Spectral Analysis of Photoemissive Yields in GaAs and Related Crystals*

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The strongest optical reflectivity peak at 5 eV in GaAs and the corresponding dip at 5 eV in the photoemissive-yield curve have long been associated with $X_{5v} \rightarrow X_{1c}$ transitions. Since recent experimental and theoretical studies indicate that $X_{1c}-X_{5v}=4.2\pm0.1$ eV, this association is invalid. Accordingly, most of the earlier estimates of $X_{1c}-X_{5v}$ and $X_{3c}-X_{5v}$ in GaAs and related crystals will have to be revised, as will empirical band models based on these estimates. An improved energy-band model for GaAs is reported.

MANY authors[1–9] have called attention to the fact that the principal dip[10] in the photoemissive-yield curve for such crystals as Si, Ge, and GaAs occurs at nearly the same energy as does the main peak in the reflectivity spectrum (or ϵ_2). This correlation has been used to justify the assignment of energies to the $X_4 \rightarrow X_1$ transitions in Si and Ge, and to the $X_{5v} \rightarrow X_{1c}$ transitions in GaAs, and several other III-V compounds.[1–9] These energy assignments play an important role in the construction of empirical energy-band models.

On the basis of our own recent experimental[11] and theoretical[12] studies of the band- structure of GaAs and related crystals, we have been able to construct rather accurate energy-band models for these crystals. With these models in hand, we have been able to examine the significance of the correlation noted above and its relationship to $X_{5v} \rightarrow X_{1c}$ and $X_{5v} \rightarrow X_{3c}$ transition energies.

In a recent paper,[11] the following experimental results are cited for GaAs: $L_{1c}-X_{1c}=0.09\pm0.02$ eV, and $X_{3c}-X_{1c}=0.58\pm0.04$ eV. One of us[12] has recently reported empirically adjusted orthogonal-plane-wave (OPW) energy-band calculations for GaP, GaAs, and GaSb, which take these and other recent experimental results into account. Our results for GaAs are sum-

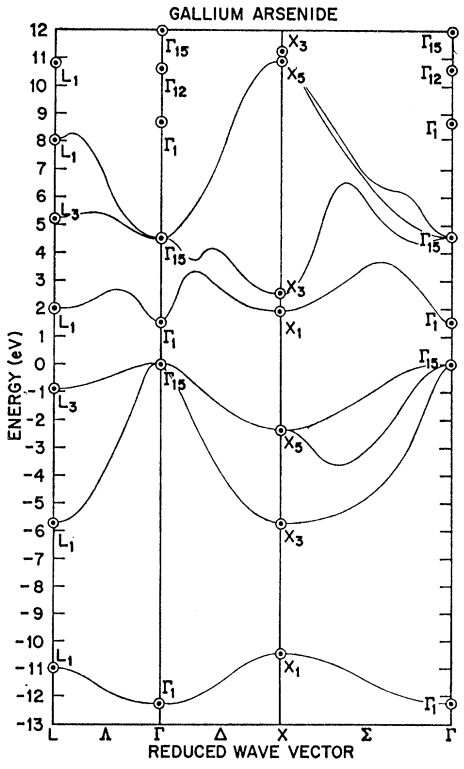

FIG. 1. Energy-band structure of GaAs (with spin-orbit splitting neglected). The circled dots correspond to the entries in Table I, column 6. The curves were drawn in freehand, with previous solutions for GaAs (Ref. 5) and Ge (Refs. 12 and 14) serving as a guide.

