Electroreflectance of GaAs and GaP to 27 eV using synchrotron radiation

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Electroreflectance of GaAs and GaP to 27 eV using synchrotron radiation

Abstract
Electroreflectance (ER) spectra of GaAs and GaP, taken with the Schottky-barrier method, exhibit to 27 eV the strong structural enhancement and high resolution characteristic of similar measurements below 6 eV. Above 20 eV, a new set of critical points is observed between the flat valence bands derived from the Ga 3d core levels and the local extrema of the sp3 conduction bands. The attained resolution, of the order of 100 meV, enables us to resolve clearly the spin-orbit splitting of 0.45 eV of the 3d-derived valence bands. The following critical-point energies have been determined in GaAs and GaP, respectively: sp3 valence conduction: E1′, 6.63 ± 0.05 eV, and 6.80 ± 0.05 eV; E1′+Δ1′, 6.97 ± 0.05 eV (GaAs only); E0″(Γv15→Γc12), 10.53 eV, and 9.38 ± 0.1 eV; E0‴(Γv15→Γc1), 8.33 ± 0.1 eV, and 10.27 ± 0.1 eV, E1″, 9.5 ± 0.2 eV, and 10.7 ± 0.2 eV. E5, E6, and E7 structures are observed at 15.1, 16.7, and 17.9 eV in GaAs, and at 14.7, 16.1, and 18.6 eV in GaP. Relative values of 3d core to sp3 conduction-band matrix elements are estimated for several states and show that the lowest 3d core-level ER structures arise from transitions terminating at the Xc1 conduction-band minimum. We calculate an exciton or core-hole interaction shift of 150 meV for GaP and 200 meV for GaAs, which indicates that core-hole effects are probably small for these materials. Spectral features with initial structure less than 100 meV in width are observed above 20 eV, showing that broadening effects are much smaller in this energy range than previously believed.

Keywords
Schottky-barrier method, critical-point energies, exciton, Ames Laboratory

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

Comments
Electroreflectance of GaAs and GaP to 27 eV using synchrotron radiation

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Electroreflectance (ER) spectra of GaAs and GaP, taken with the Schottky-barrier method, exhibit to 27 eV the strong structural enhancement and high resolution characteristic of similar measurements below 6 eV. Above 20 eV, a new set of critical points is observed between the flat valence bands derived from the Ga 3d core levels and the local extrema of the sp\(^3\) conduction bands. The attained resolution, of the order of 100 meV, enables us to resolve clearly the spin-orbit splitting of 0.45 eV of the 3d-derived valence bands. The following critical-point energies have been determined in GaAs and GaP, respectively: sp\(^3\) valence conduction: \(E_{1}^{+}, 6.63 \pm 0.05\) eV, and \(6.80 \pm 0.05\) eV; \(E_{1}^{-} + \Delta_{1}^{-}, 6.97 \pm 0.05\) eV (GaAs only); \(E_{1}^{+} (\Gamma_{5} \rightarrow \Gamma_{3}), 10.53\) eV, and \(9.38 \pm 0.1\) eV; \(E_{1}^{-} (\Gamma_{5} \rightarrow \Gamma_{3}), 8.33 \pm 0.1\) eV, and \(10.27 \pm 0.1\) eV, \(E_{1}^{+}, 9.5 \pm 0.2\) eV, and \(10.7 \pm 0.2\) eV. \(E_{1}^{+}\) and \(E_{1}^{-}\)structures are observed at 15.1, 16.7, and 17.9 eV in GaAs, and at 14.7, 16.1, and 18.6 eV in GaP. Relative values of 3d core to sp\(^3\) conduction-band matrix elements are estimated for several states and show that the lowest 3d core-level ER structures arise from transitions terminating at the \(\Gamma_{1}\) conduction-band minimum. We calculate an exciton or core-hole interaction shift of 150 meV for GaP and 200 meV for GaAs, which indicates that core-hole effects are probably small for these materials. Spectral features with initial structure less than 100 meV in width are observed above 20 eV, showing that broadening effects are much smaller in this energy range than previously believed.

I. INTRODUCTION

The effectiveness of modulation techniques in enhancing weak structure in the optical spectra of solids has been well documented in the quartz-optic energy range below 6 eV.\(^1\) By contrast, the energy region above 6 eV has been largely unexplored. Using the continuum provided by the hydrogen discharge lamp, Scouler\(^2\) and others\(^3\)–\(^7\) have measured thermoreflectance spectra of Au\(^2\) and other materials,\(^3\)–\(^7\) to 10 eV, while Menes\(^8\) has recently reported the electroabsorption spectra of the alkali iodides NaI, KI, and RbI to 8.2 eV. Although the enhancement of structure typical of modulation measurements was observed to these energies, there has been little incentive to extend modulation measurements beyond 10 eV even though a number of transitions important in energy-band theory occurred above this limit. This was due partly to the difficulty of obtaining suitably intense continuum sources, and partly to the fact that the broadening energy above 10 eV, as estimated from absorbance/reflectance spectroscopy,\(^8\)\(^9\) and x-ray,\(^10\)–\(^14\) resonance lamp,\(^14\),\(^15\) and synchrotron\(^16\)–\(^18\) photoemission measurements, was relatively large, of the order of 300 meV. Such large broadening effects would wash out fine structure in optical spectra, making modulation measurements unproductive.

