Reflectivity and $(dR/dE)/R$ of GaP between 2.5 and 6.0 eV

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The reflectivity and logarithmic derivative of the reflectivity of GaP at $T=2$ and 300 K are reported. A Δ_0 spin-orbit splitting of 80 ± 1 meV is obtained, in agreement with earlier transmission data. The E_1, $E_1+\Delta_1$ splitting is resolved and the value $\Delta_1=50\pm5$ meV is found. Reflectivity structures not observed previously have been seen between 4.5 and 6.0 eV.

INTRODUCTION

We report the reflectivity and logarithmic derivative of the reflectivity of GaP at $T=2$ and 300 K. These data, obtained with a sensitive double-beam spectrophotometer, provide a considerable improvement in sensitivity over the most recent measurement of the GaP reflectivity made by Ehrenreich *et al.*[1] in 1962. Structure in the reflectance is emphasized in the derivative function $(dR/dE)/R$ which is calculated (with a digital computer) directly from the reflectance data. These logarithmic-derivative data can be compared directly with earlier modulation spectroscopy results, such as electroreflectance,[2,3] thermoreflectance,[4] and wavelength modulation.[5] One of the main results of the present work is the determination of the E_1, $E_1+\Delta_1$ spin-orbit splitting which was not unambiguously determined by earlier work.

EXPERIMENTAL DETAILS

The GaP samples used in these experiments were grown by the Czochralski method. They were sliced parallel to a {111} face with a diamond wheel. A weak (~0.2%) bromine-methanol solution was then used as a polishing etch. The prepared surfaces were smooth, quite free of etch pits, and exhibited very little nonspecular reflection. Furthermore, the fact that the E_0 reflectance structure is as sharp as that observed (in transmission) by Dean *et al.*[6] for as-grown thin needles indicates that our surfaces were also relatively free of surface damage. The samples were approximately 1- mm thick; therefore, reflection from the back surface was not a problem for energies above 2.4 eV. The reflectance measurements were made with a sensitive double-beam spectrophotometer described previously.[7]

The absolute-reflectance values are accurate to within ±3% of the reflectivity, the greatest uncertainty being due to the spatial inhomogeneity of the cathode surface of the photomultiplier. The sensitivity of the spectrophotometer was such that the observed noise level in the logarithmic derivative at 3.8 eV was 0.02 eV^{-1} with a resolution of 1.6 Å. This noise level was determined by the shot noise in the optical signal. The light beam was within 8 deg of normal incidence.

RESULTS

The reflectivity data at 2 and 300 K are shown in Fig. 1. Our values are about 10% higher than those of Ehrenreich *et al.*[1] Our measured reflectivity at 2.4 and 2.62 eV agrees (within 1%) with that calcu-

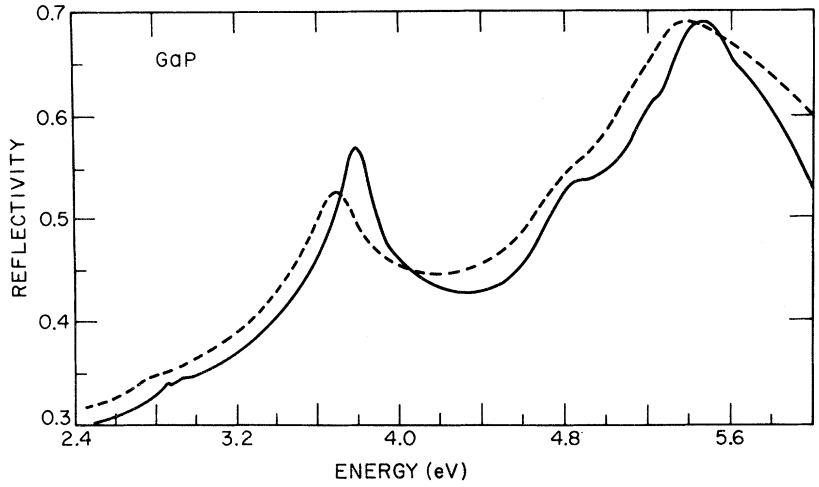

FIG. 1. Reflectivity of GaP at 300 K (dashed line) and 2 K (solid line).

