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Optical transitions via the deep O donor in GaP. II. Temperature dependence of cross sections

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A detailed experimental study of temperature dependence of optical cross sections for the GaP:O one-electron state for $T < 300$ K is presented. Broadening effects on the edge as well as temperature shift of the deep-level binding energy and spectral variations of the measured cross section with temperature are treated. In our purely optical data from bulk material the overall broadening of the edge for $\sigma_{p1}^{0}(h\nu)$ and $\sigma_{n1}^{0}(h\nu)$ is well explained ($\sim 15\%$ accuracy) by absorption of configuration-coordinate phonon quanta in the optical transitions, apart from an anomalous behavior below 30 K. The 0.9-eV O level is nearly pinned to the valence band below 175 K ($\Delta E_i/\Delta E_g = 0.90 \pm 0.10$) while above this temperature $\Delta E_i/\Delta E_g$ seems to decrease gradually. The temperature-dependent spectral behavior of the cross sections seems to be due to the presence of two different levels related to the one-electron O state where the new level is situated 80 ± 20 meV above the previously established 0.9-eV level. The apparent temperature dependence of the part of the cross sections associated with the 0.9-eV level is described in terms of a thermal activation energy of 0.4 meV.

I. INTRODUCTION

Optical cross sections for deep localized states in semiconductors can vary with temperature in several different respects. For centers which do not have strong configuration-coordinate (CC) phonon interaction in optical transitions (which is often believed to be the case for centers in Si and Ge), the problem is simply reduced to a possible variation in magnitude of the cross section (such variations are usually small) and a temperature shift due to the temperature dependence of the deep-level binding energy. For centers where CC phonon interaction cannot be neglected (we believe this is the case for most deep levels in III-V and II-VI compounds), the situation is more complicated. As was described in Part I of this study,[1] optical cross sections must in this case be considered as a convolution of an electronic spectrum with the line-shape function due to vibrational modes coupling to optical transitions via the defect state. Therefore, in addition to the temperature dependence of the electronic part of the cross section (magnitude and spectral shift), which cannot be directly measured, there are effects of phonon interaction affecting the experimentally measured curves. The effect of phonons on the temperature variation of the saturation magnitude of optical cross sections is rather small, but not negligible. The most drastic temperature dependence expected is a phonon-induced broadening of cross sections, which is normally most apparent as an edge effect.[2] The present paper covers some aspects of all these different effects of temperature dependence of optical cross sections, in relation to new experimental data.

The experiments reported in this paper are restricted to one center, the deep O donor in GaP. The main reason for this is that it is about the only deep center among the III-V compounds where the identity of the defect is established.[3] Further, large-band-gap materials like GaP are suitable for the application of our extremely sensitive methods of measuring spectral variations of optical cross sections, i.e., the photoluminescence-excitation (PLE) and -quenching (PLQ) techniques described in Part I of this study.[1] Indeed very accurate experimental data are necessary to separate different temperature-dependent effects from a measured spectral variation of optical cross sections. Measuring techniques relying on p-n junctions are not accurate enough for these measurements, since large field-induced broadening effects do occur with such methods.[1] Our earlier investigations[1,4] of data for GaP:O were restricted to the lowest temperatures to emphasize the verification of a detailed discrete model for phonon interaction. Further, we developed proper methods to describe and evaluate the electronic cross section when detailed knowledge about the phonon interaction is available.[1] In this paper, we continue the description of new experimental data for optical cross sections for GaP:O up to higher temperatures concentrating on temperature dependences up to 300 K. We shall find that the detailed knowledge about the phonon-interaction parameters displayed in Part I is indeed necessary to evaluate properly the different and quite complicated effects that occur. This is true for temperature broadening as well as temperature dependence of the spectral behavior of the electronic part of optical cross sections for GaP:O.

In Sec. II, we start the description of experimental data with the broadening effects at the very edge, which are compared with expectations from phonon broadening alone.[1] Although the major effects can be explained by such phonon broadening, additional broadening effects do occur. In Sec. III, we evaluate the temperature variation of the position of the O-donor level in the band gap below 300 K. Our accurate experimental data show that this level is approximately pinned to the valence band at low temperatures, in conflict with some previous theoretical[5] and experimental[6] results. The previously unknown complicated behavior of the electronic cross section with temperature is displayed in Sec. IV. We show that $\sigma^0_{p1,\mathrm{el}}(h\nu)$ is composed of two different spectra, one of which has a very strong temperature dependence at low temperatures in our PLE data.

In Sec. V, a more detailed discussion of the experimental results is presented, for broadening effects as well as the temperature variation of the deep-level position and the complicated behavior of the electronic spectrum. The most important conclusions from this paper are collected in Sec. VI.

II. EXPERIMENTAL BROADENING OF OPTICAL CROSS SECTIONS CLOSE TO THE EDGE

The PLE technique for measuring optical cross sections allows accurate measurements of the spectral dependence of $\sigma^0_{p1}(h\nu)$ for GaP:O over 5 orders of magnitude in the low-temperature region,[1] which makes a detailed evaluation of broadening effects with temperature in the edge region possible. In Fig. 1, such data are displayed for a number of temperatures ≤ 100 K, showing clear effects of broadening. All the curves in Fig. 1 are normalized to the shoulder of the electronic cross section at ~1.46 eV. (This shoulder constitutes about 1% of the saturation value.) Also shown in Fig. 1 are the corresponding theoretically computed curves, obtained by convolution of the electronic cross section $\sigma^0_{p1,\mathrm{el}}(h\nu)$ (evaluated at 1.5 K), with the aid of Eq. (9) of Ref. 1. Here we have used the parameters for phonon interaction deduced in Ref. 1, i.e., two phonon modes $\hbar\omega_1 = 19$ meV and $\hbar\omega_2 = 48$ meV with coupling strengths $\lambda_1 = 1.65$ and $\lambda_2 \approx 1.1$, respectively.[4] We observe in Fig. 1 an apparently larger experimental broadening at all temperatures compared to what is expected from the theoretical convolution procedure.

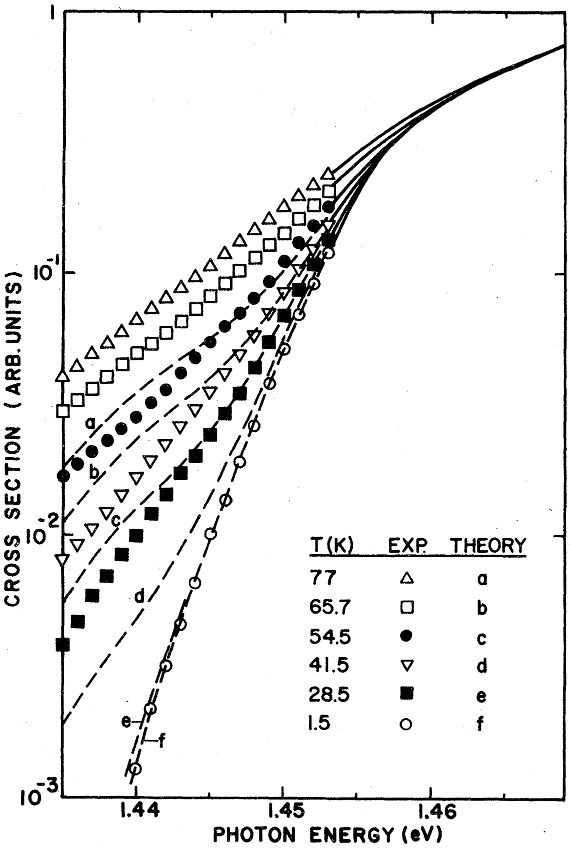

FIG. 1. PLE data for $\sigma^0_{p1}(h\nu)$ for different temperatures below 80 K. The theoretical curves shown here are convoluted cross sections from 1.5-K electronic spectra.

