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Electronic aspects of the optical-absorption spectrum of the $EL2$ defect in GaAs

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As far as its optical properties are concerned, the $EL2$ defect seems to be the same as the isolated As_{Ga} arsenic antisite defect in GaAs. Although it is widely accepted that lattice relaxation plays a role in determining the optical absorption of $EL2$, there are now reasons to question just how much lattice relaxation occurs. As an initial step towards resolving this issue, this paper presents a calculation of the optical absorption of the isolated As_{Ga} defect in which the calculational emphasis is on a realistic description of the electronic states. In this calculation, we ignore lattice relaxation altogether and, consequently, we find neither the experimentally observed zero-phonon line nor the multiphonon replicas. Aside from these and one other interesting discrepancy that can probably be explained by our neglect of lattice coupling, the spectra are reasonably similar to what is observed. One conclusion from the analysis presented here is that the hole cross section for the main donor level of $EL2$ has not been correctly measured in any of the experiments reported to date.

I. BACKGROUND

$EL2$ is a metastable native donor defect in GaAs which has been intensely studied for over a decade now.[1] There are two reasons for the intensity of this study. On the one hand, the defect is important technologically for its role in producing semi-insulating GaAs. On the other, it exhibits an optically driven metastability at low temperature. The challenge to understand both the microscopic structure and composition of this defect, and how the absorption of light causes the defect to transform from its ground state to its metastable state, has been fascinating in its own right.

The amount of experimental information and theoretical interpretation for this defect makes it one of the two most studied deep-level point defects in any material. (The other is the DX center in $Al_xGa_{1-x}As$ alloys.) In spite of all this study, there is still no microscopic model that satisfies all the present interpretations of all the existing experiments. As far as its *optical* properties are concerned, however (including mechanisms for the transformation between the ground and metastable states[2]), the $EL2$ defect seems to be the same as the isolated As_{Ga} arsenic antisite defect in GaAs. The present paper is concerned with calculations of some of the optical properties of the isolated As_{Ga} defect, and for comparison with experiment, we shall refer to optical experiments on $EL2$.

Let us review the optical processes that can occur for an isolated As_{Ga}. The isolated As_{Ga} has a state of A_1 symmetry with an energy roughly midgap. When the A_1 state is doubly occupied, the defect is neutral. The A_1 state can also be singly occupied or empty. It gives rise to two levels, $(+/++)$ at $E_1=E_v+0.54$ eV,[3] and $(0/+)$ at $E_2=E_c-0.742$ eV.[4] As shown in Fig. 1, the two levels give rise to four optical cross sections for transferring electrons between the bands and the levels.

Since the defect can exist in any of three different charge states, let n_0, n_+, and n_{2+} be the concentrations of the neutral, singly ionized, and doubly ionized As_{Ga} defects. These concentrations satisfy the constraint

$$n_0+n_++n_{2+}=N \ , \tag{1.1}$$

where N is the total As_{Ga} concentration. The optical absorption $\alpha(h\nu)$ can then be expressed in terms of the cross sections shown in Fig. 1 as

$$\alpha(h\nu)=(n_0\sigma_{n2}+n_+\sigma_{p2}+n_+\sigma_{n1}+n_{2+}\sigma_{p1}) \ . \tag{1.2}$$

Similarly, the total (positive) charge density associated with this population of defects is, in units of the charge on a hole,

$$Q=n_++2n_{2+} \ . \tag{1.3}$$

The concentrations themselves are determined by N and by kinetic and statistical considerations. At low optical flux, there are four occupation regimes at low temperature. These depend on n_D and n_A, the shallow donor and shallow acceptor concentrations, and on N. The four regimes are characterized as being n-type, semi-insulating with $E_{\rm Fermi}\approx E_2$, semi-insulating with $E_{\rm Fermi}\approx E_1$, and p

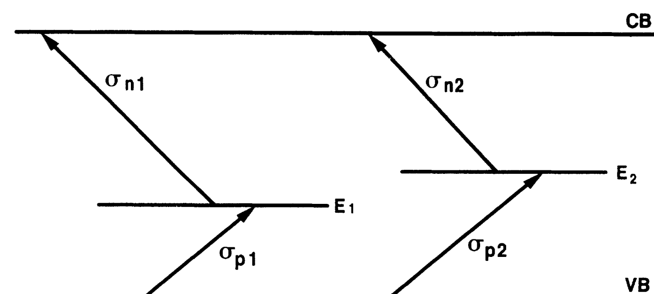

FIG. 1. Diagram defining the two energy levels and the four optical cross sections for transfer of an electron between the A_1 midgap state and the extended valence and conduction bands.