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[1] W. E. Spicer and R. E. Simon, Phys. Rev. Letters **9**, 385 (1962), Si.
[2] D. Brust, M. L. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962), Si.
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[5] T. E. Fischer, Phys. Rev. **139**, A1228 (1965), AlSb.
[6] T. E. Fischer, Phys. Rev. **142**, 519 (1966), InP.
[7] F. G. Allen and G. W. Gobeli, Phys. Rev. **144**, 558 (1966), Si and Ge.
[8] T. E. Fischer, Phys. Rev. **147**, 603 (1966), GaP.
[9] T. E. Fischer, F. G. Allen, and G. W. Gobeli, Phys. Rev. **163**, 703 (1967), InAs.
[10] This dip is usually attributed to the fact that the photoexcited electrons end up in final states which have a low escape probability, that is to say, the final states lie close to or below the vacuum level at all work functions.
[11] L. W. James, R. C. Eden, J. L. Moll, and W. E. Spicer, Phys. Rev. **174**, 909 (1968).
[12] F. Herman, R. L. Kortum, C. D. Kuglin, J. P. Van Dyke, and S. Skillman, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic Press Inc., New York, to be published in 1968), Vol. 8. This article also contains empirically adjusted OPW energy-band models for GaP and GaSb as well as improved pseudopotential energy band models for GaP, GaAs, and GaSb.

TABLE I. Energy-band structure of GaAs.[a]

Level	Slater exchange Trial	Slater exchange Pert	Kohn-Sham exchange Trial	Kohn-Sham exchange Pert	Present model Pert	Experiment E^*(Expt)	Cohen and Bergstresser Estim	Cohen and Bergstresser Calc
1	2	3	4	5	6	7	8	9
Γ_{15c}	13.37	12.06	12.24	12.11	12.1			
Γ_{12c}	10.97	10.55	10.43	10.58	10.6			
Γ_{1c}	9.33	9.40	8.32	8.67	9.0	9.1±0.2[b]		(8.1)
Γ_{15c}	4.70	4.70	4.23	4.54	4.6	4.9±0.1[b]	4.6	4.55
Γ_{1c}	1.44	1.54*	1.65	1.54*	1.54*	1.54[c]	1.5	1.45
Γ_{15v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_{1v}	−11.93	−12.46	−12.01	−12.35	−12.4			
X_{5c}	10.82	10.93	10.74	10.94	10.9			
X_{3c}	2.77	2.54	2.22	2.53	2.5	X_{1c}+0.6[d]	2.3	2.1
X_{1c}	2.89	1.90*	2.03	1.90*	1.90*	Γ_{1c}+0.36[e]	1.9	1.8
X_{5v}	−2.08	−2.21	−2.34	−2.31	−2.3	−2.4±0.1[b]	−2.7	−2.2
X_{3v}	−6.00	−5.35	−6.26	−5.64	−5.5			
X_{1v}	−9.91	−10.82	−9.73	−10.53	−10.7			
$X_{3c}-X_{5v}$	4.85	4.75	4.56	4.84	4.8		5.0	4.3
$X_{1c}-X_{5v}$	4.97	4.11	4.37	4.21	4.2		4.6	4.0
L_{1c}	9.38	8.13	8.39	8.15	8.1			
L_{3c}	5.69	5.39	5.12	5.30	5.3	5.2±0.1[b]		5.1
L_{1c}	2.06	2.00*	1.80	2.00*	2.00*	X_{1c}+0.1[d]		1.7
L_{3v}	−0.85	−0.84	−0.95	−0.91	−0.9	−1.0±0.1[b]		−0.9
L_{1v}	−5.72	−5.51	−6.07	−5.76	−5.6			
L_{1v}	−10.52	−11.24	−10.43	−11.02	−11.1			
$L_{3c}-L_{3v}$	6.54	6.23	6.07	6.21	6.2		6.4	6.0
$L_{1c}-L_{3v}$	2.91	2.84	2.75	2.91	2.9		2.5	2.6

[a] The entries in columns 2 through 6 are based on empirically adjusted OPW energy band calculations (Ref. 12). Theoretical levels that have been deliberately adjusted to experiment are denoted by an asterisk. Our "best" solution is listed in column 6. Spin-orbit split levels are everywhere represented by their weighted means. The entries in columns 8 and 9 are based on Ref. 15. All entries are in eV.

[b] R. C. Eden, Ph.D. thesis, Stanford University, 1967 (unpublished), available through University Microfilms Library Service, Xerox Corp., Ann Arbor, Michigan 48106, as Item 67-17415 R. C. Eden; see also W. E. Spicer and R. C. Eden, in Proceedings of the International Conference on the Physics of Semiconductors, Moscow, July, 1968 (to be published).