A closer inspection of the data in Fig. 1 shows that the largest deviations from theory occur at the very lowest temperatures. From theory, very little vibrational broadening is expected below 30 K. The possible reason for this discrepancy will be discussed below under Sec. V A. To compare the experimental data of Fig. 1 with theory for vibronic broadening effects,[1] it might be more appropriate to regard the 30-K curve as the proper low-temperature reference. Thus, if we subtract from the experimental data (for $T > 30$ K) the corresponding values for 30 K, the additional broadening should be explained by CC phonon absorption.[1] This is illustrated in Fig. 2, where we have plotted $\sigma^0_{p1}(h\nu)$, with the 30 K saturation background subtracted, against inverse temperature for five different photon energies below 1.45 eV. The activation energy for this tailing below 100 K is found to be 19± 2 meV for all photon energies. This is in excellent agreement with expectations from the theory presented in Part I,[1] since only the 19-meV phonon mode (and not the 48-meV one) is important in absorption below 100 K. We therefore conclude that the observations of the edge broadening of $\sigma^0_{p1}(h\nu)$ below 100 K can be reasonably well described as vibronic phonon broadening if the low temperature effects occurring below 30 K are disregarded.

In Fig. 3 are shown additional data of edge

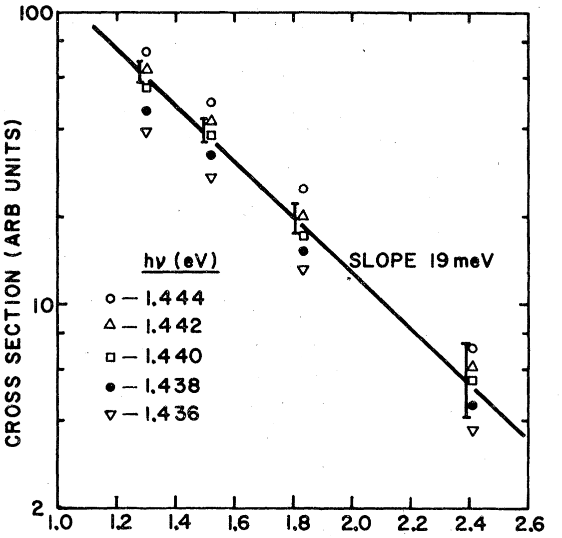

FIG. 2. Logarithmic plot of the σ_{p1}^0 cross sections for different photon energies around 1.44 eV against inverse temperature. The σ_{p1}^0 data have been corrected for the rapid low-temperature broadening below 30 K.

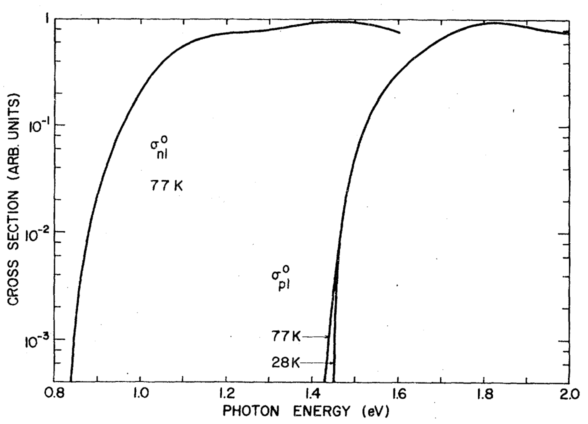

FIG. 4. $\sigma_{n1}^0(h\nu)$ and $\sigma_{p1}^0(h\nu)$ plotted on the same scale to illustrate the amount of phonon broadening to be expected for $\sigma_{n1}^0(h\nu)$ below 77 K.

broadening of $\sigma_{p1}^0(h\nu)$ over a wider photon energy region and extended from low temperatures up to room temperature. The experimental data at each temperature are also here compared with a theoretical curve obtained from convolution of the low-temperature $\sigma_{p1,\mathrm{el}}^0(h\nu)$ electronic spectrum [Eq. (9) in Ref. 1]. We conclude from Fig. 3 that the theoretical cross sections predicted from low-temperature CC phonon interaction data broaden with temperature similarly to those experimentally measured. At the lowest energies, however, the experimental broadening of $\sigma_{p1}^0(h\nu)$ at $T > 100$ K seems to be about 15% larger than expected.

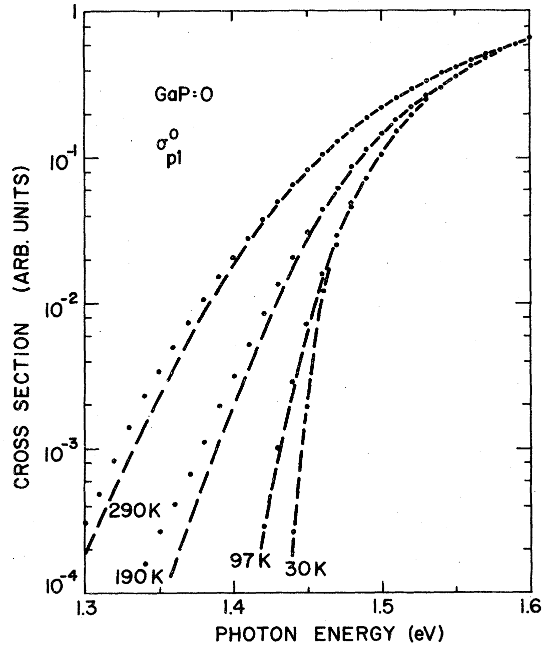

FIG. 3. Logarithmic plot of $\sigma_{p1}^0(h\nu)$ for $T = 30$ K, 97 K, 190 K, and 290 K, below 1.6 eV. The theoretical curves are convoluted spectra according to Eq. (9) in Ref. 1. They are shifted 1 meV (97 K), 7 meV (190 K), and 34 meV (290 K), respectively, to give the best fit.

The corresponding comparison between experimental and theoretical data for CC phonon broadening with temperature is more difficult for $\sigma_{n1}^0(h\nu)$, for experimental reasons. We could measure $\sigma_{n1}^0(h\nu)$ with high accuracy (≥ 3 orders of magnitude at the edge) only in the range 70–175 K, since the PLQ method[1] was less sensitive for other temperatures. But interesting effects of broadening of the $\sigma_{n1}^0(h\nu)$ edge region are observed already from the 77-K data in Fig. 4. If we compare with the behavior of the $\sigma_{p1}^0(h\nu)$-edge also shown in Fig. 4 over the same scale, we conclude that very little vibronic broadening is to be expected for $\sigma_{n1}^0(h\nu)$ between 0 and 77 K over the upper three orders of magnitude. Experimentally, we observe a very strong tail on $\sigma_{n1}^0(h\nu)$ at 77 K, in fact, the lowest measured point falls below 0.840 eV. The known value of the ionization threshold (~0.89 eV at this temperature[7,8]) occurs high up on the edge, at about 5% of the maximum value of $\sigma_{n1}^0(h\nu)$ (Fig.4), and therefore at least the lowest order of magnitude shown in Fig. 4 falls below the electronic ionization limit to conduction-band states. We must conclude that the electronic cross section in this case starts off well below the ionization limit of the 0.89-eV state. This is not too surprising, since excited states close to the conduction band are expected and also previously observed[9] for the O center. At 77 K, we do not expect to resolve any discrete states because of phonon broadening. Further in our PLQ measurements, it is reasonable to assume that electrons excited to shallow excited states ionize or tunnel to shallow traps much faster than they are recaptured into the O ground state. We conclude that the shape of such photoionization curves (each at low temperature) is not very useful for accurate evaluation of the deep-level binding energy, since the ionization threshold is not prominent on the background induced by discrete excited states.

In Fig. 5 are shown the experimental data for the edge region of $\sigma_{n1}^0(h\nu)$ at three different temperatures 77 K, 145 K, and 175 K. The full lines are the theoretical curves from convolution with the phonon line shape from luminescence.[4] The $\sigma_{\rm el}$ was chosen to fit the 77-K cross section, and the shift to fit the data determines the temperature variation of the binding energy (Sec. III). Clearly the theoretically predicted curve for $\sigma_{n1}^0(h\nu)$ at 145 and 175 K account very well for the broadening of the edge.