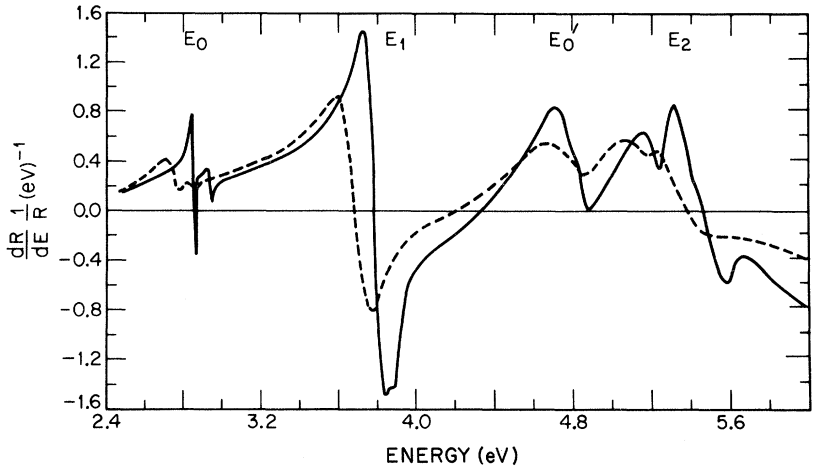

FIG. 2. Logarithmic derivative of the reflectivity at 300 K (dashed line) and 2 K (solid line).

lated from the index of refraction as measured by Folberth and Oswald[8] and by Dean *et al.*[6] There is a general shift of the spectrum to higher energy by 0.09 eV in going from 300 to 2 K.

The logarithmic-derivative data $(dR/dE)/R$, computed from the data in Fig. 1 by numerical differentiation with a digital computer, is shown in Fig. 2. The structures are labeled according to the common notation. The derivative data can be directly compared with that obtained by Braunstein and Welkowsky[5] using the wavelength modulation technique. The two types of data agree except that we are able to observe the spin-orbit splitting of the E_1 peak. We have also extended the measurements to 6 eV. A theoretical calculation of the logarithmic derivative by Walter and Cohen[9] using the empirical pseudopotential method agrees reasonably well with our results except that the experimental E_1 peak is enhanced in magnitude by Coulomb effects. The energies at which structure occurs are listed in Table I. Except for the E_0 transitions, the energy of the reflectivity peaks is given. For E_0 and $E_0+\Delta_0$ the energies are taken at the maximum negative slope in the reflectivity, which corresponds to the peaks in the absorption coefficient. We shall discuss each region in turn.

The E_0 and $E_0+\Delta_0$ structures shown in Fig. 3 are due to transitions from Γ_8^v to Γ_6^c and from Γ_7^v to Γ_6^c, respectively. (For a good diagram of the band structure see Ref. 10.) The spin-orbit splitting is 80 ± 1 meV at both 300 and 2 K. This agrees with the 78 ± 2-meV value obtained by Sell and Lawaetz's[11] analysis of the absorption data of Dean *et al.*[6]

We have calculated a reflectivity curve for E_0 using the parameters (11 meV for the exciton binding energy and 6 meV for the half-width at half-maximum) that were obtained[11] from a fit to the absorption data of Dean *et al.*[6] The calculated reflectivity curve has a stronger-positive peak and a weaker-negative peak than the observed structure. The amplitude of the structure is also a factor of 2 higher in the calculated curve, although the width in reflectivity is identical to that obtained from the absorption data. One likely explanation for these differences is the presence of exciton spatial dispersion[12] effects. As can be seen in Ref. 12, spatial dispersion effects decrease the positive peak, increase the negative peak, and decrease the amplitude of the structure, which is apparently what we are seeing.

The E_1 and $E_1+\Delta_1$ reflectivity structures in the zinc-blende materials are due to transitions from the spin-orbit-split valence band to the lowest conduction band along the Λ direction. The spin-orbit splitting of E_1 is visible in the logarithmic-derivative curve shown in Fig. 4. The two negative peaks in the derivative curve are separated by 40 meV. However, since the width of the structure is comparable to the separation of the peaks, the peaks tend to be "pulled" together, and the observed splitting is less than the true Δ_1. By taking the

TABLE I. Energies (eV) of structure in the reflectivity of GaP.