[c] Reference 19.

[d] L. W. James, Ph.D. thesis, Stanford University, 1968 (unpublished), available through University Microfilms Library Service, Xerox Corp., Ann Arbor, Michigan 48106; see also Ref. 11 and the article by Spicer and Eden cited in Ref. b above. The actual experimental values are: $X_{3c}-X_{1c}=0.58\pm0.04$ eV and $L_{1c}-X_{1c}=0.09\pm0.02$ eV.

[e] A. R. Hutson, A. Jayaraman, and A. S. Coriell, Phys. Rev. **155**, 786 (1967). According to Jayaraman (private communication), a refined experimental value for $X_{1c}-\Gamma_{1c}$ at room temperature is 0.38 eV.

marized in Table I and are sketched in Fig. 1. In Table I, the results of first-principles OPW band-calculations, based on the Slater and Kohn-Sham free-electron exchange approximations, are listed in columns 2 and 4; and the corresponding empirically adjusted solutions are listed in columns 3 and 5. The same three-parameter adjustment scheme that was previously used in studies of CdTe [13] and other II-VI compounds[14] is employed here. Energy levels that have been deliberately adjusted to experiment are denoted in Table I by an asterisk. Even though corresponding entries in columns 2 and 4 sometimes differ by as much as 1 eV, the differences between columns 3 and 5 are 0.1 eV or less for most of the energy levels of primary interest. Our "best" solution, which takes all the information in columns 2 through 5 into account, is listed in column 6. Earlier experimental estimates due to Cohen and Bergstresser[15] are given in column 8, and the results of their empirical pseudopotential energy-band calculations are shown in column 9. Subsequent optical-spectrum calculations by Saslow *et al.*[15] suggest that some of the entries in

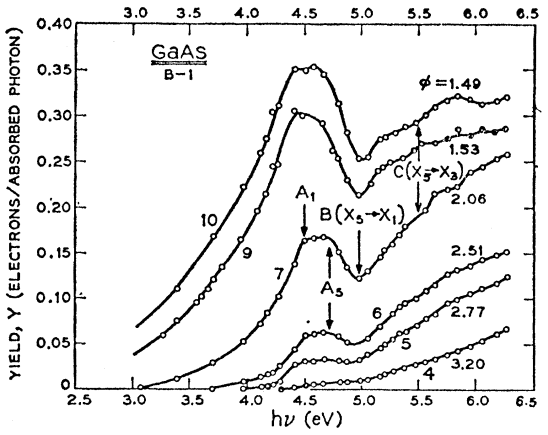

FIG. 2. Photoemissive yield of GaAs at various Cs coverages, according to the experiments of Gobeli and Allen (M. L. Cohen and J. C. Phillips, Ref. 4).

[13] J. L. Shay, W. E. Spicer, and F. Herman, Phys. Rev. Letters **18**, 559 (1967).

[14] F. Herman, R. L. Kortum, C. D. Kuglin, and J. L. Shay, in *II-VI Semiconducting Compounds, 1967 International Conference*, edited by D. G. Thomas (W. A. Benjamin, Inc., New York, 1967), p. 503.

[15] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

columns 8 and 9 should be brought closer to those in column 6.

According to Table I, $X_{1c}-X_{5v}=4.2$ eV and $X_{3c}-X_{5v}=4.8$ eV, with an uncertainty of the order of 0.1 eV. (Note that our values for X_{1c} and X_{3c} are supported by experiment,[11] while our estimate for X_{5v} is accurate to about 0.1 eV.) It is evident that there is a discrepancy of about 0.8 eV between our value for $X_{1c}-X_{5v}(=4.2$ eV) and the energy value of 5 eV at which the principal dip in the photoemissive-yield curve and the main reflectivity peak occurs. Clearly, the $X_{5v}\rightarrow X_{1c}$ transition energy cannot be determined with any degree of accuracy merely by inspecting[4] the photoemissive-yield curve or the reflectivity spectrum. The same can be said for other transition energies such as $X_{5v}\rightarrow X_{3c}$.