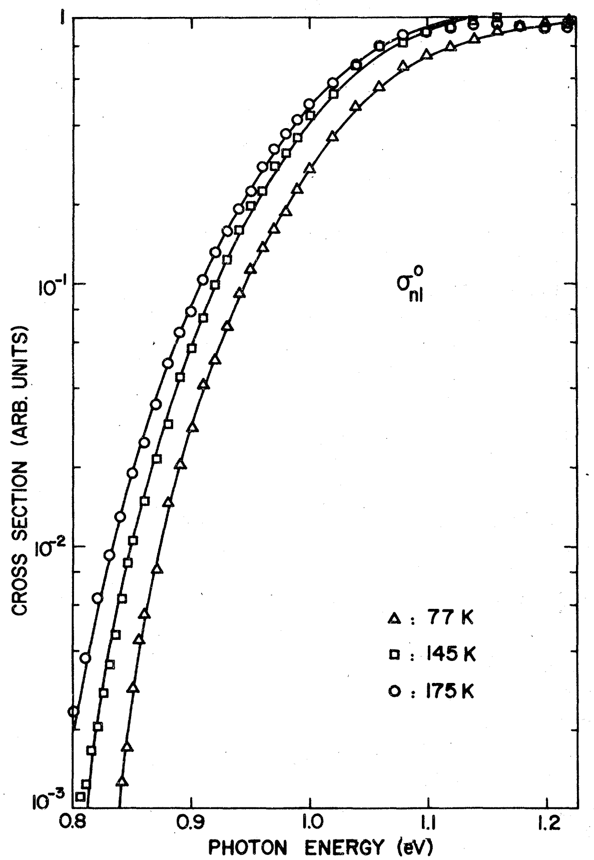

FIG. 5. Logarithmic plot of $\sigma_{n1}^0(h\nu)$ from PLQ measurement. The curves are convoluted theoretical curves. They are shifted 15 meV (145 K) and 26 meV (175 K), respectively, to give the best fit.

III. TEMPERATURE DEPENDENCE OF THE DEEP-LEVEL BINDING ENERGY

Temperature-dependent variations in the position of the electronic energy level in the forbidden gap are rather difficult to evaluate from optical spectra in cases of appreciable phonon coupling (lattice relaxation) upon change of charge state of the center. In this case, one must have a reliable measure of the shift of the electronic part of the cross section with temperature. For the one-electron O state in GaP we have shown in Part I that the electronic threshold of $\sigma_{p1}^0(h\nu)$, as well as its vibronic phonon replicas at higher photon energies, can be directly observed at low temperatures.[1] In Fig. 6, we show experimental data for $\sigma_{p1}^0(h\nu)$ measured with the PLE technique,[1] extended up to 175 K. At this temperature, phonon replicas could still be discerned. In Fig. 6, the derivative of $\sigma_{p1}^0(h\nu)$ is displayed for clarity. As long as such phonon structure can be directly followed in experimental data, very accurate evaluations of the temperature shift of the electronic level can be made. Thus, it can be observed in Fig. 6, that the temperature shift of the $\sigma_{p1,\rm el}^0(h\nu)$ structure is of the order of 1 to 2 meV up to 110 K and about 3 to 4 meV up to 175 K. (The 175-K set of data are less accurate.) This is to be com-

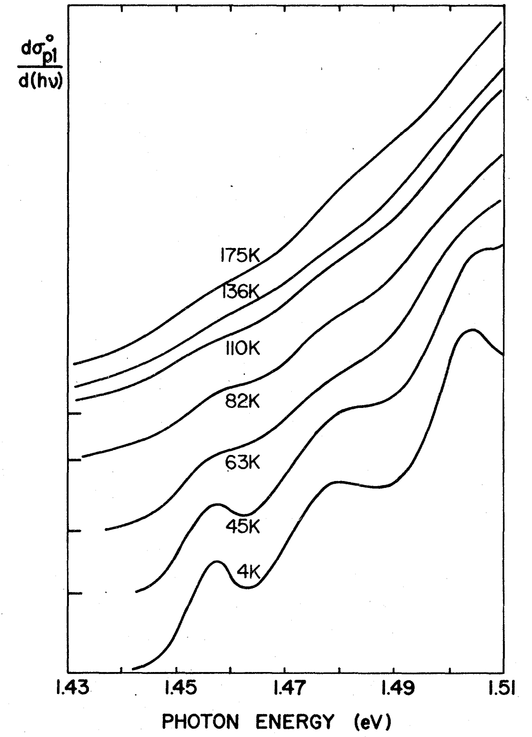

FIG. 6. Derivative spectrum $[d\sigma_{p1}^0(h\nu)/d(h\nu)]$ for different temperatures up to 175 K.

pared with the variation of the band gap up to these temperatures $\Delta E_g(110\text{ K}) \approx 15$ meV and $\Delta E_g(175\text{ K}) \approx 30$ meV.[10–12] Thus, these data indicate that this O level is nearly pinned to the valence band, a conclusion in conflict with some earlier less accurate experimental results,[6,13] and also with theoretical predictions,[5] but in agreement with other experimental data.[8]

Consistent with these results on the shift in $\sigma^0_{p1,el}(h\nu)$ we also observe a correspondingly larger spectral shift with temperature of the $\sigma^0_{n1}(h\nu)$ cross section. In this case, we did not observe any phonon replicas, partly for the reason that they would be extremely difficult to see on a $\sim(h\nu - E)^{3/2}$-dependent rise expected for this photoionization process,[1] but also due to the possible contributions from the excited states discussed above. A crude approach for the evaluation of the temperature shift of $\sigma^0_{n1}(h\nu)$ is to observe the energy shift directly on the experimental curve above 0.9 eV, where vibronic broadening effects on the edge are less important. If we normalize the $\sigma^0_{n1}(h\nu)$ curves in Fig. 5 at say ~1.15 eV, it seems that the shift in binding energy with temperature is ~30 meV between 77 and 175 K, i.e., a slightly larger shift than for the band gap (which is obviously incorrect). This example shows, that such a procedure of directly comparing experimental curves taken at different temperatures to evaluate the shift of the discrete energy level is misleading for centers showing appreciable coupling to the lattice. One reason for this is that a spectral broadening is induced from CC phonon convolution even in the saturated region of the spectrum.[1] Another reason for an anomalous behavior in this particular case is that the measured cross section appears to consist of more than one component with different temperature-dependent strengths (see below under Sec. VI and Sec. V C).

The proper procedure to evaluate the shift of the discrete level with temperature is to compare the experimental cross sections at each temperature with corresponding theoretical curves, computed by convolution of an electronic cross section with an adequate phonon line-shape function.[1] At present, the accuracy in predicting from theory a good electronic spectrum for an optical cross section is rather limited. Therefore, it is important in this procedure to use the electronic cross section evaluated directly by deconvolution of low-temperature experimental data for the spectral variation of the optical cross section.[1] Convolution of such curves for the temperatures used are also included in Fig. 5. The shift to obtain a best fit to the edge below 0.9 eV is 15 ± 5 meV at 145 K and 26 ± 5 meV at 175 K. These are our best estimates of the corresponding shift of the O-donor level with respect to the conduction band and agree perfectly well with the data from the derivative of σ^0_{p1}. In this fitting (Fig. 5), we have considered only the upper ~2 orders of magnitude of the edge below the saturated region of $\sigma^0_{n1}(h\nu)$. This is a better procedure to use than normalizing the saturated parts of the cross sections, since (as mentioned above) there is a change also in the overall shape of $\sigma^0_{n1}(h\nu)$ with temperature well above the edge (Fig. 5). For instance the spectral shape of $\sigma^0_{n1}(h\nu)$ for 77 and 175 K differ above 1.0 eV, a fact which can also be traced in previous photocapacitance data.[14]

An evaluation of the temperature shift of the $\sigma^0_{p1}(h\nu)$ threshold above 175 K, where the phonon structure could not be observed, can be done in the same way, i.e., by observing the shift of the convoluted low-temperature electronic spectrum (for the temperature in question) necessary to get a best fit to experimental curves. Such curves from PLE measurements at different temperatures are shown in Fig. 7 normalized at the peak. It is apparent from Fig. 7, that such an evaluation in this temperature region is difficult, for the reason that the spectral shape of the experimental