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type. When the optical flux is high enough (optical transitions occurring more rapidly than do spontaneous hole and electron generation, which normally establish equilibrium), then the occupations will depend on the cross sections via the following kinetic equations:

$$\frac{dn_0}{dt}=\Phi(-n_0\sigma_{n2}+n_+\sigma_{p2}) , \quad (1.4a)$$

$$\frac{dn_+}{dt}=\Phi(n_0\sigma_{n2}-n_+\sigma_{p2}-n_+\sigma_{n1}+n_{2+}\sigma_{p1}) , \quad (1.4b)$$

$$\frac{dn_{2+}}{dt}=\Phi(n_+\sigma_{n1}-n_{2+}\sigma_{p1}) . \quad (1.4c)$$

These equations can be solved to give equilibrium concentrations from which the equilibrium absorption or charge density can be evaluated using Eqs. (1.2) or (1.3). Alternatively, they can be solved to give the transient concentrations evolving from some specified initial situation after time-independent light flux Φ has been turned on. In that case, the time-dependent total absorption $\alpha(h\nu)$ or the time-dependent charge density Q can be evaluated by using these transient concentrations in Eq. (1.2) or (1.3).

These considerations give rise to various optical spectroscopic techniques for evaluating the cross sections themselves. As shown by Chantre, Vincent, and Bois,[5] there is an advantage in measuring the initial slope of the capacitance transient (i.e., the initial rate of change of the charge Q) from an initial condition having all defects in the same charge state, for instance, $n_0=N$, $n_+=0$, $n_{2+}=0$. This condition can be obtained by starting with n-type material where $n_D>n_A$. A measurement of the initial dQ/dt, N, and Φ in this case will give σ_{n2}.

Similarly, by starting with p-type material where $(n_A-n_D)>2N$, one can achieve the initial condition $n_0=0$, $n_+=0$, $n_{2+}=N$. A measurement of the initial dQ/dt, N, and Φ in this case will give σ_{p1}. Measurement of the other two cross sections by this technique are much harder to do, and we shall see later that there is reason to doubt the reported results or interpretations.

The electronic structure of the defect is such that if the GaAs forbidden gap were about 0.5 eV larger than it is, there would also be a T_2 bound state associated with the As_{Ga}. As it is, instead of a discrete state, the T_2 state mixes with the other conduction-band states and is broadened into a resonance that shows up in the optical absorption.[6] This resonance is strongly coupled to the lattice, in the sense that an electron excited into this resonance can cause the defect and the nearby atoms to relax to a position of minimum energy, just as if the resonance were indeed a discrete state. We have begun a model theory of optical absorption into a lattice-coupled resonance,[7] which can exhibit a variety of effects. A realistic application of the theory, however, requires input from a realistic calculation of the electronic cross sections. This is the motivation for the calculations to be described in this paper.

This paper presents a calculation of the purely electronic part of the four optical cross sections depicted in Fig. 1. The computational emphasis will be on the realistic description of the electronic states. In this calculation, we ignore lattice relaxation altogether and consequently, we find neither the experimentally observed zero-phonon line nor the multiphonon replicas, nor are we able to calculate the experimentally observed cross section for internal transition.[6] These last will be discussed in some detail in a later section of the paper.

In the next section, we present details of the calculation. In Sec. III, we give our calculated results, and in Sec. IV, we compare the calculated and experimental results. Section V contains a discussion of the role of lattice coupling. Section VI contains a summary, a discussion of our findings, and the implications that follow from them.

II. CALCULATIONAL DETAILS

As Petit, Allan, and Lannoo[8] have shown, a particularly useful expression for the optical absorption associated with transitions between Ψ_L, the bound state of an isolated defect, and the band states of the semiconductor containing the defect is

$$\sigma(h\nu)=-\frac{\beta}{h\nu}\mathrm{Im}\langle\Psi_L|p_zG(E_L\pm h\nu)p_z|\Psi_L\rangle , \quad (2.1a)$$

where Im denotes the imaginary part, E_L is the energy of the bound state, and the sign $+(-)$ denotes transitions to the conduction (valence) band. $G(E)$ is the Green's function for the perturbed crystal. The other symbols are defined by

$$p_z=-i\hbar\frac{\partial}{\partial z} , \quad (2.1b)$$

$$\beta=\frac{4\pi^2e^2\hbar}{m^2cn}\left[\frac{E_{\text{eff}}}{E_0}\right]^2 . \quad (2.1c)$$

The quantity n is the index of refraction, and E_{eff}/E_0 is the so-called local-electric-field enhancement factor. In the absence of a reliable way to calculate this factor of order unity, we shall take it as being equal to $n^{1/2}$, which makes β a materials-independent constant. Our ignorance of E_{eff}/E_0 could result in an uncertainty of perhaps a factor of 10 in the overall amplitude of the cross sections. The error will be the same for all four cross sections, and will be independent of $h\nu$ in the range of interest here.