The earlier $X_{5v}\rightarrow X_{1c}$ and $X_{5v}\rightarrow X_{3c}$ assignments[4] for GaAs (cf. Fig. 2) were based on an oversimplified analysis, which does not appear to be valid in the light of subsequent experimental and theoretical studies. Analogous assignments for the $X_{5v}\rightarrow X_{1c}$ and $X_{5v}\rightarrow X_{3c}$ transition energies in other III-V compounds[4–6,8,9] (and for $X_4\rightarrow X_1$ in Si [1–4,7] and Ge [4,7]) are also subject to revision for the same reason.

Recent optical-spectrum calculations[14,16] indicate that the main reflectivity peak in GaAs at 5 eV is due to interband transitions associated with a large region of the reduced zone: The principal contribution to this peak comes from $\Sigma_{2v}\rightarrow\Sigma_{1c}$ and neighboring transitions. Neither $X_{5v}\rightarrow X_{1c}$ nor $X_{5v}\rightarrow X_{3c}$ transitions contribute importantly to the main reflectivity peak. In view of the correlation noted above, it is reasonable to conclude that the dip in the photoemissive-yield curve at 5 eV (cf. Fig. 2) is also due primarily to $\Sigma_{2v}\rightarrow\Sigma_{1c}$ transitions, rather than $X_{5v}\rightarrow X_{1c}$ or $X_{5v}\rightarrow X_{3c}$ transitions.

Thus, while we believe that the main reflectivity peak and the corresponding dip in the photoemissive-yield curve are both due in large measure to the same set of interband electronic transitions, in our view, neither of these spectral features provides an accurate measure of the $X_{5v}\rightarrow X_{1c}$ or $X_{5v}\rightarrow X_{3c}$ transition energies. In several III-V compounds, including GaP, GaAs, GaSb, and InSb, our adjusted OPW band calculations[12] indicate that the $X_{5v}\rightarrow X_{1c}$ transition energy is roughly 0.7 or 0.8 eV less than the main reflectivity peak energy. This is reminiscent of earlier calculations by Kane[17] and by Herman *et al.*,[18] which indicated that in Si and Ge the $X_4\rightarrow X_1$ transition energy is roughly 0.4 or 0.5 eV lower than the main reflectivity peak energy.

In short, it is hazardous to assign energies to interband transitions at X in GaAs and related crystals on the basis of superficial interpretations of photoemissive-yield, reflectivity, or electroreflectivity[19] spectra. The same statement applies to other transitions such as $\Gamma_{15v}\rightarrow\Gamma_{15c}$, which contribute only in a minor way to such spectra. The uncertainty of many of the earlier energy assignments should be borne in mind in future attempts to construct empirical energy-band models on the basis of optical and photoemission spectra. One of the principal advantages of our empirically adjusted OPW energy-band models for GaAs and related crystals[12] is that these involve only three adjustable parameters and only make use of incisive and well-established experimental information.

The authors are grateful to Richard C. Eden and Lawrence W. James for many useful discussions of their photoemission results. The calculations leading to Table I were carried out in collaboration with Richard L. Kortum, Charles D. Kuglin, and John P. Van Dyke.

[16] W. Saslow, T. K. Bergstresser, C. Y. Fong, M. L. Cohen, and D. Brust, Solid State Commun. **5**, 667 (1967).

[17] E. O. Kane, Phys. Rev. **146**, 558 (1966).

[18] F. Herman, R. L. Kortum, C. D. Kuglin, and R. A. Short, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. O. Löwdin (Academic Press Inc., New York, 1966), p. 381.

[19] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967). None of the higher-energy electroreflectivity peaks (at 4.44, 4.63, 4.99, and 5.33 eV) appear to correspond to $X_{5v}\rightarrow X_{1c}$ or $X_{5v}\rightarrow X_{3c}$ transitions, even if we take the 0.08 eV spin-orbit splitting of X_{5v} (see Ref. 12) into account.