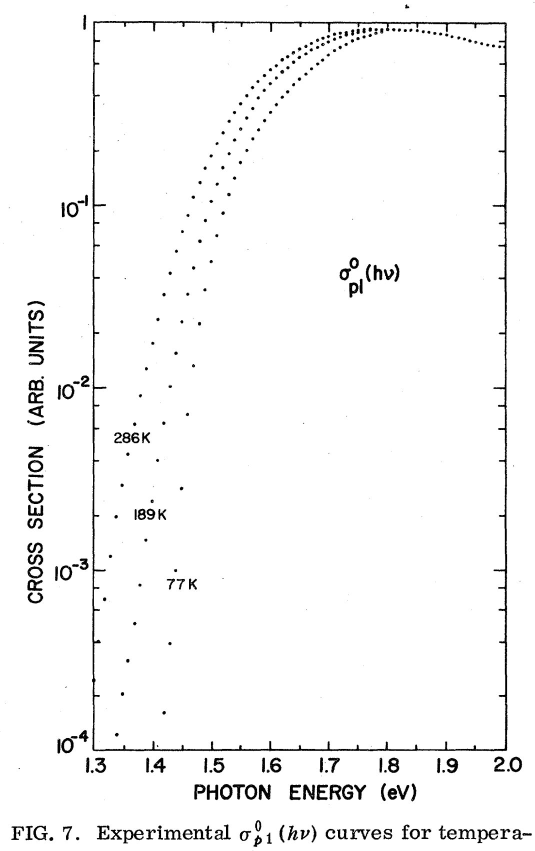

FIG. 7. Experimental $\sigma^0_{p1}(h\nu)$ curves for temperatures up to room temperature.

cross section changes drastically in the photon energy region 1.55–1.8 eV between 77 and 175 K. Therefore, like in the case of $\sigma_{n1}^0(h\nu)$ described above, a fit to the saturated region of the curve is questionable and likely to give a wrong answer. The only use of this region will thus be for a direct measurement of the shift of the photon energy giving maximum cross section. This is of course not an accurate measure of the deep level shift, but suggests a σ_{p1}^0-threshold shift of 15 ± 15 meV up to 190 K and 35 ± 15 meV up to 300 K. Note the big errors from the change in the curve form with temperature. The best way to evaluate the shift of the defect level is again to compare experimental data at a particular temperature T with the generated $\sigma(T,h\nu)$ from the low-temperature deconvoluted $\sigma_{el}(h\nu)$ in the region closest to the edge, neglecting the region close to saturation. This was done in Fig. 3, and the shifts for the σ_{p1} (electronic) thresholds are 1 ± 1 meV up to 97 K, 7 ± 3 meV up to 190 K, 20 ± 5 meV up to 256 K, and 34 ± 5 up to 290 K.

Our measurements of optical cross sections are not carried up to temperatures above room temperature, but we have attempted to extend the evaluation of the temperature shift of the O level with the aid of a set of 400-K photocapacitance data presented by Henry and Lang.[14] Because the broadening of the edge in these experiments is dominated by effects other than phonon broadening, an evaluation from these data cannot be very accurate. A crude evaluation gives for $\sigma_{p1}^0(h\nu)$ a shift up to 400 K of 50 ± 20 meV. A similar comparison based on the $\sigma_{n1}^0(h\nu)$ data gives an apparent shift of 60 ± 20 meV.

In Fig. 8, we summarize our results for the temperature variation of the position of the one-electron 0.9-eV O level in the gap. It is clear from these data that this level is approximately pinned to the valence band below 175 K. Above 175 K, the band-gap shrinkage starts to become more equally shared between the two distances E_i and $E_g - E_i$ between the deep level (of binding energy E_i) and the band edges. It is encouraging to observe that within estimated experimental errors the data for ΔE_i and $\Delta(E_g - E_i)$ add up to the known value of the band-gap shrinkage ΔE_g at all temperatures; a necessary criterion for a correct result. These data will be discussed in more detail, in comparison with previous experimental and theoretical results, under Sec. V B.

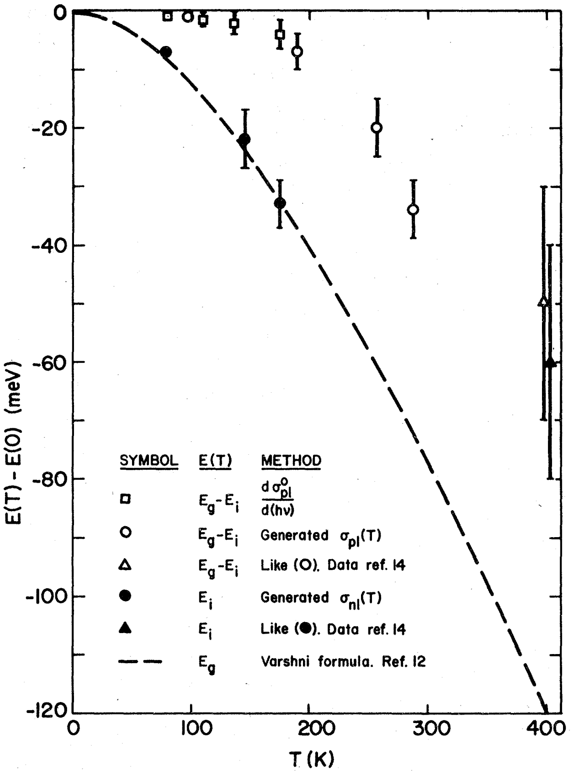

FIG. 8. Experimental results for the temperature dependence of the threshold energies E_i and $E_g - E_i$ from the structure in $[d\sigma_{p1}^0/d(h\nu)]$ and from the convolution procedure to generate $\sigma_{p1}^0(h\nu,T)$ and $\sigma_{n1}^0(h\nu,T)$. The dashed curve is the Varshni formula for the variation of the bandgap with parameters from Thurmond, Ref. 12.

IV. TEMPERATURE VARIATION OF THE SPECTRAL DEPENDENCE OF ELECTRONIC CROSS SECTIONS

As it has appeared in different parts of the previous description of experimental data, the usual assumption that the electronic part of the optical cross section for an impurity level is essentially independent of temperature (apart from a possible rigid shift) is not valid for GaP : O, judged from our PLE data. This fact was not revealed by previous investigations,[2,13,14] partly due to a lower sensitivity in spectral measurements, but also due to a less detailed analysis of data neglecting the lattice-relaxation effects. Dishman and Di Domenico actually did observe a change in slope of the $\sigma_{p1}^0(h\nu)$ edge at low temperatures, but they did not explore the possible origin of this effect.[15]

In Fig. 9 are shown three different experimental σ_{p1}^0 cross sections at 1.5, 4.2, and 30 K, measured by PLE technique, showing substantial spectral differences up to 1.8 eV. The main peak in $\sigma_{p1}^0(h\nu)$ occurs at ~1.8 eV, but it turns out that a second peak at about 1.65 eV becomes more and more dominant as the temperature is lowered below ~30 K. It was established that the presence of two spectral peaks was not an artifact of the experimental (PLE) measuring technique; the above-mentioned spectral contributions have been found

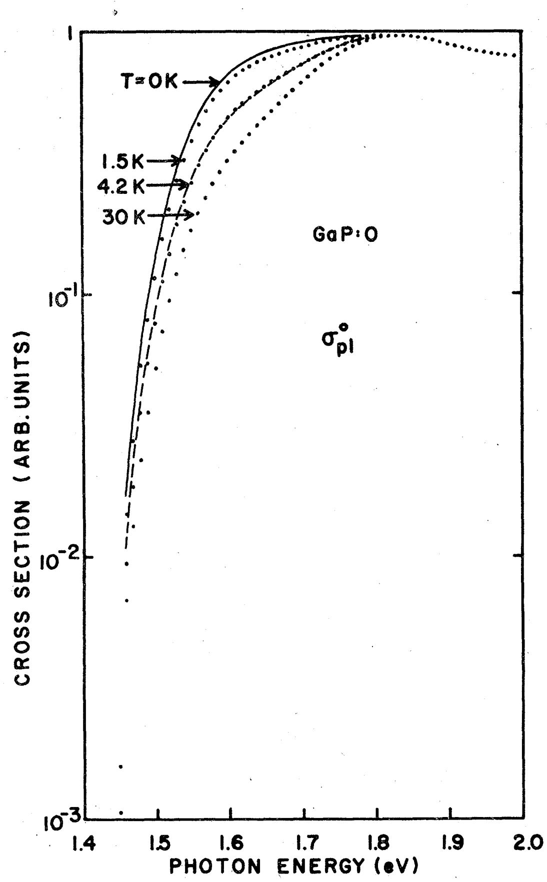

FIG. 9. Logarithmic plot of experimental $\sigma^0_{p1}(h\nu)$ cross sections for $T=1.5$, 4.2, and 30 K. The dashed curve is the generated 4.2-K curve and the full curve is the expected curve for $T=0$ K.