	300 K	2 K
E_0	2.780 ± 0.002	$2.869^a\pm0.001$
$E_0+\Delta_0$	2.860 ± 0.002	2.949 ± 0.001
E_1	3.693 ± 0.002	3.785 ± 0.005
$E_1+\Delta_1$		3.835 ± 0.005
E_0'	4.77 ± 0.01	4.77 ± 0.01
		4.85 ± 0.01
E_2	5.12 ± 0.01	5.21 ± 0.01
	5.34 ± 0.02	5.36 ± 0.01
		5.50 ± 0.02

[a]We find that there is a 4-meV unexplained discrepancy in the exciton energy as obtained from our reflectivity results and that from the absorption curves of Dean, Kaminsky, and Zetterstrom (Ref. 6).

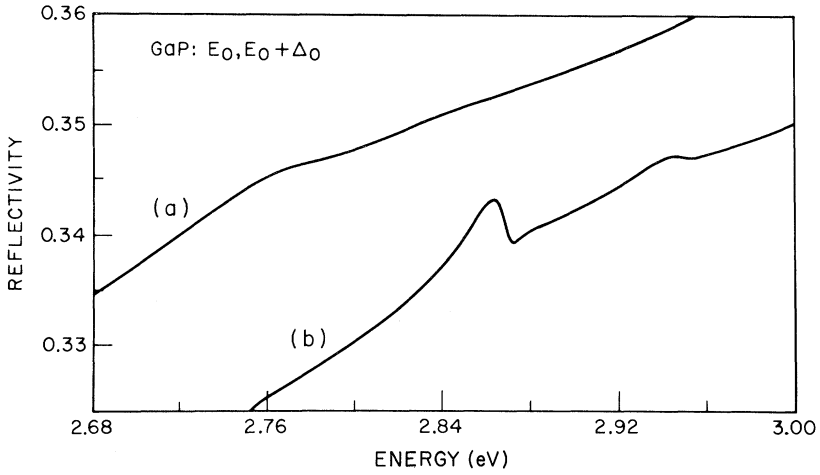

FIG. 3. E_0 and $E_0+\Delta_0$ direct-gap reflectivity structures at (a) 300 K and (b) 2 K.

second derivative of the reflectivity, we are able to determine that the Δ_1 spin-orbit splitting is 50 ±5 meV. The only reported data which show the splitting of E_1 are the electroreflectance results[2,3] in which a value of 0.11 eV was obtained. However, due to the difficulty in interpreting electroreflectance structures, especially when two transitions overlap, those results were somewhat preliminary.

According to the "two-thirds rule," $\Delta_1 \simeq \frac{2}{3}\Delta_0$. It is expected to be satisfied for GaP, and our results indicate that this is the case. A recent calculation by Wepfer *et al.*[13] of the spin-orbit splittings in GaP, along with other III-V compounds, gives the values $\Delta_0 = 0.09$ eV and $\Delta_1 = 0.06$ eV, in agreement with our experimental values.

There are two reflectivity peaks split by ~0.08 eV in the E_0' region. Others [3,5] using modulation techniques have given this splitting as 0.06 eV. Various band calculations have associated the E_0' structure with Γ_{15}^v-to-Γ_{15}^c transitions, or with transitions from Δ_3^v, Δ_4^v to Δ_1^c either near Γ or from an extended region along the Δ symmetry line. The 80-meV splitting does suggest that we may be seeing the Γ_7^v-to-Γ_8^c and Γ_8^v-toΓ_8^c transitions. However, the Γ_8^v-toΓ_7^c transition should also be seen, in this case, at about 4.59 eV if $\Delta_{15} = 0.18$ eV as calculated by Wepfer *et al.*[13] (The Γ_7^v-to-Γ_7^c transition is forbidden.) On the other hand, if the transitions originate along Δ_3^v and Δ_4^v, band calculations indicate that the splitting of the Δ valence bands should be considerably smaller than 80 meV obtained at Γ. The E_0' structure can be followed through the Ga (As, P) alloy system[14,15] and appears at 4.4 eV in GaAs. Photoemission results on GaAs[16] place the Γ_{15}^v-Γ_{15}^c energy at 4.5±0.3 eV, which, therefore, does not rule out the possibility that the E_0' structures are due to Γ_{15}^v-Γ_{15}^c transitions. Walter and Cohen[9] find theoretically that the reflectivity struc-

