[13]K. C. Pandey and J. C. Phillips, Phys. Rev. B 9, 1552 (1974).
[14]J. A. Appelbaum and D. R. Hamann, Phys. Rev. Lett. 32, 225 (1974).
[15]K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 32, 1433 (1974).
[16]W. Gudat, E. E. Koch, P. Y. Yu, M. Cardona, and C. M. Penchina, Phys. Status Solidi (b) 52, 505 (1972).
[17]J. Shaw, unpublished.
[18]D. E. Eastman and J. Freeouf, unpublished.

Electroreflectance of GaP to 27 eV*

D. E. Aspnes
Bell Laboratories, Murray Hill, New Jersey 07974

and

C. G. Olson
Ames Laboratory USAEC and Department of Physics, Iowa State University, Ames, Iowa 50010
(Received 29 October 1974)

We report the first electroreflectance spectra obtained above 7 eV. The large number of new critical points observed includes a group in the energy range above 20 eV which occur between the 3*d* valence bands, derived from the deep-lying Ga 3*d* core levels, and the sp^3 conduction bands. The resolution, currently limited by the monochromator band pass, enables us to resolve directly the 0.50 ± 0.03 eV spin-orbit splitting of the Ga 3*d* core levels for the first time.

We report the first electroreflectance (ER) spectra measured in the energy range above 7 eV. The ER signals are large, of the order of 10^{-3} in the relative reflectance ratio $\Delta R/R$, and show the high resolution and critical-point enhancement characteristic of ER measurements at lower energies[1-3] up to our current measurement limit of 27 eV. In addition to a number of new sp^3 valence-band–conduction-band critical-point features which appear in this energy range, we also observe structure from a new class of critical points: those which occur between flat, deep-lying valence bands derived from atomic core levels (here, the 3*d* levels of Ga) and the sp^3 conduction bands. The monochromator band pass of 150 meV obtained here improves by a factor of 3 to 6 the actual resolution limits attained by alternative spectroscopic techniques, such as absorptance-reflectance spectroscopy,[4,5] or x-ray,[5-8] resonance-lamp,[8,9] or synchrotron[10,11] photoemission, which have also been used to study electronic states in this energy range in semiconductors. For example, the improved resolution enables us to observe directly the spin-orbit splitting $\Delta_{\mathrm{III}d}$ of the Ga 3*d* core states and to obtain a new and reliable value, $\Delta_{\mathrm{III}d} = 0.50 \pm 0.03$ eV, for this quantity.

Measurements were performed using the high-energy photon source of the Synchrotron Radiation Center of the Physical Sciences Laboratory of the University of Wisconsin. Details of the modulation-spectroscopy configuration used in these experiments have been published elsewhere.[12] All data reported herein were obtained on a ⟨111⟩ face of an *n*-type, Te-doped, single-crystal GaP wafer having a carrier concentration of 5×10^{17} cm^{-3}. A standard Schottky-barrier electroreflectance configuration[13] was used, in which the modulating electric field was generated normal to the surface by applying a reverse voltage across the barrier formed by evaporating a semitransparent, 4-nm Ni film on the Syton[14]-polished sample surface, as described previously.[3]

The experimental results are shown in Figs. 1 and 2, which cover the spectral ranges 2.5–14 eV and 14–27 eV, respectively. The structures observed below 6 eV consist of a combination of primary critical-point features and Franz-Keldysh oscillations. Critical-point assignments in this energy range have been given previously[2] and will not be discussed here. The dominant new features observed above 6 eV include two relatively large structures at 6.80 and 9.30 eV. The particularly large size of the 6.80-eV structure indicates an $L_{3v} \to L_{3c}$ (E_1') critical-point origin for this spectral feature, in good agreement with estimates of this energy from band-structure calculations.[15,16] The magnitude and sharpness of the 9.30-eV structure suggest[3] that this spectral feature originates at or near the

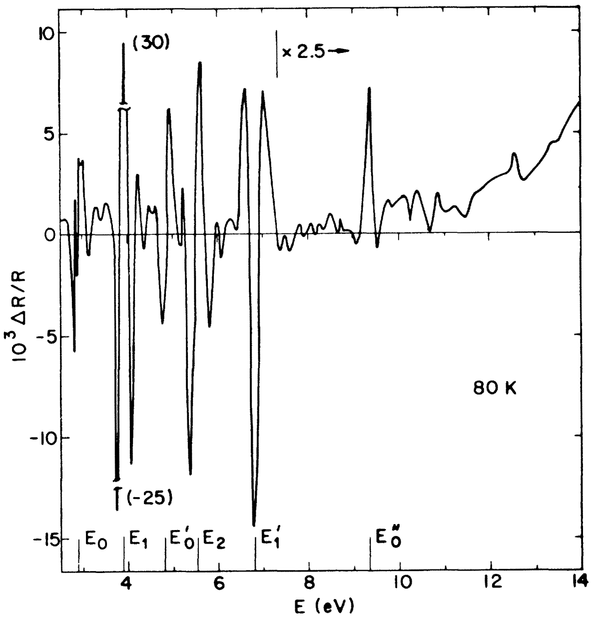

FIG. 1. Electroreflectance spectrum of GaP from 2.5–14 eV measured by synchrotron radiation. The rising background above 10 eV is a spurious effect due to luminescence.