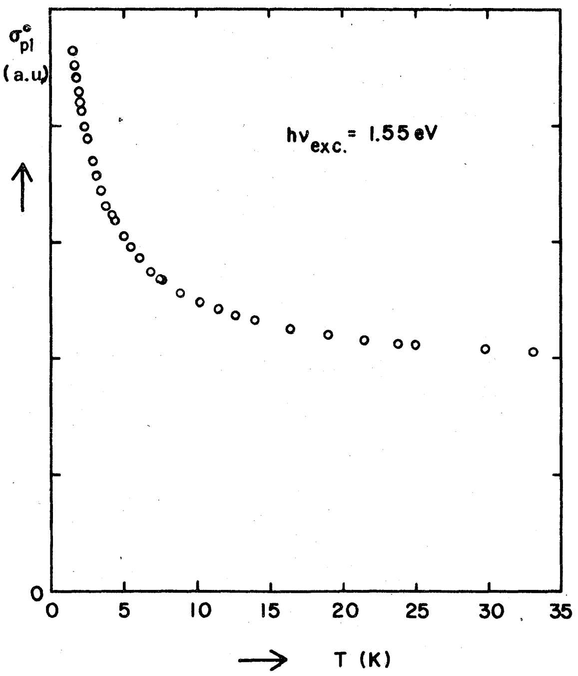

FIG. 10. Linear plot of σ^0_{p1} ($h\nu=1.55$ eV) against temperature.

to be exactly the same in data taken by photocapacitance and junction photocurrent[16] techniques at 77 K. The temperature dependence of the extra spectral contribution peaking at ~1.65 eV was monitored in the PLE experiment (selecting $h\nu=1.55$ eV), and the result is shown in Fig. 10. It is apparent that the process responsible for the peak at 1.65 eV becomes very prominent at the very lowest temperatures, a behavior indicating the presence of a thermal quenching process. The spectral dependence of this extra temperature-dependent contribution to $\sigma^0_{p1}(h\nu)$ can be extracted separately by measuring curves such as those in Fig. 10 at a number of photon energies, and observing the variation of the temperature-dependent part with photon energy. The result of such an evaluation is shown in Fig. 11. It appears that this temperature-dependent part of $\sigma^0_{p1}(h\nu)$ peaks at ~1.63 eV with a half-width of ~0.2 eV. Its overall shape resembles very much the Poisson distribution expected for low-temperature optical cross sections with moderate CC phonon interaction.

If we deconvolute the experimental cross sections in Fig. 9 (using the formalism of Ref. 1), the development of this extra electronic peak at the lowest temperature is very evident, Fig. 12. It seems that the temperature-dependent part of the cross section peaks at ~1.55 eV, only ~100 meV from the threshold. The main (temperature independent) part of $\sigma^0_{p1,\mathrm{el}}(h\nu)$ peaks at ~1.72 eV. It

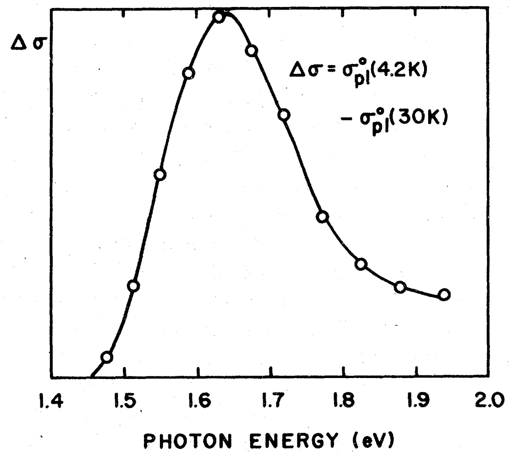

FIG. 11. Plot of the difference between σ^0_{p1} ($h\nu$) at two temperatures to illustrate the spectral variation of the temperature dependence.

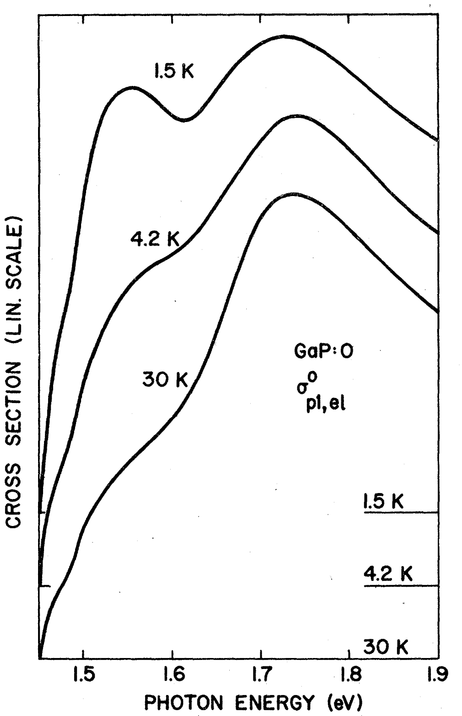

FIG. 12. $\sigma^0_{p1,el}$ for different low temperatures plotted linearly against $h\nu$.

should be noted that the electronic cross sections in Fig. 12, which are the relevant ones for comparison with theoretical models for the electronic excitation process for the deep level, have quite a different spectral dependence from the observed experimental data (Fig. 9). This fact has been overlooked in previous theoretical studies of the spectral behavior of GaP:O cross sections.[17]

From the data just described it is apparent that the most drastic changes in the $\sigma^0_{p1,el}(h\nu)$ spectrum occur below 30 K, in the region 30–77 K the spectral shape stays essentially constant. However, as we noted above in the description of the O-level shift, a definite change in character occurs for the experimental cross section $\sigma^0_{p1}(h\nu)$ between 1.6 and 1.8 eV for temperatures in the range 77–175 K (see Fig. 7). These changes can most easily be explained as a corresponding spectral change in the electronic cross section. Since a direct deconvolution of experimental cross sections at elevated temperatures requires a very complicated formalism, we have adopted the simpler procedure of convolution of electronic trial spectra. Above 77 K, the near threshold peak of $\sigma^0_{p1,el}(h\nu)$ again gains in relative importance compared to the main 1.73-eV peak. While the temperature dependence of the spectral shape below 30 K can be shown to be restricted to the narrow near-edge contribution, we have not established whether the near-edge peak rises again above 77 K, or if the 1.73-eV peak decreases in magnitude instead.

The electronic cross section $\sigma^0_{n1,el}(h\nu)$ corresponding to the measured $\sigma^0_{n1}(h\nu)$ PLQ spectra shown above could not be evaluated accurately by deconvolution, for the reason that the PLQ measurements of sufficient sensitivity could only be carried down to 70 K. We have already noted in our discussion of spectral broadening of $\sigma^0_{n1}(h\nu)$, that excited states might determine a sizeable part of the rise in $\sigma^0_{n1}(h\nu)$ close to the photoionization threshold. However, (as already mentioned) it can be concluded from the spectra in Fig. 5, that in addition to the importance of excited states there are spectral changes in the region $h\nu \geq 1.0$ eV of the same order of magnitude as those observed for $\sigma^0_{p1}(h\nu)$ (see above). These variations have been observed also in photocapacitance[14,16] and photoconductivity[16] data. Consequently, both $\sigma^0_{p1}(h\nu)$ and $\sigma^0_{n1}(h\nu)$ data suggest that we are facing a more complex electronic structure for the one-electron GaP:O state, than previously assumed.[9,17]

V. DISCUSSION

A. Broadening effects on optical cross sections

As it has appeared from our experimental data on optical cross sections for GaP:O, it is very important to recognize the presence of different broadening effects for a proper evaluation of both electronic properties and lattice-relaxation phenomena for a deep impurity state. In Ref. 1, Fig. 3, we have shown that the electric field in a *p-n* junction does remarkably influence the low-energy edge of the optical cross section $\sigma^0_{p1}(h\nu)$ for GaP:O, actually the electric field broadening in this case was found to be a larger effect than the broadening of the edge caused by CC phonon absorption (lattice relaxation). Additional evidence for electric field induced broadening of the optical cross sections for the GaP:O case has recently been observed in *p-n*-junction measurements with different values of reverse bias.[16] Similar quite large effects of electric fields on thermal emission rates (normally used for evaluation of carrier capture cross sections for a center) have been observed for the Zn-O center in GaP from transient capacitance measurements on *p-n* junctions.[18] Such *p-n*-junction or Schottky-barrier measurements have given the overwhelming majority of data presently available on deep center properties[19] such as binding energies, spectral distribution of optical cross sections and capture cross sections. The conclusion is that unless the junction electric field is proved to have a negligible effect for the center under study, these measurement techniques may be unreliable for evaluation of bulk properties.