The recent measurements of the thermoreflectance (TR) spectrum of Au to 35 eV,\(^19\) the electroreflectance (ER) spectrum of GaP to 27 eV,\(^20\) and the high-resolution reflectance spectrum of GaSe,\(^21\) using synchrotron radiation,\(^22\) were therefore surprising and significant for a number of reasons. First, first-derivative (TR), second-derivative (calculated numerically from reflectance), and third-derivative (low-field ER) techniques were shown to be effective to much higher energies than previously supposed. The spectra observed were large, with \(\Delta R / R\) of the order of 10\(^{-3}\) to the highest energies measured. Since the highest energies attained were a result of specific experimental conditions and not due to any intrinsic limitations of the techniques, these experiments demonstrated that it should be possible to measure spectra to even higher energies. Secondly, the spectra were not only highly structured but the structure observed was much sharper than expected. Certain transitions in these spectra showed widths of the order of 100 meV at energies as high as 25 eV. It was therefore clear that the broadening energies observed in previous spectroscopic measurements did not represent intrinsic limits of bulk processes. Although the optical work was probably resolution limited, the photoemission spectra were certainly broadened additionally due to effects arising from the shallow escape depth
of photoemitted electrons and the necessarily close proximity of the nominally bulk initial and final states to the surface. It was therefore apparent that optical-derivative spectroscopy, unlike electron spectroscopy, would provide spectra characteristic entirely of bulk phenomena. Thirdly, the improved resolution obtained by optical-derivative techniques, relative to previous spectroscopic measurements, allowed many previously undetected critical-point features to be observed and interpreted. In particular, the 0.50-eV spin-orbit splitting of the Ga 3d valence bands were resolved for the first time.\textsuperscript{26, 27} Fourth, the ER results showed that useful modulation spectra could be obtained from the extremely flat valence bands arising from atomic core levels. Since these levels show no curvature on the scale of experimental energy resolution of 100 meV, critical-point spectra arising from these core bands are qualitatively different from the usual ones involving the $s\sigma^*$ valence bands, in that each critical point of a core spectrum occurs at a local extremum of the conduction bands. By determining the absolute energy of the core level from photoemission measurements, it is therefore possible to obtain absolute energies of these conduction-band local minima and maxima. By performing symmetry analysis\textsuperscript{23, 24} on these critical-point features, it should be possible to assign these structures conclusively to different regions of the Brillouin zone, and therefore to determine, for instance, the energies of the local conduction-band minima at $\Gamma$, $X$, and $L$ directly.

The objective of this paper is to discuss more thoroughly the Schottky-barrier ER spectra of GaP given in our preliminary report,\textsuperscript{20} and to present new ER results for GaAs. A comparison of these two Ga compounds is particularly informative since they share in the 20–26-eV range the same flat valence bands derived from the 3$d$ core levels of the cation, and the spectra obtained from transitions out of this valence band simply reflect the similarities of and differences between the conduction-band topology of the two materials. The ER spectrum of GaAs below 6 eV has previously been measured in detail,\textsuperscript{25} and very accurate nonlocal pseudopotential band-structure calculations\textsuperscript{26, 27} are available to assist in interpreting the core-level spectra. The conduction-band structure of GaP is not known as accurately, but the much smaller spin-orbit splitting of P relative to As makes the core-level spectra of GaP intrinsically simpler than that of GaAs. The experimental details are discussed in Sec. II. The spectra are presented and analyzed in Sec. III. The results are summarized and discussed in Sec. IV.

II. EXPERIMENTAL

Schottky-barrier ER measurements\textsuperscript{26, 28} were performed using the high-energy photon source of the Synchrotron Radiation Center of the Physical Sciences Laboratory of the University of Wisconsin. A 1-m McPherson model-225 normal-incidence monochromator with a 600-line/mm grating was used to cover the energy range of 3–27 eV. Slit widths of 100 to 250 $\mu$m gave spectral resolutions of 1.6 to 4 Å. The output beam size at the sample was 1 $\times$ 5 mm and was reflected with predominantly $p$ polarization from the sample at a 30° angle of incidence. An EMI 9514 photomultiplier was used in conjunction with a sodium salicylate phosphor as a detector in the energy range below 14 eV. At higher energies, an EMI model 9603/2B electron multiplier was used because of its higher sensitivity and its complete lack of response to scattered light below 10 eV. Further details of the optical system, including the cold-finger sample Dewar, have been given elsewhere.\textsuperscript{16, 29}

Electroreflectance samples used in this experiment consisted of $n$-type Te-doped single-crystal slices of GaP and GaAs, with $\{111\}$ surfaces and net donor concentrations of $5 \times 10^{17}$ and $4 \times 10^{17}$ cm$^{-3}$, respectively. The back or $B$ surfaces were sand blasted and rhodium plated to form an Ohmic contact. The front or $A$ surfaces were optically polished with Syton,\textsuperscript{30} and Schottky barriers were formed by evaporating semitransparent metal films on these surfaces as described previously.\textsuperscript{25} All GaP spectra were taken with Ni as the barrier metal, whereas both Ni and Au were used for measurements on GaAs. Au films worked well in the vacuum-uv range below 14 eV, and the GaAs spectra from 6 to 14 eV were taken with Au as the barrier metal. The high reflectance of Au in the 17–25-eV range\textsuperscript{19} resulted in substantial attenuation of the ER spectra, so Ni was used as the barrier metal above 14 eV. Except for the difference in attenuation, the ER spectra measured above 14 eV appeared to be essentially the same for either Ni or Au barrier samples. For optical measurements, the samples were mounted directly on the Dewar cold finger with silver paste. Measurements were performed at liquid-nitrogen temperature (ca. 80 K) with ambient pressures in the 10$^{-8}$-Torr range.

Most spectra were taken with square-wave modulation of amplitude 1.0 to $\pm$3.0 V for GaAs and 1.0 to $\pm$5.0 V for GaP. The negative-voltage limits were determined by the reverse breakdown limits of the barriers, and corresponded to calculated surface fields of the order of 700 kV cm$^{-1}$. This is near the absolute dielectric breakdown
limit of these materials, and the actual field magnitudes obtained were probably somewhat less. A modulating frequency of 104 Hz was used for these measurements. A phase lag of 45° was observed between the modulation voltage and the ER response, indicating that the series resistance had only a minor effect in charging the barrier at this frequency.

The spectra were measured by phase-sensitive detection. Signal averaging for 20–60 sec per data point was obtained by integrating the output of the phase-sensitive detector with a V-to-f converter and accumulating the resultant pulses in a SSR model-1110 digital synchronous computer. These data were normalized by simultaneously recording the dc output of the detector. The usual factor of 2.22 was used to convert the rms output scale of the phase-sensitive detector to an equivalent square-wave modulation amplitude as seen at the photomultiplier output.