The Green's function for the perturbed crystal is related to G^0, that of the perfect crystal, by Dyson's equation,

$$G=G^0+G^0VG . \quad (2.2)$$

A general discussion of evaluation of G^0 and the solution of Eq. (2.2) is given in Ref. 9. Briefly, we first solve the local-density approximation (LDA) Kohn-Sham equations self-consistently for the perfect crystal. We use a Gaussian local orbital basis set consisting of 19 orbitals per site; s, p, d, and an additional r^2 function with decay constant $\alpha=0.6$, and longer range s, p, and d functions with $\alpha=0.2$. This set has been selected to yield reasonable results for group-IV elemental and III-V compound semiconductors when compared with converged plane-wave calculations. We employ standard norm-conserving

pseudopotentials and we use the Ceperly-Alder form of electron-gas correlations, as parametrized by Perdew and Zunger. Self-consistency is achieved with 10 **k** points in an irreducible portion of the Brillouin zone.

The 38-orbital-per-cell set gives an LDA gap for GaAs of $E_g = 0.89$ eV at Γ, 1.1 eV at *X*, and 1.17 eV at *L*. A **k**-dependent "scissors-operator" adjustment (described below and, in more detail, in the Appendix) is subsequently carried out prior to the evaluation of the Green's function.

For the orbital expansion in G^0 and G, we retain the As_{Ga} antisite, its 4 As neighbors, and their 12 Ga neighbors, 3 atomic shells in all with a total of 323 orbitals. Since we are interested in details of the optical cross-sections near threshold, we use a fine **k**-space sampling grid, corresponding to 615 **k** points in the irreducible portion of the Brillouin zone. This gives an energy resolution of ≈ 0.03 eV. The symmetry of the system is the T_d point group: no lattice distortions are considered.

Dyson's equation (2.2) is iterated to self-consistency using a complex contour integration scheme for evaluating the charge density in the fully occupied valence band, and occupying the A_1 gap state with 0, 1, or 2 electrons corresponding to the $++$, the $+$, or the 0 charge state of the antisite. The optical cross sections are then evaluated using analytic dipole matrix elements between the Gaussian orbitals, and numerical sums over the products of optical matrix elements and Green's-function matrix elements.

We now discuss certain new features of the present calculation. Self-consistent LDA calculations systematically underestimate the band gaps of semiconductors.[10] At the present time, the only fully satisfactory way to remedy this problem is to perform quasiparticle calculations.[11] It has been found that quasiparticle wave functions agree closely with those calculated by LDA, even for such localized states as those that appear at the surface of a semiconductor.[12] Applying this finding to Eq. (2.1a), the cross section can be accurately calculated using LDA wave functions, provided that the energy of the bound state and those of the extended states (as contained in the Green's function) are given correctly. There are limitations on what we can do calculationally in the self-consistent defect problem. For this reason, we shall use LDA wave functions and the LDA Green's function to calculate the cross section, but we shall make three empirical adjustments to the energies of the states involved. The first is an adjustment to the energy of the states of the perfect crystal to overcome the problem of the incorrect LDA band gap. For this purpose, we employ the **k**-dependent scissors operator, a generalization of the so-called scissors operator[13] we introduced into LDA defect calculations.[14] (The specific **k**-dependent form we use here is described in the Appendix.) The second adjustment is a slight scaling of the overall strength of the defect potential. The purpose of this scaling is to allow us to study how the A_1-T_2 transition gains intensity and sharpens up when the T_2 final state moves downward through the lower part of the conduction band as it might do under the influence of external parameters, e.g., hydrostatic pressure. (More accurately, the T_2 state moves up slightly relative to the valence-band maximum, but the conduction-band minimum moves up so much more rapidly that the net effect is to move T_2 state into the gap.) The last adjustment is to the energy of the A_1 localized state. We set that energy to its experimental value (E_1 or E_2) because we recognize that simply using the **k**-dependent scissors operator while adjusting the strength of the defect potential alters the calculated energy of the A_1 state. None of the conclusions we reach are dependent on these adjustments; they are simply calculational conveniences allowing us to carry out this study.

III. CALCULATED RESULTS

One of the main points made in the paper of Petit, Allan, and Lannoo[8] was that the presence of a point defect in the semiconductor has two strong effects on the electronic structure. The first is that it introduces localized states in the gap. The second is that it strongly modifies the band states in its immediate neighborhood, a fact that had been almost universally overlooked in earlier calculations of optical cross sections. They illustrated this point by calculating the optical cross section using two different formulas, namely

$$\sigma^0(h\nu) = -\frac{\beta}{h\nu} M^0(E_L \pm h\nu) , \tag{3.1a}$$

$$\sigma(h\nu) = -\frac{\beta}{h\nu} M(E_L \pm h\nu) , \tag{3.1b}$$

where

$$M^0(E) = \mathrm{Im}\langle \Psi_L | p_z G^0(E) p_z | \Psi_L \rangle , \tag{3.2a}$$

$$M(E) = \mathrm{Im}\langle \Psi_L | P_z G(E) p_z | \Psi_L \rangle . \tag{3.2b}$$

$\sigma^0(h\nu)$ is thus the cross section calculated using the localized state of the defect crystal and the band states of the perfect crystal, while $\sigma(h\nu)$ is the cross section calculated using that same localized state and the band states of the defect crystal. Petit, Allan, and Lannoo exhibited σ and σ^0 for several defects and showed that, in general, there were large differences between the two.