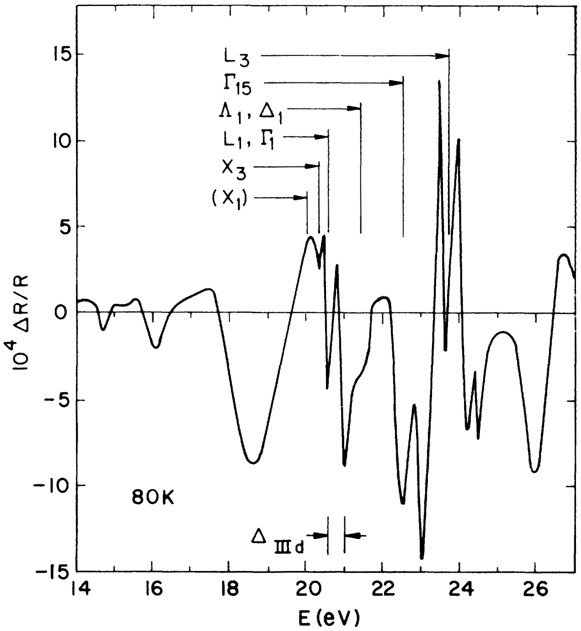

FIG. 2. Electroreflectance spectrum of GaP from 14–27 eV measured by synchrotron radiation. The critical-point assignments shown are discussed in the text.

sp^3 states forming the $\Gamma_{15v}-\Gamma_{12c}$ (bonding p-like to antibonding d-like) critical point E_0''. This assignment is in good agreement with the calculations of Cohen and Bergstresser.[17] Other features in Fig. 1 include Franz-Keldysh oscillations extending from the E_1' structure to higher energies, and a number of weakly resolved sp^3 critical points above E_0''. The rising background above 10 eV is a spurious effect due to luminescence. It is not seen with the solar-blind detector used for energies above 13 eV.

In Fig. 2, a new set of features, superimposed upon the relatively broad sp^3 background structure, is seen to appear at 20.3 eV and extend to higher energies. These new structures form a striking pattern of clearly resolved doublets of narrow line shapes, and originate from critical points that occur between the flat $3d$ valence bands, derived from the Ga $3d$ core states, and the sp^3 conduction band. The spin-orbit splitting, $\Delta_{IIId}=0.50\pm0.03$ eV, obtained accurately from these spectra, is in very good agreement with the theoretical value of 0.53 eV.[18] Our measured value is somewhat larger than that obtained from resonance photoemission (0.4 ± 0.1 eV),[8] and much less than that obtained from x-ray photoemission (0.67 eV),[7] neither of which have shown sufficient resolution in this energy range to separate these features.

For brevity, we shall discuss in detail only the critical-point assignments of the lower-energy components of the doublet structures, which arise from the upper spin-orbit $3d$ valence band. In order to make definite assignments, we note first that in this energy range

$$\Delta R/R \cong 1.6[\Delta\epsilon_1+\Delta\epsilon_2], \qquad (1)$$

where $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are the field-induced changes in the real and imaginary parts of the dielectric function, respectively. Equation (1) follows from the generalized Seraphin coefficient expression[19] of the three-phase vacuum-Ni-GaP system, using the values $\epsilon_{Ni}\cong 0.8+i0.8$[20] and $\epsilon_{GaP}\cong 0.87+i0.34$,[5] which are slowly varying over this energy region. Assuming three-dimensional M_0 low-field line shapes,[21] Eq. (1) predicts that each critical point will generate a single strong negative peak in $\Delta R/R$, which means, for example, that the relevant critical-point feature is the valley at 23.65 eV and not the positive peaks on either side. With this identification, the Γ_1 and Γ_{15} assignments at 20.55 and 22.50 eV, respectively, follow directly from magnitude considerations and the energy difference of 1.95 eV between these structures. This difference is in excellent agreement with the known difference of 1.94 eV which follows from an analysis[22] of absorption-edge data,[22] which places Γ_{1c} 2.87 eV above Γ_{15v} and high-resolution reflectance measurements,[24] which show an average $\Gamma_{15c}-\Gamma_{15v}$ separation of 4.81 eV. The L_1 and L_3 assignments, at 20.55 and 23.65 eV, respectively, follow similarly from our previous identification of the E_1' transition at 6.80 eV in Fig. 1 and from high-resolution reflectance measurements which place the averaged E_1' structure at 3.81 eV.[24] We note that the coincidence of the Γ_1 and L_1 critical points observed here fixes L_{3v} at 0.95 ± 0.05 eV below Γ_{15v}, in essential agreement with photoemission measurements[8] if the $3d$ valence bands are flat on our energy scale of 0.1 eV. This is a good approximation: theoretical estimates[25] show the expected width of the $3d$ band to be of the order of 0.1 meV. Further assignments include a relatively broad Λ_1, Δ_1 feature at 21.3–21.5 eV, and a very sharp structure at 20.30 eV which signals the onset of the $3d$ transitions. This latter structure clearly involves the X_3 conduction-band minimum, which lies 0.25 eV below Γ_1 and 0.29 eV above X_1, the true conduction-band minimum. The fact that X_1 is not seen (to within our experimental uncertainty of $\pm 2\times10^{-5}$ in $\Delta R/R$ in this energy range) gives further proof of the importance of matrix-element effects in core–to–conduction-band transitions.[10] Here, the electron is localized about Ga in the X_3 state and P in the X_1 (true minimum) state[26]; hence a significant overlap with the Ga $3d$-core wave function should be expected for the former and not the latter, in agreement with experiment.