III. RESULTS AND DISCUSSION

A. ER spectra below 14 eV

The Schottky-barrier ER spectra of GaAs from 5 to 14 eV and GaP from 2.5 to 14 eV are shown in Figs. 1 and 2, respectively. Numerous structures can be seen which arise from critical points between the $sp^3$ valence and conduction bands. Structure below 6 eV is in agreement with that previously measured and discussed in ER spectra for both GaAs and GaP. Critical-point energies determined from these spectra by the three-point method are given for GaAs and GaP in Table I. Since the present ER spectra are not low-field spectra in this energy range, the values of critical point energies obtained from these spectra are expected to deviate somewhat from the corresponding low-field values. No measurements were taken below 5 eV for GaAs since Schottky-barrier ER data are already available in the literature. For completeness, we also list in Table I the energies of selected critical points as determined by low-field ER, high-resolution energy derivative reflectance (EDR), and thermoreflectance measurements, and the results of recent nonlocal pseudopotential band-structure calculations based principally upon the low-field Schottky-barrier ER data. We note that the $E_2$ critical-point energy determined from the present experiment is in very good agreement with that obtained from low-field ER measurements in the overlap region between 5 and 6 eV.

Experimental results for GaP listed in Table I include all major critical points for GaP, although high fields were used and consequently the spin-orbit splittings were not resolved. The single exception occurs for the $E_0$ and $E_1 + \Delta_0$ transitions, where well-developed $n = 1$ exciton lines were observed in both cases. The critical-point energies for these latter transitions were calculated by adding to the exciton line structures the known 11-meV binding energy of the $n = 1$ $E_1$ exciton. The discrepancy between our measurements and those from high-resolution energy-derivative-reflectance data also shown in Table I may be due to the higher doping levels of our samples. This is certainly the case for the $E_2$ transition. The corresponding difference for the average of

![Figure 1](image1.png)

**FIG. 1.** Schottky-barrier ER spectrum of GaAs from 5 to 14 eV. The barrier metal for this spectrum was Au.

![Figure 2](image2.png)

