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FUNDAMENTAL REFLECTIVITY OF GaAs AT LOW TEMPERATURE

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Recent work¹ has shown that the main ultra-violet reflectivity peak in C, Si, and Ge is due to transitions at or near the X point of the Brillouin zone (zone edge, $\langle 100 \rangle$ direction). The double degeneracy of the conduction band at X is removed for crystals without inversion symmetry and thus this peak should split for group III-V semiconductors. Using low-temperature (80°K) reflectivity measurements on etched single crystals, we have observed this splitting in GaAs, GaSb, InAs, and InSb. No splitting is observed in either Si or Ge. These results confirm the assignment of the main reflectivity peak in zincblende semiconductors to X transitions. The use of low temperatures, in addition to sharpening the main reflectivity peaks considerably, has revealed weak structure in all the materials studied. The general systematics of the band structure of diamond and zincblende crystals¹⁻⁴ make it possible to give reasonable assignments to nearly all of the new experimental peaks. The experimental curve for GaAs is shown in Fig. 1, and the results for the four materials are summarized in Table I.

Phillips, Ehrenreich, and Philipp¹ have given a tentative value of 0.9 eV for the X_1-X_3 gap in

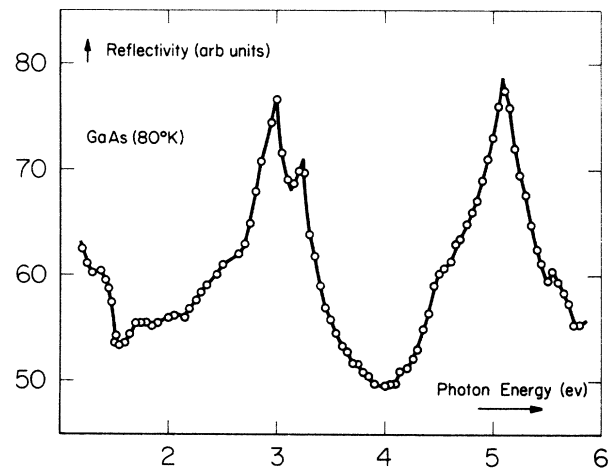


FIG. 1. Reflectivity of etched GaAs at 80°K.

GaAs. However Paul has shown⁵ that this splitting should be small (<0.3 eV). The value of 0.43 eV from Fig. 1 is in better agreement with this estimate. Also, the splitting for ZnSe should be double this value, and Aven, Marple, and Segall⁶ have obtained a room-temperature reflectivity curve for ZnSe which clearly shows a splitting of 0.9 eV. The 8.5-eV peak in ZnSe

Table I. Experimental reflectivity peaks in GaAs, GaSb, InAs, and InSb at 80°K between 1.2 and 6.0 eV.

	$L_{3'} - L_1$	$\Gamma_{25'} - \Gamma_{15}$	$X_5 - X_1$	$X_5 - X_3$	$X_1 - X_3$	Other peaks
GaAs	2.99 3.23	4.2? 4.52	5.12	5.55	0.43	1.4, 1.75 = $(\Gamma_{25'} - \Gamma_2')$ 2.3, 2.6 = $(L_{3'} - L_1)$?
GaSb	2.08 2.55	3.74	4.33	4.70	0.37	5.7 = $(L_{3'} - L_3)$ 1.4, 1.9 = $(L_{3'} - L_1)$?
InAs	2.57 2.85	4.63	4.83	5.30	0.47	2.2, 2.45 = $(L_{3'} - L_1)$?
InSb	1.87 2.45	2.8? 3.45	4.20	4.70	0.50	5.4 = $(L_{3'} - L_3)$

attributed in reference 1 to X_5-X_3 transitions is more reasonably assigned to the low-energy peak of the $L_3'-L_3$ transitions. The 4.52-eV peak in GaAs is ascribed to $\Gamma_{25}'-\Gamma_{15}$ transitions and agrees well with a calculated value of 4.5 eV.⁷ This peak is visible at room temperature in InSb (3.4 eV) and has previously been identified.¹ It is therefore reasonable to assign the corresponding peaks in InAs and GaSb to these transitions. The Γ_{25}' valence band in GaAs should have a splitting of 0.33 eV due to spin orbit interaction and it is possible that structure at 4.2 eV in Fig. 1 is associated with this mechanism. There is further evidence of this splitting from the peaks at 1.75 eV and 1.4 eV; the latter peak corresponds to the direct gap for GaAs. These two peaks can thus be assigned to $\Gamma_{25}'-\Gamma_{2}'$ transitions. The cause of the rise in reflectivity at energies less than 1.5 eV is not clear, as the carrier concentration of the specimen ($6 \times 10^{17}/\text{cc}$) is not sufficient to cause appreciable free carrier reflectivity at these energies. All previous work has associated the low-energy doublet (3.02 and 3.23 eV in GaAs at 80°K) with $L_3'-L_1$ transitions split by spin-orbit interaction of the valence band. Recent band structure calculations on germanium by Brust, Phillips, and Bassani⁸ have shown the possibility that this peak in Ge is caused by $\Lambda_3-\Lambda_1$ transitions at the (0.17, 0.17, 0.17) point of the Brillouin zone. According to the critical point theory,⁹ reflectivity edges can occur wherever the condition

$$\nabla_k (E_k^c - E_k^v) = 0$$

is satisfied. Normally this occurs at zone edges when the gradients of the bands are zero, but

the condition is also satisfied when both valence and conduction bands have the same gradient. The treatment of Brust *et al.* predicts that for Ge the reflectivity edges due to $L_3'-L_1$ transitions occur at slightly lower energies than $\Lambda_3-\Lambda_1$ and are much weaker. The general systematics indicate that the interpretation might also hold for GaAs. If this is true then the 3.0- and 3.2-eV peaks are due to $\Lambda_3-\Lambda_1$ transitions; the $L_3'-L_1$ transition should be responsible for the weak structure with thresholds near 2.2 and 2.5 eV. Approximately the same value of the spin-orbit splitting is observed for both $\Lambda_3-\Lambda_1$ and $L_3'-L_1$ transitions, which occur at quite different points in the Brillouin zone. This is in agreement with the germanium calculations of Kane¹⁰ which show that the spin-orbit splitting (Δ_0) of the valence band at Γ reaches the L -point value of $\frac{2}{3}\Delta_0$ very near to the center of the Brillouin zone.

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ENERGY MIGRATION AND TRANSFER IN SOLID ARGON AND KRYPTON AT LOW TEMPERATURES*

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In the study of free radicals produced by γ irradiation of various substances trapped in an argon matrix at 4.2°K, we made the surprising observation that strong electron spin resonances (ESR) of H atoms and CH_3 radicals were produced from impurity concentrations of less than one part in 10^4 of CH_4 in the matrix with a moderate γ -ray dosage of 10^5 r. The same amount of CH_4 in the pure form, given the same dosage at 4.2°K, would not give a

detectable signal with our spectrometer. It seems evident that a large portion of the γ -ray energy impinging on the argon matrix was being transferred to, and absorbed by, the slight CH_4 impurity. We found a similar effect for small concentrations of CH_4 in a krypton matrix. Because all samples of highest purity of argon which we could obtain had slight CH_4 impurity which gave H and CH_3 signals upon γ irradiation, we resorted to the