The same situation as that illustrated by Petit, Allan, and Lannoo is also true here: Here, the defect modifies the conduction-band states by, among other things, creating a fairly strong T_2 resonance. This can be most easily seen in Fig. 2 where we have plotted $M^0(E)$ and several different $M(E)$ for energies E in the conduction band. The various $M(E)$ differ from each other because we have artificially varied the position of the resonance peak. To produce these different plots, we have replaced V, the self-consistently determined defect potential used in Eq. (2.2), by V/λ. Since the defect potential for As_{Ga} is essentially attractive, increasing λ makes the potential less attractive and allows the T_2 resonance to shift to higher energies.

Referring still to Fig. 2, for $\lambda < 0.9$, (not shown) the resonance lies below the L-band minimum. Any scattering state near the resonance energy developed from an unperturbed state whose **k** vector lay in the Γ conduction-band valley. Not only is the overall density of states small in the Γ valley, but the density of T_2 states

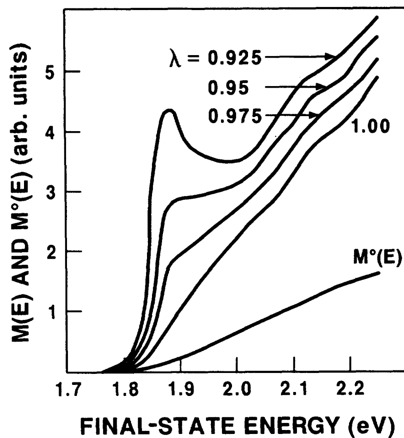

FIG. 2. $M(E)$ and $M^0(E)$, proportional to the square of the transition probability from the A_1 state to states at energy E in the conduction band. M^0 is calculated using the conduction-band states of the perfect crystal. M is calculated using the states of the defect crystal. It depends sensitively on the energy of the T_2 conduction-band resonance. This energy is controlled by the parameter λ.

is particularly small. For this reason, there is a *very* weak background of T_2 symmetry states to interact with and broaden the T_2 resonance. The resonance produces essentially a δ-function cross section (not shown). As λ increases, the resonance moves into the L band and very quickly broadens and loses intensity. By the time it is ≈ 0.15 eV above the L-band edge, it has completely lost its independent identity. As the resonance moves and changes its width, the oscillator strength of the nearby background also changes.

The difference between $M^0(E)$ and $M(E)$ for energies E in the valence band is shown in Fig. 3. Spin-orbit coupling is not included in our calculations. The presence of the defect reduces the density of states at the top of the

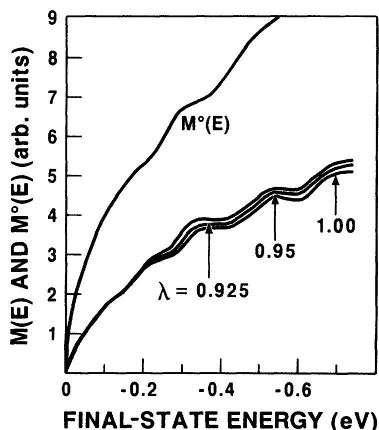

FIG. 3. $M(E)$ and $M^0(E)$ for states in the valence band. The sensitivity of $M(E)$ to the value of λ is far less because there is no resonance at these energies.

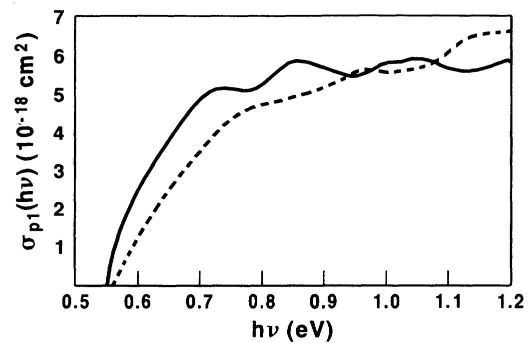

FIG. 4. Solid curve: $\sigma_{p1}(h\nu)$ evaluated for $\lambda=1$. Dashed curve: measured values as given in Ref. 3.

valence band near the defect, as would be expected for an attractive potential. This can be inferred because $M(E)$ for final energies near the valence-band maximum is smaller than $M^0(E)$, the value for the unmodified valence-band states. Although varying λ does vary the potential and thus the perturbed states to some extent, small changes in λ produce proportionately small effects, unlike the situation in the conduction band where a small change in position of the resonance has a profound effect on whether or not the resonance was broadened. Figure 3 also exhibits a small amplitude oscillation which we attribute to **k**-space and energy-grid sampling noise in the calculations.