**FIG. 2.** Schottky-barrier ER spectrum of GaP from 3 to 14 eV. The barrier metal for this spectrum was Ni.
<table>
<thead>
<tr>
<th>Critical points</th>
<th>This work</th>
<th>GaAs</th>
<th>Theory</th>
<th>GaP</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0 (\Gamma'_0 \rightarrow \Gamma'_0)$</td>
<td>$1.5177 \pm 0.0005$</td>
<td>$1.5192 \pm 0.0002$</td>
<td>1.51</td>
<td>$2.85 \pm 0.05$</td>
<td>2.880 \pm 0.001</td>
</tr>
<tr>
<td>$E_0 + \Delta_0 (\Gamma'_1 \rightarrow \Gamma'_0)$</td>
<td>$1.859 \pm 0.001$</td>
<td>$1.859 \pm 0.002$</td>
<td>1.86</td>
<td>$2.93 \pm 0.05$</td>
<td>2.960 \pm 0.001</td>
</tr>
<tr>
<td>av $\Gamma'_1 \rightarrow \Gamma'_1$</td>
<td>1.632</td>
<td>1.632</td>
<td>1.638</td>
<td>1.63</td>
<td>2.87</td>
</tr>
<tr>
<td>$E_1 (\Lambda'_0,3 \rightarrow \Lambda'_0)$</td>
<td>$3.0439 \pm 0.001$</td>
<td></td>
<td>3.03</td>
<td></td>
<td>3.785 \pm 0.005</td>
</tr>
<tr>
<td>$E_1 + \Delta_1 (\Lambda'_0 \rightarrow \Lambda'_0)$</td>
<td>$3.2636 \pm 0.001$</td>
<td></td>
<td>3.25</td>
<td></td>
<td>3.835 \pm 0.005</td>
</tr>
<tr>
<td>av $L'_0 \rightarrow L'_1$</td>
<td>3.1338</td>
<td>3.18</td>
<td>(3.14)</td>
<td></td>
<td>3.91 \pm 0.1</td>
</tr>
<tr>
<td>$E'_1 (\Gamma'_0 \rightarrow \Gamma'_0)$</td>
<td>$4.488 \pm 0.01$</td>
<td></td>
<td>4.54</td>
<td></td>
<td>4.77, 4.85</td>
</tr>
<tr>
<td>$E'_1 + \Delta'_1 (\Gamma'_1 \rightarrow \Gamma'_0)$</td>
<td>$4.659 \pm 0.01$</td>
<td></td>
<td>4.71</td>
<td></td>
<td>4.77, 4.85</td>
</tr>
<tr>
<td>$E'_1 + \Delta'_1 + \Delta_0 (\Gamma'_0 \rightarrow \Gamma'_1)$</td>
<td>$5.014 \pm 0.01$</td>
<td></td>
<td>5.05</td>
<td></td>
<td>4.85</td>
</tr>
<tr>
<td>av $\Gamma'_1 \rightarrow \Gamma'_3$</td>
<td>4.716</td>
<td>4.657</td>
<td>(4.77)</td>
<td></td>
<td>4.87 \pm 0.1</td>
</tr>
<tr>
<td>$E_2 (2)$</td>
<td>$5.15 \pm 0.05$</td>
<td>$5.137 \pm 0.01$</td>
<td>5.03</td>
<td>5.13</td>
<td>5.07</td>
</tr>
<tr>
<td>$E_2 (X'_0 \rightarrow X'_0)$</td>
<td>$4.937 \pm 0.01$</td>
<td></td>
<td>4.92</td>
<td></td>
<td>5.21, 5.26</td>
</tr>
<tr>
<td>$E_2 (X'_1 \rightarrow X'_0)$</td>
<td>$5.014 \pm 0.01$</td>
<td></td>
<td>5.01</td>
<td></td>
<td>5.21, 5.26</td>
</tr>
<tr>
<td>$E_2 (X'_1 \rightarrow X'_0)$</td>
<td>$5.339 \pm 0.01$</td>
<td></td>
<td>5.38</td>
<td></td>
<td>5.36, 5.38</td>
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<tr>
<td>$E_2 (X'_0 \rightarrow X'_1)$</td>
<td>$5.415 \pm 0.01$</td>
<td></td>
<td>5.38</td>
<td></td>
<td>5.50</td>
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<tr>
<td>av $X'_1 \rightarrow X'_1$</td>
<td>4.975</td>
<td>4.96</td>
<td>(4.96)</td>
<td></td>
<td>4.6</td>
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<tr>
<td>av $X'_1 \rightarrow X'_1$</td>
<td>5.377</td>
<td>5.34</td>
<td>(5.33)</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>$E_1 + \delta$</td>
<td></td>
<td></td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E'_1 (\Lambda'_0,3 \rightarrow \Lambda'_0,3)$</td>
<td>$6.63 \pm 0.05$</td>
<td></td>
<td>6.62</td>
<td></td>
<td>6.80 \pm 0.05</td>
</tr>
<tr>
<td>$E'_1 + \Delta_1 (\Lambda'_0 \rightarrow \Lambda'_0)$</td>
<td>$6.97 \pm 0.05$</td>
<td></td>
<td>6.9</td>
<td></td>
<td>7.6</td>
</tr>
<tr>
<td>av $L'_3 \rightarrow L'_3$</td>
<td>6.87</td>
<td>6.74</td>
<td>6.74</td>
<td></td>
<td>6.4</td>
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<tr>
<td>$E_3$</td>
<td></td>
<td></td>
<td>7.55</td>
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*Table 1. Energies of selected sp³ valence–conduction interband critical points in GaAs and GaP. All values are in eV. Experimental uncertainties are given where known.*
<table>
<thead>
<tr>
<th>Critical points</th>
<th>This work</th>
<th>Experiment Low-field ER$^a$</th>
<th>GaAs</th>
<th>GaP</th>
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</thead>
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<tr>
<td>$E''_{1}(\Gamma_1^0 \rightarrow \Gamma_2^0)$</td>
<td>10.42 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E''<em>{1} + \Delta</em>{a}(\Gamma_1^0 \rightarrow \Gamma_2^0)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>av $\Gamma_1^0 \rightarrow \Gamma_2^0$</td>
<td>10.53 (7)</td>
<td>10.41$^f$</td>
<td>9.38 ± 0.1</td>
<td>9.3</td>
</tr>
<tr>
<td>$E''''_{1}(\Gamma_1^0 \rightarrow \Gamma_2^0)$</td>
<td>8.24 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E''''<em>{1} + \Delta</em>{b}(\Gamma_1^0 \rightarrow \Gamma_2^0)$</td>
<td>8.50 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>av $\Gamma_1^0 \rightarrow \Gamma_2^0$</td>
<td>8.33 ± 0.1</td>
<td>8.29$^f$</td>
<td>10.27 ± 0.1</td>
<td>9.8</td>
</tr>
<tr>
<td>$E''_{1}(\Lambda_1^0 \rightarrow \Lambda_2^0)$</td>
<td>9.35 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E''<em>{1} + \Delta</em>{c}(\Lambda_1^0 \rightarrow \Lambda_2^0)$</td>
<td>9.60 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>av $L_3^0 \rightarrow L_2^0$</td>
<td>9.47?</td>
<td>9.37$^f$</td>
<td>10.7 ± 0.2</td>
<td>10.7</td>
</tr>
<tr>
<td>$E_s$</td>
<td>15.1 ± 0.2</td>
<td></td>
<td>14.7 ± 0.15</td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>16.7 ± 0.2</td>
<td></td>
<td>16.1 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>$E_{1}$</td>
<td>17.9 ± 0.2</td>
<td></td>
<td>18.6 ± 0.2</td>
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<tr>
<td>$E_{s}$</td>
<td>19.3 ± 0.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$^{a}$ Aspnes and Studna, Ref. 25.  
$^{b}$ Sell et al., Ref. 34.  
$^{c}$ Sell and Stokowski, Ref. 35.  
$^{d}$ Guizzetti et al., Ref. 36.  
$^{e}$ Pandey and Phillips, Ref. 26.  
$^{f}$ Steklowsky and Cohen, Ref. 27.  
$^{g}$ Stokowski and Sell, Ref. 38.  
$^{h}$ Cohen and Bergstresser, Ref. 40.  
$^{i}$ J. C. Phillips (private communication).
the $E_i$ and $E_i + \Delta_i$ transitions probably includes in addition broadening effects that occur at the high fields used in these measurements. A number of separate transitions in the $E'_0$ and $E'_3$ structures are indicated but not resolved. Presumably, low-field measurements can obtain the necessary separation to identify the component critical points in these regions of the spectrum, as has been possible for GaAs. A number of subsidiary or Franz-Keldysh oscillations are present in the spectra of Fig. 2 as well as the primary structures associated with the critical points themselves. These are most apparent in the energy ranges just above the $E'_0 + \Delta'_0$, $E'_1$, and $E'_2$ critical points, and in principle can be used to obtain the interband reduced masses of these critical points.