The physical effect responsible for the electric field induced broadening of optical cross sections can be explained as a variety of the so-called Franz-Keldysh effects previously studied for fundamental interband transitions.[20–22] To our knowledge this effect has not been experimentally studied for the case of optical cross sections for impurity centers in semiconductors.

We have demonstrated above under Sec. II that for measurements performed on bulk material in the absence of high electric fields the spectral broadening of optical cross sections is indeed dominated by the most obvious mechanism, i.e., absorption of CC phonon quanta, below the edge of the electronic cross section. This effect explains the magnitude of the observed broadening between 30 K and room temperature for our GaP : O data. The excess broadening (~15%) is slightly larger than the possible error in the determination of parameters for CC phonon interaction,[1,4] indicating a weak additional broadening process. This extra broadening could be induced by the electric field from randomly distributed impurities or from a slow variation of the phonon coupling parameters with temperature.

A different broadening behavior is observed at temperatures below 30 K. The relatively strong broadening below 1.445 eV in this temperature region shown in Fig. 1 cannot at all be fitted into the scheme of CC phonon absorption with phonon modes of energy $\geqslant 19$ meV.[1,4] This effect seems to occur over a very narrow temperature range, and appears to saturate around 30 K. It is important to note that the curves in Fig. 1 are normalized at the ~1.46-eV shoulder, where $\sigma^0_{p1}(h\nu)$ actually has a strongly temperature-dependent magnitude (Fig. 9). Therefore a different (weaker) variation in magnitude with temperature of the tail region relative to the main 1.46-eV shoulder would contribute to the observed broadening behavior below 30 K. The origin of this complicated broadening effect is presently unclear. Similar broadening phenomena are observed in the luminescence spectra for the O donor in the same temperature range. In Fig. 13 is shown a plot of the no-phonon peak of the O-Zn pair recombination studied at different temperatures below 35 K. As in the $\sigma^0_{p1}(h\nu)$ spectrum, only minor broadening is observed here below 20 K, but over the range 20–30 K a drastic broadening occurs. Such a broadening effect starting up within a fairly narrow temperature region could be a contribution from a range of very low-energy (~1 meV) acoustic phonons to the line-shape function of CC phonon interaction in $\sigma^0_{p1}(h\nu)$ as well as in luminescence. Actually, one usually observes a featureless background in discrete distant pair luminescence spectra.[23] This effect might be due to a weak interaction with a rather low-energy phonon spectrum. At higher temperature, this broadening would be of minor importance compared to the one induced by the main larger CC phonon modes.

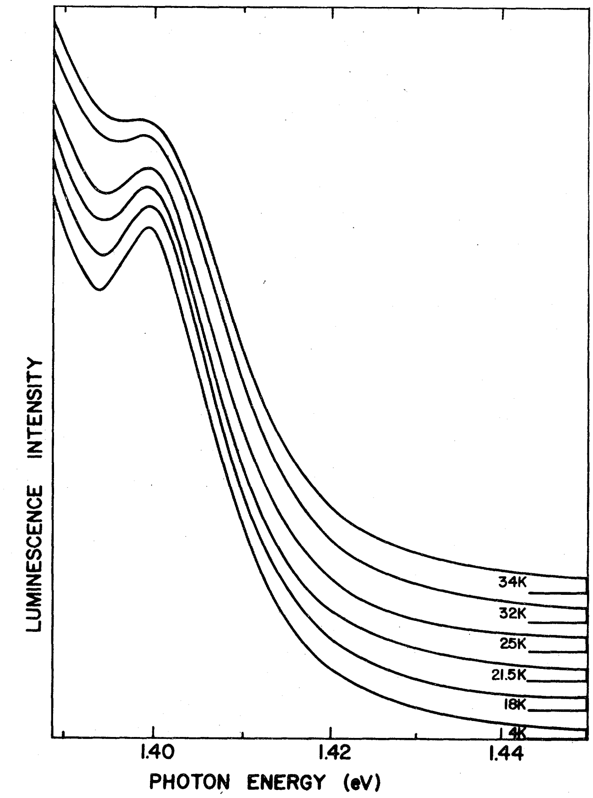

FIG. 13. Temperature variation of the line shape in the donor-acceptor pair recombination for GaP:O, Zn showing broadening that starts around 20 K.

B. Temperature shift of the deep-level position

The general background obtained from previous research efforts in this field is incomplete and partly confusing. Many conclusions drawn in the literature from the few measurements that exist on temperature variation of deep impurity level binding energies in semiconductors seem to be fairly unreliable. Different methods of measuring such temperature variations have given strikingly different results as, e.g., the Au^- center in Si.[24,25] We feel the most foolproof way of determining such shifts is by evaluating accurate measurements of the spectral behavior of optical cross sections for the center at different temperatures. As we have shown such spectra are broadened by the lattice-relaxation effects, and therefore a direct comparison of experimental spectra taken at different temperatures is adequate only when the no-phonon part of the spectrum is clearly observable. This was done in our case for the first time, in the temperature range $T < 175$ K for O in GaP. When the phonon structure cannot be resolved, evaluation of the shift of the deep level based directly on comparison between experimental spectra taken at different temperatures is often inadequate. The procedure we have used involves the computation of a theoretical spectrum at each temperature from a knowledge of the spectral behavior of the electronic cross section (evaluated at the lowest temperatures) and parameters for phonon interaction.[1] The rigid shift necessary to obtain overlap between such computed convoluted curves and the measured experimental spectrum is the most reliable measure of the deep-level shift with temperature in the absence of resolved phonon replica.[26]

Earlier less accurate evaluations of the shift of the deep O level with temperature give a somewhat confusing picture. From luminescence data, Dishman has concluded that the level is pinned to the valence band below 80 K[8]; measurements at higher temperatures reported by Bhargava lead to the same conclusion.[27] Direct evaluation of shifts observed for optical cross sections by Braun and Grimmeiss[13] lead to the conclusion that the level was pinned to the valence band above room temperature [at lower temperatures their evaluated optical thresholds for $\sigma_{n1}^0(h\nu)$ and $\sigma_{p1}^0(h\nu)$ did not add up to the band gap]. The most recent evaluation of the shift of the O level with temperature was reported by Kopylov and Pikhtin,[6] who claimed that the O level was essentially pinned to the conduction band below room temperature. These authors made an effort to include lattice-relaxation effects in their analysis, but they have not based their conclusions on any analysis of spectra measured at different temperatures. Rather they use a model electronic spectrum which they convolute and fit to a quite incorrect experimental spectrum obtained from photoconductivity data[28] (peaking at about 1.6 eV instead of the correct value ~1.81 eV[1]). Further, they obtain the O binding energy at room temperature by subtracting the Franck-Condon shift $\Delta = 0.09$ eV from their electronic edge $E_0 = 1.46$ eV to obtain E_D as $E_D = E_g - E_0 + \Delta = 0.89$ eV at room temperature. Obviously this is a grossly inadequate procedure, since electronic (zero-phonon) thresholds have to add up to the band gap at all temperatures.

If we therefore disregard the results from Ref. 6, previous measurements seem to indicate that the level is pinned to the valence band. Our accurate data reveal that this is approximately true. The three different ways we have used to evaluate the no-phonon binding energy as a function of temperature gave for $T \leqslant 175$ K (see Fig. 8) the firm conclusion that $\Delta E_i \approx (0.90 \pm 0.10) \times \Delta E_g$. At higher temperatures (200–400 K) $\Delta E_i / \Delta E_g$ is no longer a constant and the band-gap shrinkage seems to become more equally divided between the two energy gaps.