In Figs. 4–7, we exhibit calculated values of σ_{p1}, σ_{n1}, σ_{p2}, and σ_{n2}, respectively. The self-consistent potential used in evaluating these cross sections was that calculated for the neutral $\mathrm{As_{Ga}}$. We verified that there were only small changes in cross section if we used the potential for singly ionized $\mathrm{As_{Ga}}$, except for those changes directly associated with the position of the T_2 resonance. The energy of the A_1 state, as was explained in Sec. II, has been set by hand for the purposes of evaluating the cross sections. The hole cross sections σ_{p1} and σ_{p2}, which are very weakly affected by the value of λ in the range $0.9<\lambda<1.0$, as can be seen in Fig. 3, were evaluated for $\lambda=1.0$.

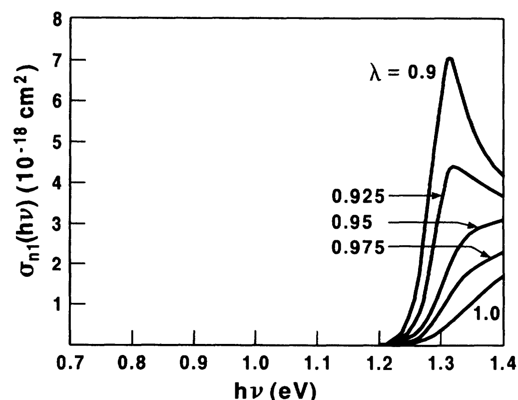

FIG. 5. $\sigma_{n1}(h\nu)$ evaluated for various values of λ.

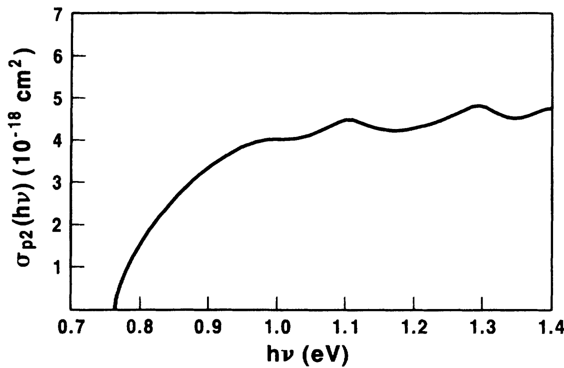

FIG. 6. $\sigma_{p2}(h\nu)$ evaluated for $\lambda=1$.

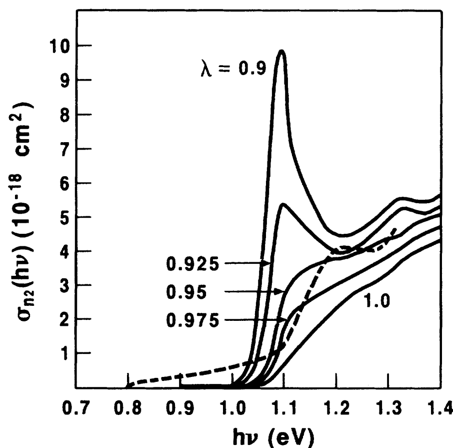

FIG. 7. Solid curves: $\sigma_{n2}(h\nu)$ evaluated for various values of λ. Dashed curve: measured value as given in Ref. 5.

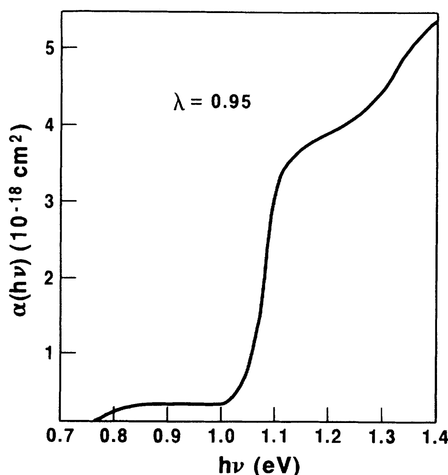

FIG. 8. Optical absorption $\alpha(h\nu)$ evaluated for n-type material in which 5% of the As_{Ga} have been ionized into the singly ionized state by the action of the light itself, or for semi-insulating material where the ionization is caused by a small concentration of lower-lying acceptors.

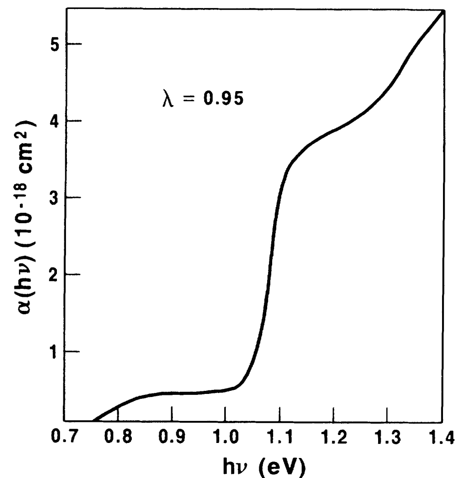

FIG. 9. Same as Fig. 8 except that the fraction of ionized As_{Ga} is 10%.