The identification of $sp^3$ valence-conduction-band critical points in the previously unexplored region above 6 eV is greatly facilitated by examining the GaAs and GaP spectra for similar structures, and comparing the energies obtained with the results of band-structure calculations. Since recently developed nonlocal pseudopotential methods have not yet been applied to GaP, we shall place the most emphasis on agreement with band-structure calculations for GaAs. The dominant spectral features above 6 eV are the $E'_1$ transitions with measured critical point energies 6.63 and 6.80 eV in GaAs and GaP, respectively. These energies are in good agreement with those obtained from thermoreflectance measurements and also with the energies obtained from reflectance measurements and with those at which measured reflectance reach local maxima. A clearly defined secondary structure is observed in GaAs at a critical point energy of 6.97 ± 0.05 eV, as shown in Fig. 3. The energy of the secondary critical point is obtained by assuming that its line shape is the same as that of the main structure, and that it is simply superimposed on the high-energy tail of the latter. This energy is also in good agreement with that obtained from thermoreflectance measurements. A similar secondary structure may exist in GaP, but its presence is masked by the multiplicity of structures in the 7.3–9.0-eV region for this material. Spectra were obtained at several different modulation voltages for GaAs in order to verify that the secondary structure was an intrinsic property of the material, and not a subsidiary oscillation. Two such spectra are shown in Fig. 3. Except for small discrepancies, the two spectra are the same and are observed to scale approximately linearly with the modulating voltage. This verifies that these spectra were obtained under low-field conditions. The separation energy of 0.34 ± 0.05 eV for these transitions is substantially greater than the value, 0.220 ± 0.002 eV, observed for the spin-orbit splitting of the $E_1$ and $E_1 + \Delta_1$ transitions. This shows that the respective transitions are localized in somewhat different regions of the Brillouin zone, as has been demonstrated previously for the equivalent transitions in Ge.

The multiplicity of structures above $E'_1$ in Figs. 1 and 2 is exceeded only by the multiplicity of interband critical points that occur in the calculated energy band structures for these materials. We shall therefore discuss only the most prominent of the remaining features, reserving analysis of the remainder until polarization data are available. The sharp positive peak at 9.38 eV in GaP, labeled $E'_2$ in Fig. 2, is clearly related to the corresponding peak at 10.42 eV in GaAs in Fig. 1. The anomalous sharpness relative to the surrounding structures is characteristic of zone-center transitions, and the strength is suggestive of a large matrix element and possibly of contributions from a somewhat extended region of the Brillouin zone. Band-structure calculations for GaP show that the $\Gamma_{13} - \Gamma_{12}$ critical point is the most probable cause of this structure, not only because it is a zone-center critical point between bonding $p$-like and bonding $d$-like states, but also because the energy bands are very nearly parallel for a short distance from $\Gamma$ along $\Lambda$, contributing to the oscillator strength. Finally, band-structure calculations for both GaAs and GaP place this energy in very good agreement with our measured values, as shown in Table I. The calculated energies of these critical points are known

![Fig. 3. Schottky-barrier ER spectra of GaAs in the vicinity of the $E'_1$ and $E'_1 + \Delta'_1$ transitions at two values of the modulating voltage. The spectra taken at the lower field are shown larger by a factor of 3.5 to facilitate comparison of the line shapes.](image)
to be very insensitive to changes in pseudopotential parameters.\textsuperscript{45} For these reasons, the assignment of these structures appears firm. The lack of a definite spin-orbit-split structure for this transition is taken as an indication that contributions from the parallel-band region along \( \Lambda \) are also important in generating this spectral feature, because if this is correct, then the missing structure will contain contributions from regions of the valence band having both zone-center (0.341 eV) and \( \Lambda \)-axis (0.220 eV) spin-orbit splittings. It would consequently be expected to be illdefined and therefore rather weak.

In GaAs, an equally strong feature occurs at 9.35 \( \pm \) 0.1 eV in Fig. 1 and is labeled \( E''_\delta \). From line-shape similarities, we believe that the structure in the GaP spectrum of Fig. 2 at 10.7 \( \pm \) 0.2 eV arises from the same type of critical point. In the latter case, this corresponds to a parallel-band region along \( \Lambda \) centered about the \( L'_s-L''_s \) critical point.\textsuperscript{40} The calculated energy of the corresponding feature in the GaAs band structure\textsuperscript{38} is 9.97 eV, about 0.5 eV higher than the experimental average separation. We do not view this discrepancy as serious, since the \( L'_s-L''_s \) energy is sensitive to the pseudopotentials chosen in the calculation.\textsuperscript{45} If the structure at 9.60 \( \pm \) 0.1 eV is the spin-orbit-split companion, as seems likely, then the difference (0.25 eV) is very close to the spin-orbit splitting (0.220 eV) of the valence bands at \( L \). We view this agreement as added support for this assignment.

The critical point structures at 8.24 \( \pm \) 0.1 and 8.50 \( \pm \) 0.1 eV in the GaAs spectrum of Fig. 1 are assigned to the \( \Gamma^6 \), \( \Gamma^6 \rightarrow \Gamma^5 \) transitions, which have the average value 8.29 eV in the band-structure calculations.\textsuperscript{26,45} The line shape cannot be interpreted clearly; we assume that the individual contributions, if separated, should have essentially the same shape as the \( E''_\delta \) structure adjacent to it at higher energy. The interpretation given leads to a spin-orbit splitting of 0.25 eV, less than that of the \( \Gamma^6 \), \( \Gamma^6 \) symmetry points. From its sharpness, the spectral feature at 10.27 \( \pm \) 0.1 eV appears to represent the equivalent critical point in GaP.

An inspection of the band structure at high energies\textsuperscript{40} shows a large number of possibilities for the remaining features shown in Fig. 1. We feel that any further interpretation at this stage is premature, and will discuss these assignments in a future publication as further data become available. The slowly rising background above about 10 eV that appears in both Figs. 1 and 2 is a spurious effect due to luminescence, which does not occur with the solar-blind detector used above 14 eV.

\textbf{B. ER spectra from 14 to 27 eV}

Schottky-barrier ER spectra from 14 to 27 eV are shown in Figs. 4 and 5 for GaAs and GaP, respectively. A new set of features, characterized by a striking pattern of sharp clearly resolved doublets, is seen to appear above 20 eV superimposed on the relatively broad \( sp^3 \) background structure. These doublet structures arise from critical points that occur between the flat valence bands derived from the 3d atomic core levels of Ga, which are split by the spin-orbit interaction. Since the curvature of these 3d bands is of the order of 0.1 meV,\textsuperscript{45,46} which is negligible on the scale of resolution of this experiment, the energies of these critical points determine rigorously the relative energies of local minima and maxima of the \( sp^3 \) conduction band to the extent that electron-hole interaction effects\textsuperscript{37,48} can be ignored. When combined with absolute determinations of the energy of the 3d core valence bands by photoemission measurements,\textsuperscript{10-12} absolute energies of the conduction-band extrema, in principle, can be obtained.