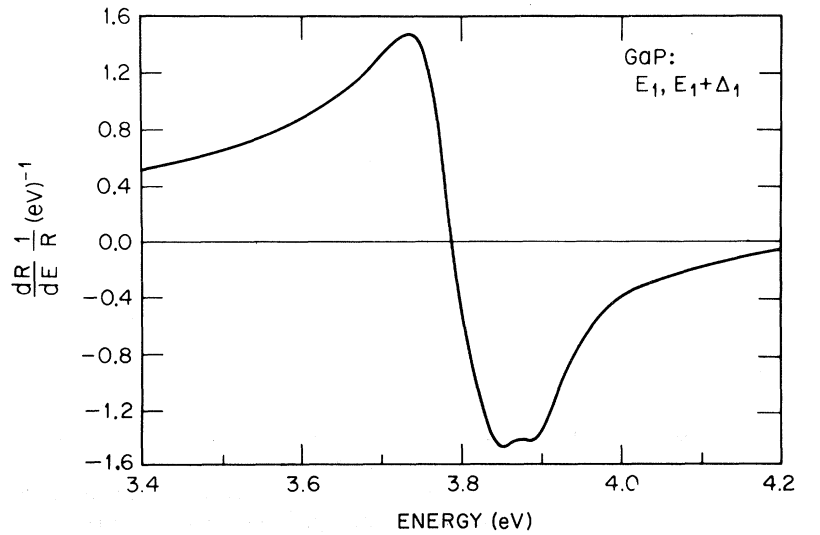

FIG. 4. Logarithmic derivative of the E_1 reflectivity peak at 2 K, showing the spin-orbit splitting.

ture due to the Γ_{15}^v-Γ_{15}^c transitions is much smaller than the observed E_0' structure, although Coulomb effects, which they did not consider, could enhance the structure. In the E_0' region of Ge[17,18] and GaSb,[19] $\Gamma_{15}^v \rightarrow \Gamma_{15}^c$ transitions have been identified. In Ge[18] these Γ transitions are superimposed upon a broad structure which could arise from Δ transitions. These results suggest a similar behavior for GaP; however, the available data do not allow an unambiguous identification.

In the E_2 region we find at least three transitions, of which only one (5.27 eV) is seen in the electroreflectance spectrum at room temperature. The transitions which may give rise to these structures include $X_5 \rightarrow X_1$, $X_5 \rightarrow X_3$, $\Delta_5 \rightarrow \Delta_1$, and $\Sigma_2 \rightarrow \Sigma_1$. However, no definite assignment will be attempted here.

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Singularities of One- and Two-Dimensional Origin in Three-Dimensional Lattice Spectra*

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Recently a new type of singularity has been discovered in the spectrum of an fcc lattice problem with second-neighbor interactions. Arising as a consequence of a surface of analytic critical points, it does not fit into van Hove's classification of the isolated variety. A simple modification of his scheme accommodates this case and predicts further singularities, characteristic of one- and two-dimensional lattices, in three-dimensional model problems. Implications for real materials are discussed.

In a classic paper van Hove[1] has classified the isolated analytic critical points (cp), zeros of the group velocity $\nabla_{\vec{k}}\epsilon_{\vec{k}}$, of a general lattice spectrum and also analyzed their contributions to the singularities in the spectral density (or density of states). The rationale for only studying isolated cp was that other forms of cp would only result from special relationships between force constants that could not be realized in real materials.[1] However, such special relationships are well known in the spectra of some basic model systems: for a long time in the nearest-neighbor bcc tight-binding dispersion function,[2] and more recently in the corresponding fcc problem.[3] In the latter case a line of cp (one-dimensional manifold) occur along the edge XW[4] of the irreducible portion of the Brillouin zone. Of course pure nearest-neighbor cases will not occur in real systems because there will