There are two factors to note in these figures. First of all, there is a generic similarity in shape between σ_{p1} and σ_{p2}. All the differences between these two cross sections can be understood in terms of the 0.24-eV difference in energy of the final A_1 midgap state. The calculated $M(E)$ agrees to within 10% when V^0 for the neutral defect is replaced with V^+ for the singly ionized defect. We are not aware of a physical mechanism which should make these two cross sections inherently different in shape. The same is true (except for the changes engendered by the shifts of the T_2 resonance) for the pair of cross sections σ_{n1} and σ_{n2}.

The second factor to note is that the density of T_2 symmetry states below the L-band minimum is so small that there is very little electron cross section σ_{n1} or σ_{n2} to final states whose energy lies within the Γ valley range.

In Figs. 8 and 9, we exhibit the optical absorption as evaluated using Eq. (1.2) and concentrations appropriate for semi-insulating type material. These have been evaluated using $n_0=f_0$, $n_+=1-f_0$, and $n_{2+}=0$, $0\le f_0\le 1$. For $f_0=1$, the optical absorption is identical to σ_{n2}, as shown in Fig. 7. This has an extremely small cross section in the range 0.77 eV $<h\nu<1.04$ eV and is zero below 0.77 eV. With as little as 5% (Fig. 8) or 10% (Fig. 9) of the defects in the singly ionized state, the cross section in the range $0.77<h\nu<1.04$ approaches experimentally observed values. However, it is clear that the increase in this range is due to the onset of the hole cross section σ_{p2} and not the electron cross section σ_{n2}.

IV. COMPARISON WITH EXPERIMENT

The first measurements of the optical cross sections of $EL2$ (then known as the "O" defect) were made by Chantre, Vincent, and Bois[5] using the deep-level optical spectroscopy technique they pioneered. At that time, however, the existence of a *second* donor level of $EL2$ was unknown, and so, instead of Eqs. (1.1)–(1.4), they interpreted their experiments assuming that there were only two charge states of the defect:

$$n_0+n_+=N \ . \tag{4.1}$$

The absorption would then be given by

$$\alpha(h\nu)=(n_0\sigma_{n2}+n_+\sigma_{p2}) \ , \tag{4.2}$$

the charge would be given by

$$Q=n_+ \ , \tag{4.3}$$

and the kinetic equations governing the transient populations would be

$$\frac{dn_0}{dt}=\Phi(-n_0\sigma_{n2}+n_+\sigma_{p2}) \ , \tag{4.4a}$$

$$\frac{dn_+}{dt}=\Phi(n_0\sigma_{n2}-n_+\sigma_{p2}) \ . \tag{4.4b}$$

Their technique was to measure the initial slope of a photocapacitance signal. To obtain σ_{n2}, they achieved the initial condition $n_0=N$, $n_+=0$ (and, unbeknownst to them, $n_{2+}=0$) by using an electrical pulse to flood all the centers with electrons. Analyzing the results using either Eqs. (1.1)–(1.4) or Eqs. (4.1)–(4.4) leads in this case to the same result: the initial slope provides a direct measure of σ_{n2}, the electron cross section. Their results for σ_{n2} at 77 K are shown as a dotted curve on Fig. 7. The normalization of their cross section was not determined, and we have chosen a normalization which is convenient to the scale of the calculated results.

In order to measure the hole cross section (σ_{p2} in our notation), Chantre, Vincent, and Bois started from an initial condition $n_0=0$, $n_+\approx N$, which they achieved by emptying the (0/+) level thermally. (The initial value of n_{2+} that this would have produced is not clear to us.) Incorrectly using the equations of this section to analyze the data would make it appear that the initial slope of the capacitance transient is proportional to σ_{p2}. If the data is analyzed correctly using the equations of Sec. I, then (under the assumption that $n_{2+}=0$), the quantity being measured is really $\sigma_{p2}-\sigma_{n1}$. If some of the defects are initially in the doubly ionized state, then the quantity measured is even less directly related to σ_{p2}.

Another measurement of an optical cross section was done by Lagowski *et al.*[3] Knowing that $EL2$ was a double donor, they measured the initial slope of capacitance transient in p-type material. Starting from an initial condition $n_0=n_+=0$, and $n_{2+}=N$, they obtained σ_{p1}. Their analysis gave the best estimate of the level E_1, namely $E_1=E_v+0.54\pm0.02$ eV. They also gave an order of magnitude for the absolute value of the cross section they measured, namely $\approx 10^{-17}$ cm^2. We have reproduced the cross section they obtained as the dotted curve on our Fig. 4. The exact normalization is not given in Ref. 3, and we have normalized the experimental and theoretical curves to agree at $h\nu=1.0$ eV.