A cursory inspection of Figs. 4 and 5 shows a remarkable similarity between the Schottky-barrier ER spectra of GaAs and GaP in the 19–25-eV range, which is emphasized by the extended-scale display of these spectra in Fig. 6. Before discussing these spectra in detail, we consider first the remaining \( sp^3 \) valence-conduction-band critical points above 14 eV. In accordance with the notation introduced by Cardona\textsuperscript{49} and extended by Guizzetti \textit{et al.}\textsuperscript{30} to include volume critical points

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig4.png}
\caption{Schottky-barrier ER spectrum of GaAs from 14 to 27 eV. The barrier metal for this spectrum was Ni.}
\end{figure}
$E_9$ and $E_6$, we term the probably related structures at 15.1, 16.7, and 17.9 eV in GaAs and 14.7, 16.1, and 18.6 eV the $E_6$, $E_9$, and $E_7$ structures, respectively. The $E_6$ transition in GaAs is quite probably a multiplet. A final structure labeled $E_9$ occurring at 19.3 eV in GaAs appears either to be absent or to be obscured by core-level transitions in GaP. None of these structures coincides with the bulk plasmon energies of 14.7 and 16.9 eV for GaAs and GaP, respectively, determined from the peak in the loss function calculated from reflectance measurements.\textsuperscript{41}

We consider finally the 3d-core-valence-$sp^3$-conduction-band critical-point spectrum shown in detail in Fig. 6. The doublets are well resolved and can be used to provide an accurate measurement of the spin-orbit splitting, $\Delta_{3d} = 0.45 \pm 0.03$ eV. This value, which agrees with that measured by Thiry \textit{et al.} in high-resolution reflectance measurements of GaSe,\textsuperscript{21} is given most accurately by the $\phi = 60^\circ$ spectrum shown at the bottom of Fig. 6 and was determined from this curve. We believe the 0.45 eV value to be more reliable than our previous value of 0.50 eV,\textsuperscript{20} which was obtained from analysis of $\phi = 30^\circ$ spectra for which the signal-to-noise ratio was not as good. The spin-orbit splitting is therefore noticeably less than the theoretical value of 0.53 eV calculated by Herman and Skillman,\textsuperscript{50} and slightly less than the value 0.49 $\pm$ 0.05 eV determined by Eastman and Freeouf.\textsuperscript{51}

Previous experimental values for this quantity, determined from unresolved structure, ranged from 0.4 eV (Ref. 14) and 0.6 eV (Ref. 15) in resonance-photoemission measurements, to 0.57 and 0.67 eV in x-ray-photoemission measurements.\textsuperscript{13}

When this paper was first written, we had interpreted the structure observed in the top and middle spectra in Fig. 6 on the basis of energy differences that agreed well with the known energy differences between the high-symmetry $\Gamma$, $L$, and $X$ band extrema of the conduction band. But Freeouf\textsuperscript{52} pointed out that the assignment of one feature in this interpretation, to the critical point at $X^2_5$, was untenable because this state was prin-

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**FIG. 5.** Schottky-barrier ER spectrum of GaP from 14 to 27 eV. The barrier metal for this spectrum was Ni.

**FIG. 6.** Comparison of ER spectra of GaAs (top) and GaP (middle) over the energy range dominated by contributions between the 3d-core valence bands and the $sp^3$ conduction bands. The GaP spectrum at the bottom, shown with its Kramers-Kronig transform $\Delta \omega$, differs primarily in that a 60° angle of incidence was used. The vertical scale differs for the top two curves to facilitate comparison of the line shapes. The upper scales on the zero lines of the spectra indicate conduction-band energies referenced to the $I^2_5$ top of the valence band (see text).
cipally s-like about the Ga core. If \( \chi_s \) were detectable, then a much larger structure should be expected at \( \chi_j^s \), which is \( p \)-like about the Ga core but which was not assigned in the previous interpretation. \( S \)-like conduction-band wave functions should have small matrix elements because the \( 3d \)-valence-band wave functions should be represented accurately by \( 3d \)-atomic wave functions centered about the Ga site. Group theory provides no information here since it indicates only that all \( 3d \)-core to \( sp^3 \)-conduction-band transitions are allowed. The \( 3d \) levels form irreducible representations of \( \Gamma_{13} \) and \( \Gamma_{15} \) symmetry at the zone center in the single-group notation, and hence no selection rules are obtained that forbid transitions to any of the major symmetry points of the lower \( -sp^3 \) conduction bands. The same conclusion is obtained in the double-group representation, for which the \( j = \frac{1}{2} \) (upper) state consists of \( \Gamma_j \), and the \( j = -\frac{1}{2} \) (lower) state belongs to the representation \( \Gamma_6 \).

To obtain further information to resolve this point, we estimated the matrix elements between the \( 3d \)-core wave functions and selected conduction-band states as follows: We calculated the first two terms of the power-series expansion about the Ga site of the \( \Gamma_j \), \( L_j^s \), \( X_j^s \), and \( X_j^p \) conduction-band wave functions from the recent nonlocal pseudopotential results of Pandey and Phillips. The results are shown in Table II. While the constant and linear terms in these expansions are not strictly proportional to the \( s \)- and \( p \)-like parts of the conduction-band wave functions, they nevertheless give a reasonable estimate of the magnitude of the matrix element to be expected between the core level and the selected symmetry point. It is clear from these results that the \( X_j^p \) matrix element should be larger (probably by over an order of magnitude) than the next-largest possibility, the \( L_j^s \) critical point, and that the \( \Gamma_j \) and \( X_j^s \) contributions are probably negligible. Our previous assignment could not therefore have been correct. We conclude that the dominant structures at 20.55 and 21.00 eV in GaP are the spin-orbit-split doublet arising between the Ga \( 3d \) core levels and the \( X_j^p \) absolute minimum of the conduction band.