In conclusion, we have demonstrated that the improved resolution and sensitivity to weak critical-point structures seen in ER below 6 eV continues well into the far uv not only for sp^3 valence-band–conduction-band transitions but also for core states as well. The large signals, together with the polarized nature of synchrotron radiation, are expected to make symmetry analysis of these structures practical. Further discussion of these points will be given in a forthcoming paper.

One of us (D.E.A.) is pleased to acknowledge a number of useful conversations with J. C. Phillips. We have also benefited from discussions with J. H. Weaver, and the cooperation of E. M. Rowe of the Synchrotron Radiation Center staff.

*During the course of this project, the Synchrotron Radiation Center was supported by the U. S. Air Force Office of Scientific Research under Contract No. F44620-70-0029 and by the National Science Foundation under Grant No. DMR-74-15089.

[1]B. O. Seraphin, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors*, edited by M. Hulin (Dunod, Paris, 1964), p. 165.

[2]M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[3]D. E. Aspnes and A. A. Studna, Phys. Rev. B 7, 4605 (1973).

[4]M. Cardona, W. Gudat, E. E. Koch, M. Skibowski, B. Sonntag, and P. Y. Yu, Phys. Rev. Lett. 25, 659 (1970).

[5]W. Gudat, E. E. Koch, P. Y. Yu, M. Cardona, and C. M. Penchina, Phys. Status Solidi (b) 52, 505 (1972).

[6]R. A. Pollak, L. Ley, S. Kowalezyk, D. A. Shirley, J. D. Joannopoulos, D. J. Chadi, and M. L. Cohen, Phys. Rev. Lett. 29, 1103 (1972).

[7]T. Lane, C. J. Vesely, and D. W. Langer, Phys. Rev. B 6, 3770 (1972).

[8]N. J. Shevchik, J. Tejeda, and M. Cardona, Phys. Rev. B 9, 2627 (1974).

[9]W. D. Grobman and D. E. Eastman, Phys. Rev. Lett. 29, 1508 (1972).

[10]D. E. Eastman and J. Freeouf, Solid State Commun. 13, 1815 (1973).

[11]W. D. Grobman, D. E. Eastman, J. L. Freeouf, and J. Shaw, in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, Germany, 1974,* edited by M. Pilkuhn (Teubner, Leipzig, 1974), p. 1275.

[12]C. G. Olson, M. Piacentini, and D. W. Lynch, Phys. Rev. Lett. 33, 644 (1974).

[13]D. E. Aspnes, Phys. Rev. Lett. 28, 913 (1972).

[14]Manufactured by Monsanto Corp., St. Louis, Mo.

[15]F. H. Pollak, C. W. Higginbotham, and M. Cardona, J. Phys. Soc. Jpn., Suppl. 21, 20 (1966).

[16]J. P. Walter and M. L. Cohen, Phys. Rev. 183, 763 (1969).

[17]M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966). A more extended version is shown in Fig. 63 in R. C. Eden, Stanford Electronics Laboratory Technical Report No. 5221-1, 1967 (unpublished).

[18]F. Herman and S. Skillman, *Atomic Energy Levels* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[19]D. E. Aspnes, J. Opt. Soc. Amer. 63, 1380 (1973).

[20]R. C. Vehse and E. T. Arakawa, Phys. Rev. 180, 695 (1969).

[21]D. E. Aspnes and J. E. Rowe, Solid State Commun. 8, 1145 (1970), and Phys. Rev. B 5, 4022 (1972).

[22]D. D. Sell and P. Lawaetz, Phys. Rev. Lett. 26, 311 (1971).

[23]P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. 38, 3551 (1967).

[24]S. E. Stokowski and D. D. Sell, Phys. Rev. B 5, 1636 (1972).

[25]J. C. Phillips, private communication, and Phys. Rev. Lett. 22, 285 (1969).

[26]T. N. Morgan, Phys. Rev. Lett. 21, 819 (1968).