Omling, Silverberg, and Samuelson[15,16] also were concerned with measuring $EL2$ cross sections. For some reason, the analysis in their earlier paper[15] is carried out ignoring the second donor level. The intent in this paper is to obtain absolute values for σ_{n2} and σ_{p2}, and to determine that energy for which the two cross sections are equal. As was the case in the work of Chantre, Vincent, and Bois,[5] the quantity assumed to be σ_{p2} is, at best, $\sigma_{p2}-\sigma_{n1}$. Since, however, $\sigma_{n1}\equiv 0$ for $h\nu<0.97$ eV, the analysis and the consistency checks they use are valid in this photon energy range. It is fairly straightforward to reanalyze the work presented in Ref. 15 using the equations of Sec. I and to assess, thereby, the validity of the hole cross section at energies above 1.0 eV. There is no problem with their measurement of σ_{n2}, and they were able to obtain not only its shape, but also its absolute magnitude.

In Ref. 16, the same authors measured σ_{p1} in n-type material over an energy range 0.5 eV $<h\nu<0.8$ eV by using photons of energy $h\nu=1.38$ eV to fully ionize all the $EL2$ before the start of the capacitance transient experiment. The results confirm those of Ref. 3 obtained in p-type material, but now there is also a determination of the absolute value of the cross section. This paper also presents an ingenious method of measuring σ_{n1}. The method relies on having previous knowledge of σ_{p2}. Since the papers cited above which claimed to have measured σ_{p2} have at best measured $\sigma_{p2}-\sigma_{n1}$, the σ_{n1} spectrum presented in Ref. 16 cannot be accepted without a discussion of whether the σ_{p2} used in deriving it is, in fact, correct. The biggest question here is whether the decrease in σ_{p2} at $h\nu>1.0$ eV[5,15] is real, or whether it reflects the onset of σ_{n1}.

The measurement of σ_{p1} in Ref. 3 on the one hand, and those of σ_{p2} in Refs. 5 and 15 on the other hand, yield cross sections that are profoundly different in shape. Our calculations yield two cross sections that are generically similar, basically because the calculated $M(E)$ for the two situations are virtually the same. This discrepancy is no surprise because, as we have just noted, the actual cross section measured could not have been σ_{p2}.

There is another striking discrepancy between our calculated result and the experimental one, namely for σ_{n2}. Experimentally, this cross section has a threshold at about 0.77 eV, corresponding to the transfer of electrons from the A_1 localized state to states near the Γ conduction-band minimum. The calculated cross section is extremely small from 0.77 eV up to 1.03 eV, the L-band minimum. The reason for this is that the final state of an optical transition from an A_1 symmetry initial state will have T_2 symmetry, and there is an exceedingly small density of T_2 states in the Γ valley. (There *are* T_2 states even at the bottom of the L minima.) As we shall discuss in the next section, the most likely reason for the discrepancy is that the forbidden $A_1\rightarrow\Gamma$ valley transition is made possible by emission of LO phonons of T_2 symmetry, an effect not included in our purely electronic calculation. This same effect borrows oscillator strength from transitions higher in the band. Both features are apparent in the comparison of calculated and measured cross sections in Fig. 7.

V. ROLE OF LATTICE COUPLING

The cross sections discussed in Sec. III were calculated using a purely electronic Hamiltonian, with no coupling

between the electrons and the lattice. Experimentally, however, there are several manifestations of the role of the lattice in the various optical cross sections. The first piece of evidence is that some of the cross sections are temperature dependent.[5,17] The second piece of evidence is the appearance of zero-phonon lines (ZPL's) and phonon replicas, both in the absorption spectra[6] and in emission spectra.[18,19] The third piece of evidence is the existence of an internal transition.[6] There has recently been some controversy about the interpretation of the ZPL and the amount of lattice relaxation associated with the internal transition. For that reason, it is useful to review the situation with regard to the second and third items above.

Discovery of the metastability of $EL2$ occurred in a series of photocapacitance experiments[19–21] in which it was demonstrated that the stable state of the defect and the metastable state have the same charge. From the fact that they do have the same charge, it is likely that the optical absorption causing the transformation would leave the excited electron on the defect center, i.e., would be an intracenter transition. This was demonstrated to be so by Kaminska *et al.*[6] in an experiment where optical absorption and photocurrent were measured simultaneously. These were found to track each other except over a limited range of photon energies. In the range 1.05 eV $< h\nu < 1.32$ eV, there were photons absorbed for which no electrons were collected. The difference between the optical absorption and the photocurrent gives $\sigma_{\mathrm{intr}}(h\nu)$, the cross section for exciting an intracenter transition.