Since the \( X_j^p \) absolute conduction-band minimum in GaP lies 2.333 \( \pm \) 0.001 eV above the top of the valence band at low temperature, we can determine the apparent energy of the \( 3d \) core levels from the spectra in Fig. 6. Applying the three-point method to the \( \phi = 60^\circ \) spectra, we find that the \( j = \frac{1}{2} \) and \( j = -\frac{1}{2} \) singularities occur at 20.55 and 21.00 eV, respectively. Thus, the \( 3d \) core levels—neglecting exciton effects—are located at \(-18.22 \) and \(-18.67 \) eV relative to the top of the valence band. Taking into account the 6:4 occupation of these levels, we calculate the average energy of the \( 3d \) core levels to be 18.40 eV below the top of the valence band. XPS measurements determine this energy to be \(-18.55 \pm 0.05 \) eV. The 150-meV difference can be attributed to exciton effects, since in the presence of a strong exciton line the three-point method yields \( E_x - E_{\text{con}} \). The energy difference between the optical and XPS measurements is small enough to indicate that large core-hole effects are not significant in core-level spectra of semiconductors.

For GaAs, the \( X_j^p \) level lies 0.43 eV above \( \Gamma_j^p \), while \( \Gamma_j^f \) lies 1.519 eV above \( \Gamma_j^f \). The energy of the known \( X_j^s \) singularity on the \( \phi = 30^\circ \) GaP spectra, and using the obvious similarity between the GaAs and GaP \( \phi = 30^\circ \) spectra, we find the \( X_j^s \) singularities to be at 20.35 and 20.80 eV in Fig. 6. The \( 3d \) core levels—again neglecting exciton effects—are located in GaAs at \(-18.40 \) and \(-18.85 \) eV relative to the top of the valence band. The average \( 3d \) core energy of \(-18.60 \) eV determined here is about 200 meV higher than the XPS value, \(-18.82 \) eV. The difference is similar to that determined for GaP, supporting the position that core-hole shifts are not significant in core-level ER spectra of semiconductors.

The location of the \( X_j^p \) singularity energies allows us to also reference structure in Fig. 6 to an energy scale relative to the top of the valence band. By using singularity energies throughout, we do not need to explicitly remove the electron-hole interaction energy, but we do have to assume that it is the same (or nearly the same) for each structure. The energy scale for conduction-band structure relative to the top of the valence band is given for each spectrum on top of its zero line.

The remaining core-level ER structures are of interest for two reasons: first, there exist known critical points for which structures do not appear,

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Constant</th>
<th>Linear</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_j^f )</td>
<td>2.6</td>
<td>0</td>
</tr>
<tr>
<td>( L_j^s (111) )</td>
<td>1.4</td>
<td>(-0.3Gz')</td>
</tr>
<tr>
<td>( X_j^s (001) )</td>
<td>0</td>
<td>(2.2Gz)</td>
</tr>
<tr>
<td>( X_j^p )</td>
<td>1.8</td>
<td>0</td>
</tr>
</tbody>
</table>
and second, major (obvious doublet) structures are seen in these spectra that are not related to any known high-symmetry critical points. Obvious doublet structures occur at 22.35 (22.80) eV and 23.50 (23.95) eV in GaP as seen in the $\phi = 60^\circ$ spectrum. The corresponding energies of the $j = \frac{3}{2}$ member, referenced to the top of the valence band, are 4.15 and 5.30 eV. The equivalent major structures in GaAs occur at 22.15 (22.60) eV and 23.45 (23.90) eV, and the corresponding $j = \frac{3}{2}$ energies relative to the top of the valence band occur at 3.75 and 5.05 eV, respectively. We list the results of the comparison in Table III and discuss them below.

The first known critical point occurs at $\Gamma^6_2$ in GaAs. The $\Gamma^6_2$ transition at 2.88 eV in GaP could be masked by the larger $X^6_1$ structures, but it should occur below the lower $X^6_2$ structure in GaAs. Its absence in the spectrum in Fig. 6 shows that its matrix element is small, as expected.

The $L^6_2$ structures should appear near 2 eV in GaAs and near 2.7 eV in GaP, although these energies are very uncertain because it is difficult to determine the $L^6_2$ singularity in UPS and XPS. They may in fact lie up to 0.3 eV higher. In either case, the structure would be masked in GaAs by the $X^6_2$ structures. The structure near 3.2 eV in the $\phi = 60^\circ$ GaP spectrum could conceivably be the $j = \frac{3}{2}$ member of the doublet, but its lineshape and field dependence indicate strongly that it is a subsidiary oscillation associated with the $X^6_2$ structure.

The $X^6_2$ structures should be quite weak, according to Table II. From the values given in Table III, only the $j = \frac{3}{2}$ components should be seen. The weak structure near 2.6 eV in GaAs is most probably a subsidiary oscillation of the $X^6_1$ structure, as in GaP. Accordingly, we also indicate this

| TABLE III. Comparison of energies of core-level ER structures of GaAs and GaP with energies of selected conduction-band states. Only transitions from the $j = \frac{3}{2}$ core levels are considered. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| $\Gamma^6_2$ Expt, sp\(^3\) | GaAs Expt, this work | Theory | GaP Expt, sp\(^3\) | Expt, this work |
| $\Gamma^6_2$ | 0 \(^a\) | 0 \(^a\) | 0 \(^a\) |
| $\Gamma^6_1$ | 1.519 \(^b\) | (not seen) | 1.524,\(^c,d\) 1.51 \(^c\) | 2.883 \(^f\) | (not seen) |
| $X^6_2$ | 1.95 \(^g\) | 1.95 \(^h\) | 2.02 \(^c,d\) | 2.333 \(^f\) | 2.33 \(^h\) |
| $L^6_2$ | 1.95 \(^i\) | (not seen) | 1.87,\(^c,d\) 1.72 \(^c\) | 2.65 \(^j\) | (not seen) |
| $X^6_2$ | 2.35 \(^k\) | (not seen) | | 2.62 \(^f\) | (not seen) |
| (3d ER) | | 3.75 | | 4.15 | |
| $\Gamma^6_2$ | 4.49 \(^l\) | | | |
| $\Gamma^6_2$ | 4.66 \(^l\) | | | 4.83 \(^m\) |
| (3d ER) | | 5.05 | | 5.30 | |
| $L^6_2$ | 5.6 \(^n\) | | 5.6 \(^o\) | | |