Recent theoretical developments on the temperature shift of defect-related electronic levels within the band gap of a semiconductor indicate that accurate experimental data give a great deal of useful information on physical properties of the defect state.[5] For shallow impurity levels which can be described with a Coulombic potential with a moderate central cell correction, the bound carrier has a very delocalized wave function, and therefore it has almost the same effect as a free carrier on lattice modes. Therefore the "mode softening" believed to be responsible for temperature variations of impurity binding energies[5] should be small, and the binding energy of a carrier in such a shallow bound state is expected to stay constant with varying temperatures. This idea seems to be confirmed by ir-absorption data on shallow levels.[29] In cases where central cell corrections to the defect binding energy are large, the prediction of the shift of the energy level in the band gap with temperature is less obvious. In Ref. 5, a simple trial wave function for the O-donor state was used to estimate the temperature shift of this energy level. The result was that the O-donor level binding energy E_i was expected to vary little with temperature with respect to the conduction band, and essentially the full amount $\Delta E_g(T)$ (= temperature variation at the band gap E_g) with respect to the valence band.

These theoretical predictions clearly disagree with our accurate experimental data. We believe that within the framework of Ref. 5 this discrepancy arises from the choice of impurity wave function. It appears that a more localized wave function than the one used in Ref. 5 would be appropriate. The proper choice of wave function for the one-electron O state is indeed not clear at the moment, probably contributions from valence bands must also be included in an adequate description. The observation of a temperature-dependent ratio $(\Delta E_i / \Delta E_g)$ for $T > 175$ K is interesting, since such dependence has not been predicted by existing theories.

C. Temperature dependence of the spectral distribution of electronic optical cross sections

As it became apparent from the description of experimental data under Sec. IV above, quite unexpected temperature variations of the electronic part of optical cross sections are present in the case of O in GaP. From the data of Figs. 9–12 it is apparent that the optical cross section $\sigma^0_{p1}(h\nu)$, for which the most detailed experimental data were obtained, is composed of two different parts, one of which (closest to the threshold) has a temperature-dependent strength (Fig. 10). Such dramatic temperature effects have not previously been described for optical cross sections in semiconductors.

Changes with temperature in luminescence output for a particular excitation photon energy can be due to a corresponding change in the optical cross section for the center, or alternatively to a change in the radiative to nonradiative branching ratio for the measured O recombination. Experimentally, we know that the detected quantity in these PLE spectra is always the O-related luminescence[3,4] between the 0.9-eV O donor and the valence band (or shallow acceptor states at low temperatures). This was ascertained by the result that the same luminescence spectrum was obtained for a number of excitation photon energies between 1.45 and 1.8 eV.

We have observed that the luminescence intensity is almost temperature independent up to 77 K for exciting photon energies at the main peak (~1.8 eV) of the optical cross section (Fig. 9). This indicates that only the near-edge part of the σ^0_{p1} cross section (Fig. 11) is temperature dependent, while the main part peaking at ~1.8 eV is not. As a complementary experiment we have studied the shallow donor-acceptor ($S_P - Zn_{Ga}$) pair recombination peaking at ~5700 Å, excited with infrared light via the oxygen donor. For the same excitation photon energy, the (two-step) excitation of this green luminescence has a similar temperature dependence to the infrared oxygen luminescence. This result suggests that the temperature dependence occurs either in the σ^0_{p1}-excitation process or in the total lifetime of the neutral state, and not in the radiative efficiency for the recombination following the excitation. From this we conclude that thermalization effects should be searched for either in the initial state for the near-edge σ^0_{p1} transition or in a nonradiative recombination process for the final state reached in the optical excitation. Since the two different parts of the PLE spectrum produce the same neutral oxygen ground state (detected in luminescence) we find it difficult to explain the different temperature dependence for these two parts as being due to nonradiative recombination processes.

The spectral behavior of the two different parts of $\sigma^0_{p1}(h\nu)$ can be extracted from a careful inspection of PLE curves such as those in Fig. 9. It is found that the difference in spectral shape due to overlap between the temperature-dependent part and the temperature-independent part is constant (in a log-plot) below the photon energy employed for Fig. 10. This suggests that the temperature-independent part of $\sigma^0_{p1}(h\nu)$ is negligible in this energy region. Therefore, a fairly straightforward separation procedure based on the knowledge of the temperature variation of the strength of the near-edge part can be applied. (The present description neglects minor broadening effects of the edges.) Thus, we consider $\sigma^0_{p1}(h\nu, T)$ as composed of

$$\sigma^0_{p1}(h\nu, T) = \sigma^0_{p1,A}(h\nu, T) + \sigma^0_{p1,B}(h\nu) , \qquad (1)$$

where $\sigma^0_{p1,B}(h\nu)$ is the temperature-independent part of the cross section. The temperature dependence of $\sigma^0_{p1,A}(h\nu, T)$ is well described by an expression of the type

$$\sigma^0_{p1,A}(h\nu, T) = \sigma^0_{p1,A}(h\nu, 0)[1/(1 + Ce^{-\Delta/kT})] \qquad (2)$$

as shown in Fig. 14 (employing the data in Fig. 10). The resulting values are $\Delta = 0.40 \pm 0.05$ meV and $C = 1.68 \pm 0.10$. The estimated uncertainties in

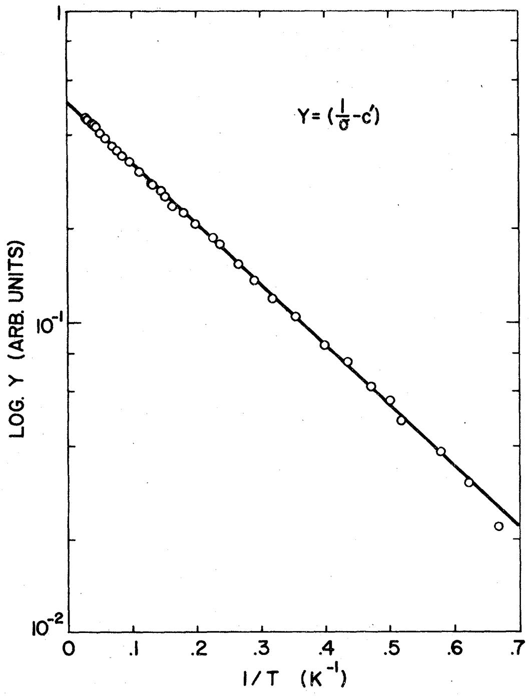

FIG. 14. Logarithmic plot of $Y = 1/\sigma^0_{p1} - c'$ against $1/T$ to test model with a split state where the upper state does not contribute to σ^0_{p1}. The photon energy used is 1.55 eV.

Δ and C are obtained from the spread in these parameters evaluated from plots like Fig. 14 for a number of different photon energies between 1.48 and 1.55 eV.

Without a detailed knowledge of the origin of the splitting Δ, it can be worth noting that C is very close to the rational number $\frac{5}{3}$. With a picture of a splitting of the initial state for the σ_{p1}^0 transition, where only the lowest state (of degeneracy g_1) but not the higher (of degeneracy g_2) is allowed for the dipole transition, Eq. (2) can be written

$$\sigma_A(T)=\sigma_A(0)[g_1/(g_1+g_2e^{-\Delta/kT})].$$

The value found for g_2/g_1 then suggests that we are dealing with two closely spaced sublevels characterized by total angular momentum quantum numbers $J=1$ and 2 from which dipole transitions are allowed only from the $J=1$ component, i.e., to a final state of $J=0$ character. This kind of exchange splitting has been found for excitons bound to isoelectronic centers in GaP.[30,31] The validity of such a two-particle picture for an initial state involving a valence band continuum, is not clear at present.[32]

Using the temperature dependence of Eg. (2) and the two sets of experimental data at 1.5 and 30 K from Fig. 9 (which were not related to each other in absolute magnitude), both curves $\sigma_{p1,A}^0(h\nu)$ and $\sigma_{p1,B}^0(h\nu)$ can easily be computed. The cross sections for two temperatures (like $T_1=1.5$ K and $T_2=30$ K) can be written

$$\sigma(T_1)=c_1[f(T_1)\sigma_A+\sigma_B]\,, \tag{3a}$$

$$\sigma(T_2)=c_2[f(T_2)\sigma_A+\sigma_B]\,, \tag{3b}$$

where we know $f(T)$ from Fig. 14. By shifting the curves (in a log plot) to make the low-energy part (σ_A) the same, we directly get c' in

$$c_1f(T_1)\sigma_A=c'c_2f(T_2)\sigma_A\,. \tag{3c}$$

Hence, we get from Eqs. (3a), (3b), and (3c),

$$\gamma\sigma_A=\sigma(T_1)/f(T_2)-c'\sigma(T_2)/f(T_1)\,, \tag{4a}$$

and

$$\gamma\sigma_B=c'\sigma(T_2)-\sigma(T_1)\,, \tag{4b}$$

where

$$\gamma=c_1[f(T_1)/f(T_2)-1]\,. \tag{4c}$$

The resulting $\sigma_{p1,A}^0$ and $\sigma_{p1,B}^0$ are shown in Fig. 15 and show that indeed the T-independent part $\sigma_{p1,B}^0$ is very weak close to the edge, and has no significant value below ~1.53 eV. The high-energy part of $\sigma_{p1,A}^0$ in Fig. 15 is more uncertain due to subtraction of two large numbers.

