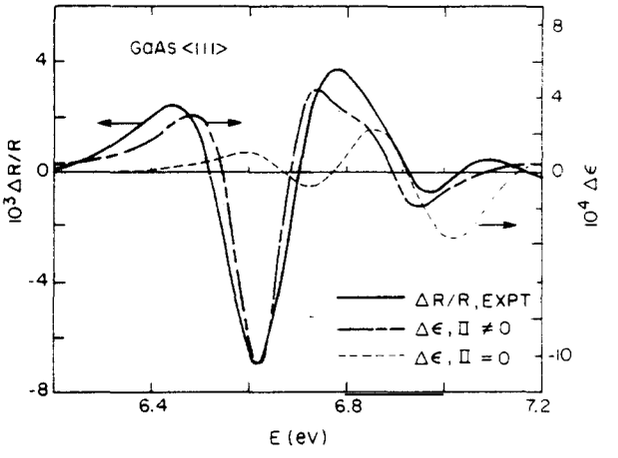

Fig. 2. Calculated $\Delta\epsilon$ lineshapes with and without k-linear coupling, compared to experimental $\Delta R/R$ spectrum.

are $\mathbf{k} \cdot \mathbf{p}$ averages over the active 80% of the ⟨111⟩ axes. Other parameters were taken from the literature with the exception of E_1', which was adjusted to fit ER spectra as will be discussed.

The effect of Π_c in the two-band Hamiltonian is to cause $\Lambda_{4,5}^{cu}$ and Λ_6^{cu} to repel each other for increasing k. For $\Lambda_{4,5}^{cu}$ the effect is finally overcome near $k = 0.057\hbar G_0$ by the free electron term and the interaction with Λ_6^v. These bands are essentially independent of θ.

For $\Lambda_{4,5}^v$ and Λ_6^v, the situation is similar for small k, but quite different for large k owing to the strong coupling to Λ_6^{cl}. Here, a finite Π_v in the three-band Hamiltonian generates via Λ_6^{cl} a threefold rotationally symmetric distortion of the valence bands whose strength is proportional to $k^3\Pi_v P^2$. Maximum and minimum spreading of the valence bands occurs at $\theta = -30° \pm n \cdot 120°$ and $+30° \pm n \cdot 120°$, respectively. For $\theta = -30°$ the Λ_6^v band is forced up sufficiently so that the absolute interband minimum with $\Lambda_{4,5}^{cu}$ is pushed off the symmetry axis, forming a triplet of critical points at $k = 0.057G_0$ with an interband energy 80 meV less that that at $k = 0$. The appearance of this triplet and suppression of the interband minimum greatly increases the oscillator strength of E_1' relative to $E_1' + \Delta_1'$ and increases Δ_1' above Δ_1^c, in accordance with experiment.

2. ELECTROREFLECTANCE SPECTRUM

To compare theory to experiment [3] we calculate the E_1' and $E_1' + \Delta_1'$ electroreflectance (ER) lineshapes using the five-band model. Because the complete Franz–Keldysh calculation for nonparabolic bands requires multiple integrations [16], we use a low-field locally parabolic approximation where the interband reduced mass in the field direction is evaluated at each point k by

the definition $\mu_T^{-1}(k) = \hbar^{-2}\, d^2E_{cv}(k)/dk^2$. We assume cylindrical symmetry (infinite longitudinal mass) for an active region comprising 80% of the ⟨111⟩ axes. The radial variation is taken to be that for $\theta = -30°$, which somewhat overemphasizes the k-linear effects but greatly simplifies the calculation.

With these approximations the low-field expression for the $\Lambda_{4,5}^v - \Lambda_{4,5}^{cl}$ and $\Lambda_6^v - \Lambda_6^{cu}$ transitions becomes

$$\Delta\epsilon = \frac{1024\sqrt{3}\hbar^2Q^2\Omega^2(Ry)^2(e^2\mathcal{E}^2a_B^2)}{405(a_0/a_B)E^2} \times \int \frac{k\,dk}{\mu_T(k)[E - E_{cv}(k) + i\Gamma]^4} \quad (6)$$

where $Ry = 13.6\,\text{eV}$, $\Omega = \hbar^2G_0^2/(2m_e)$, a_0 is the lattice constant, and Γ is the phenomenological broadening parameter. The expression for the transitions $\Lambda_{4,5}^v - \Lambda_6^{cu}$ and $\Lambda_6^v - \Lambda_{4,5}^{cu}$ is 5/4 larger owing to matrix element and field direction effects (a [111] field is assumed throughout).

The ER lineshape calculated for $\Gamma = 0.16\,\text{eV}$, $\epsilon = 100\,\text{kV cm}^{-1}$, and $E_1' = 6.71\,\text{eV}$, and properly weighting the four contributions, is shown in Fig. 2 with the experimental spectrum $\Delta R/R$. To obtain this fit the threshold energy E_1' at $k = 0$ was adjusted to 6.71 eV, and the normalized linear combination $\Delta\epsilon = 0.78(\Delta\epsilon_2 - 0.80\Delta\epsilon_1)$ was constructed to reproduce the $\Delta R/R$ asymmetry. Also shown is the curve calculated with the same parameters but with $\Pi_v = \Pi_c = 0$. It is clear that the k-linear effects are substantial and explain almost completely the lineshape differences between experiment and the simple theory. In particular, the enhancement of E_1' relative to $E_1' + \Delta_1'$ and the anomalously large value of Δ_1' follow directly.

Using literature values [17] of n and k for GaAs at 6.7 eV we estimate in the linear approximation that for bare GaAs

$$\Delta R/R \cong -0.13\Delta\epsilon_1 + 0.00\Delta\epsilon_2 \quad (7)$$

which differs in phase by about 50° from the normalized linear combination in Fig. 2. The phase discrepancy is similar to, but less than, that found in a previous lineshape comparison for Ge [2], and is in the direction predicted by the contact exciton approximation to describe the effect of the electron–hole Coulomb interaction in modulation spectra [18]. Amplitudes can be compared by using the fact that $\Delta R/R$ was measured at $\mathcal{E} \cong 700\,\text{kV cm}^{-1}$. From equations (6) and (7) and Fig. 2, we calculate the negative peak amplitude of $\Delta R/R$ to be 0.006, in good agreement with experiment. Thus a quantitative description is obtained.

The enhancement of E_1' relative to $E_1' + \Delta_1'$ is also seen in GaP where Δ_1^v and Δ_1^c are much less than for GaAs. The actual $k = 0$ thresholds of Λ^{cu} for GaP will also be underestimated if calculated directly from experiment. The difference for GaP should also be of the order of 80 meV as for GaAs. It is presumably less for α–Sn and the III-Sb compounds where the spin–orbit splitting is much larger. A more complete discussion will be given elsewhere.

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