\(^a\) Reference level.
\(^b\) Pandey and Phillips, Ref. 26.
\(^c\) Chelikowsky and Cohen, Ref. 27.
\(^d\) Dean, Kaminsky, and Zetterstrom, Ref. 56.
\(^e\) Value obtained from $\Gamma^6_2$ level plus 0.43 eV separation between $\Gamma^6_2$ and $X^6_2$ from Balslev, Ref. 57.
\(^f\) Value chosen to agree with optical value, fixing energy of all states in this column.
\(^g\) Calculated from $L^6_2$ average energy, $\approx 1.2$ eV, from UPS (Refs. 14 and 58) and XPS (Ref. 12) measurements, together with $L^6_2 \rightarrow L^6_2$ ER (Ref. 25) value from Table I.
\(^h\) Calculated from $L^6_2$ average energy, $\approx 1.15$ eV, from UPS (Ref. 14) and XPS (Ref. 12) measurements together with $L^6_2 \rightarrow L^6_1$ EDR (Ref. 38) value from Table I.
\(^i\) Value from $X^6_2$ plus 0.40 eV $X^6_2 - X^6_2$ splitting (Ref. 25).
\(^j\) Aspnes and Studna, Ref. 25.
\(^k\) From Table I and (i) above.
\(^l\) From Table I and (i) above.
transition as not seen.
One should expect a number of possible origins for the higher-energy structures, such as local extrema along \( \Delta \) or \( \Sigma \) symmetry lines, which may originate from \( p \)-like atomic states centered about Ga. \( P \)-like states of known energy include the \( \Gamma_{\alpha}^0 - \Gamma_{\beta}^0 \) set, and the higher-lying \( L_{\delta}^0 \) points. Although structure does exist in the core-level ER spectra near these energies, it is clear that the assignment of the major structure to \( X_{\delta}^0 \) results in considerable discrepancies between these high-symmetry states and the dominant ER structures discussed earlier. We conclude that these major structures, at 3.75 and 5.05 eV in GaAs, and at 4.15 and 5.30 eV in GaP, terminate at band extrema whose location is not yet known. It is unlikely that exciton shifts should be so large to cause these discrepancies. More reasonably, the critical points exist and remain to be assigned.

IV. CONCLUSION

We have demonstrated in this paper that ER is a powerful technique for detecting weak structures, resolving closely spaced critical points, and accurately determining critical-point assignments and energies well up into the vacuum uv. The spectra obtained are large, and it is clear that the technique should be useful on a wide range of materials, to higher energies than those obtained here. The observation of sharp spectra from core-level valence bands which are flat on the scale of energy determined by the experimental resolution (ca. 0.1 eV) is particularly exciting, since it not only opens up a new critical-point spectrum to local minima and maxima in the conduction bands, but also enables these energies to be determined absolutely from measurements of core-level energies and also enables the absolute energies of related high-symmetry \( sp^3 \) valence-band states to be determined more accurately than currently possible with electron spectroscopic techniques.

Previous spectroscopic work\(^{10-18} \) indicated that intrinsic broadening energies of the order of 0.3 eV could be expected in the 10–20-eV range. Since ER spectra depend on the third derivative of the dielectric function, the amplitudes of these spectra vary inversely with the third power of the broadening parameter.\(^{43,46} \) Since spectra of the order of 10\(^{-3} \) in \( |\Delta R/R| \) are observed with 50–100-meV broadening below 6 eV, and since there is no reason to expect significantly different matrix elements at higher energies, it follows that a sixfold increase in \( \Gamma \), from 30 to 300 meV, should result in ER spectra of the order of 10\(^{-4} \), near experimental resolution limits and too small to be useful or possibly even to be detected. It is clear from the results presented here that the intrinsic broadening is much less than 300 meV. The sharpest structures that we have observed, e.g., the rises in \( \Delta R/R \) at 23.4 eV in Fig. 6, appear to have widths of the order of 100 meV. The inability of electron spectroscopies to achieve these widths appears to be due to an admixture of surface and bulk effects. The small broadening obtained here indicates also that the core hole has a longer lifetime than expected, which is probably due to the centrifugal barrier imposed by the 3d wave functions.\(^{46} \) Significantly, the best resolution exhibited by the electron spectroscopies have also involved transitions from the 3d core levels\(^{41} \) in GaAs (to a sharp surface state) or from 2p core levels in light atoms (Si).\(^{61} \) This may show that measurements from core levels may prove to be particularly useful in semiconductor spectroscopy.

ACKNOWLEDGMENTS

One of us (D.E.A.) wishes to express his appreciation to J. C. Phillips for numerous useful conversations concerning the results of these experiments, and to L. Derick, A. Pisarchik, and S. Lorimer for providing the GaP and GaAs wafers used in these measurements. We also wish to thank J. L. Freeouf for his comments concerning the relative importance of the \( X_{\delta}^0 \) matrix element. We have also benefited from conversations with J. H. Weaver and the cooperation of E. M. Rowe and the Synchrotron Radiation Center Staff. 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.

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The energy quoted in Table I for the $E_0 + \Delta_1$ transition was obtained from a more accurate line-shape analysis (D. D. Sell (private communication)).


J. C. Phillips (private communication).


J. L. Freeouf (private communication).


K. C. Pandey, (private communication).


D. D. Dow (private communication).