As a test of the model we have generated $\sigma_{p1}(h\nu, 4.2\text{ K})$ from Eqs. (1) and (2). The result is shown as the dashed curve in Fig. 9. The full curve in this figure is the expected zero-temperature $\sigma_{p1}^0(h\nu, 0)$ cross section.

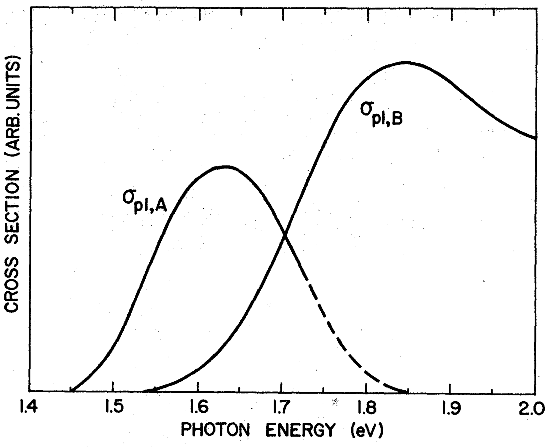

FIG. 15. Cross sections $\sigma_{p1,A}^0(h\nu)$ and $\sigma_{p1,B}^0(h\nu)$ spectrally separated.

As noted above, the two components, $\sigma_{p1,A}^0$ and $\sigma_{p1,B}^0$, of the optical cross section σ_{p1}^0 which we have separated spectrally from their different temperature properties seem to have *different* thresholds in photon energy. In our opinion, the most plausible explanation is a complex behavior of discrete oxygen states so that there is a split-off state situated about 80 ± 20 meV above the ground state (which is at ~0.9 eV from the conduction-band edge at low T).[33] Clearly the existence of both these states, as well as the small splitting producing the temperature dependence, are properties of the same center, the isolated oxygen atom in GaP, since we always find a constant ratio between $\sigma_{p1,A}^0(h\nu)$ and $\sigma_{p1,B}^0(h\nu)$ at a specific temperature for different O-doped samples.

This model of more than one level associated with the one-electron O center would also have consequences for interpretation of other oxygen-related transitions. The experimental observation that the spectral shape of *both* σ_{n1}^0 and σ_{p1}^0 changes with temperature (above 77 K) in our PLE and PLQ data speaks in favor of the picture of more than one deep neutral oxygen state. Some of these spectral variations have also been observed[26] in photocapacitance[2,16] and photoconductivity[16] measurements. The observation in Ref. 27 that the peak of the infrared luminescence (from electrons bound to oxygen recombining with free holes) shifts much less than the band gap for $300 \leqslant T \leqslant 400$ K could probably be explained with excited deep states being thermally populated. At high temperatures, such states will contribute to the luminescence and, thus, make the high-energy side of the emission stronger.

The accuracy of the separation procedure does not allow a detailed evaluation of the $\sigma^0_{p1,B}(h\nu)$ edge, but some qualitative conclusions on the spectral behavior of these cross sections can be drawn on the bases of the model just presented. The shape of $\sigma^0_{p1,A}(h\nu)$ (Fig. 11) is typical for an allowed transition between an s-like bound state and the p-like top of the valence band, where the cross section is expected to peak very close to the edge [see Eq. (4) and Fig. 1 in Ref. 1]. The general appearance of $\sigma^0_{p1,B}(h\nu)$ is actually not much different, this cross section peaks only ~0.3 eV from the threshold (while $\sigma^0_{p1,A}$ peaked ~0.18 eV from the threshold) (Fig. 15). The deconvoluted curves of Fig. 12 reveal that the corresponding electronic curves, $\sigma^0_{p1,A,\mathrm{el}}(h\nu)$ and $\sigma^0_{p1,B,\mathrm{el}}(h\nu)$, peak at ~1.55 eV and ~1.72 eV, respectively, i.e., only 0.10 eV, respectively, 0.20 eV from the edge.[34] This general similarity in appearance suggests that dipole transitions are allowed to both of these one-electron O levels (Fig. 1 of Ref. 1).[35]

VI. CONCLUSIONS

A detailed experimental study of temperature dependence of optical cross sections related to the GaP:O one-electron state has been presented. The evaluation of data gives information on mechanisms for broadening of the edge, the shift of the electronic level within the band gap, and also spectral effects of temperature on electronic cross sections. It is noted that the electric field in a p-n junction can cause a large Franz-Keldysh type broadening effect on the edge of optical cross sections for band-to-impurity transitions. The overall broadening of the edge in our optical bulk data can be well explained as due to absorption of CC phonon quanta in the optical transition, consistent within 15% with the data obtained for phonon energies and coupling strengths from the low-temperature spectra. Below 30 K, an additional broadening process occurs, possibly partly due to very low-energy phonons.

The shift of the electronic level with temperature within the band gap could be studied accurately below 175 K, since the phonon structure from convolution of the electronic spectrum was still observable at these temperatures. At higher temperatures, the shift of the electronic level was established as the rigid shift in energy necessary to obtain overlap between the experimental curve and a theoretically computed curve obtained by proper phonon convolution of the low-temperature electronic spectrum. The results are that the 0.90 eV O level is nearly pinned to the valence band, i.e., $\Delta E_i = (0.90 \pm 0.10)\Delta E_g$ below 175 K. In terms of the theory of Van Vechten and Thurmond[5] this means, that a substantially more localized wave function for the bound state has to be used than the one they assumed.

The most drastic new results are obtained on the spectral behavior of the electronic cross sections. Clearly two different cross sections $\sigma^0_{p1,A}(h\nu)$ and $\sigma^0_{p1,B}(h\nu)$ can be separated, of which $\sigma^0_{p1,B}(h\nu)$ seems to have a higher threshold (~1.53 eV) compared to $\sigma^0_{p1,A}(h\nu)$ which starts at ~1.45 eV.[1] This suggests that the one-electron O center actually has at least two deep states; the well-known ~0.90 eV state and a second state ~80 meV higher up in the band gap. The general shape of the two curves further suggests they both have s character. The temperature dependence of $\sigma^0_{p1,A}(h\nu)$ between 1.5 and 30 K can be explained in terms of a thermal activation energy of 0.4 meV.

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[32] Note, that in this picture the temperature dependence is explained as a population effect, while the magnitude of the cross section comes out temperature independent, as expected.

[33] Note that the treatment of σ_{p1}^0 only separates the temperature-dependent part, $\sigma_{p1,A}^0$, from the temperature-independent part, $\sigma_{p1,B}^0$. Therefore, e.g., an excited level with similar properties as the ground state will be included in $\sigma_{p1,A}^0$.

[34] For this deconvolution we have assumed that the phonon interaction for the $\sigma_{p1,B}^0(h\nu)$ cross section is the same as for $\sigma_{p1,A}^0$. Note that the only case where the details of the phonon interaction have been extracted is for the lowest 0 level (Ref. 4).

[35] The conclusion that the one-electron 0 state appears to have two deep s-like levels is the most obvious way of explaining our experimental data on the spectral variations of $\sigma_{p1}^0(h\nu)$ with temperature. Such behavior, however, is not predicted by general theories for impurity states, where even for a deep level only one deep s state is expected. An alternative explanation of our data associates the $\sigma_{p1,A}^0(h\nu)$ spectrum with the valence-band top, while the $\sigma_{p1,B}^0(h\nu)$ curve is due to transitions from the split-off valence band. The main reason why we reject such an explanation is that we see no way of explaining a different temperature dependence of optical cross sections associated with different subbands near Γ at the GaP valence-band top, when the same defect state is involved.