The large width of $\sigma_{\mathrm{intr}}(h\nu)$ suggested to Kaminska *et al.*[6] that lattice relaxation was responsible for broadening the absorption line. In such cases, there is often ZPL marking the lowest energy in the broadened line and phonon replicas above it. A high-resolution study of the $EL2$ optical absorption at low temperature did find such features, seemingly confirming that lattice relaxation was indeed involved in the absorption process. By using uniaxial stress to split the ZPL, Kaminska, Skowronski, and Kuszko[22] identified the intracenter transition as an A_1-T_2 transition. This finding was taken as proof that $EL2$ was an *isolated* $\mathrm{As_{Ga}}$ defect.

The reasoning behind ascribing the width of the absorption feature to lattice coupling was based on the classical Huang-Rhys[23] description of optical absorption in a system with lattice coupling. Figure 10 illustrates the essence of the Huang-Rhys theory. The theory applies to absorption between two *discrete* electronic states which are coupled to the lattice. The intensity distribution of the transitions is governed by the overlap of the initial- and final-lattice wave functions and is greatest for the transition that corresponds classically to the lattice being fixed in the initial configuration. This is the so-called vertical transition and is indicated on the configuration coordinate diagram of Fig. 10. (Strictly speaking, however, adjustments to the Huang-Rhys theory are called for in this situation because the vertical transition is *not* to a discrete state but to a T_2-symmetry electronic resonance lying low in the conduction band. This situation has been studied by us in Ref. 7.)

For the $EL2$ intracenter absorption, the peak in the ex-

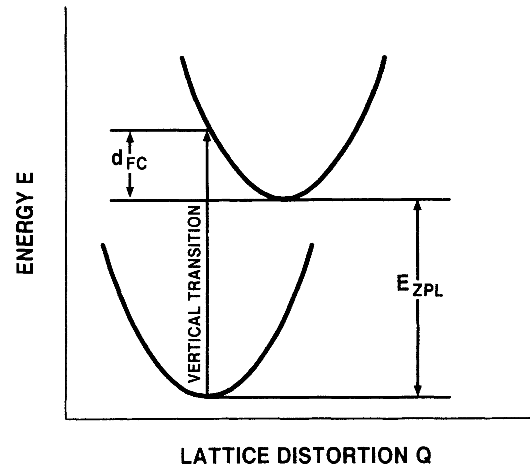

FIG. 10. Schematic representation of the Huang-Rhys theory of optical absorption in a two-level electronic system coupled to molecular degrees of freedom.

perimental absorption spectrum was ascribed to a vertical transition at 1.18 eV. Since the ZPL was observed at 1.04 eV, the lattice relaxation energy, d_{FC}, was 0.14 eV. The phonon energy $\hbar\omega$ observed in the high-resolution absorption spectra was 11 meV. Consequently, the Huang-Rhys factor $S_{\mathrm{HR}} = d_{FC}/\hbar\omega$ was close to 13. However, this aspect of the interpretation was soon attacked on the grounds that, according to the simple Huang-Rhys theory, the integrated intensity of the ZPL should be a fraction $\exp(-S_{\mathrm{HR}}) \approx 10^{-6}$ of the total, a fraction much smaller than observed.

Various suggestions for overcoming this difficulty have been put forward. One is that the 11-meV phonon observed was really the transverse optical phonon of the GaAs crystal, while the lattice relaxation phonon was really 24 or 33 meV, approximately two or exactly three of the observed 11-meV phonons.[24] Either would be close to the 29-meV phonon energy needed[25] to account for the 0.15-eV half-width of the optical absorption. Another suggestion is that the ZPL and the peak are really features which belong to different electronic transitions,[26] which means that different final electronic states of the same defect are involved. Still another is that the ZPL and its phonon replicas are not lattice vibration features at all, but are instead the lowest and higher-lying transitions in a hydrogenic series of states[27] arising from the effective-mass states split off from the L valley by the Coulomb potential of the defect.[28,29]

There has been evidence accumulating to support some of these explanations: Under hydrostatic pressure, the ZPL is observed to ride up to onto the shoulder of the peak ascribed to lattice broadening of the electronic transition.[26] Since the ZPL is supposed to mark the lower limit of the lattice-broadened transition, this would seem to be a conclusive argument that the broad peak is not simply a lattice broadened electronic transition or that the "ZPL" is not really a zero-phonon line.[27–29]

Additional information about the lattice coupling and degree of electronic relaxation has been extracted from reanalysis of the uniaxial stress-splitting experiments.[22]

Baraff[30] has shown that the total amount of lattice relaxation that can be assigned to the ε and τ models of lattice relaxation is far smaller than the 0.14 eV assigned to d_{FC}, and he made crude estimates that the a-mode coupling might possibly be enough to account for the rest. Davies,[31] in a more thorough analysis of the same problem, identified and removed one of the tacit assumptions used both in the original analysis of the stress splitting data and in Baraff's reanalysis. He reconfirmed the limit Baraff had found on relaxation caused by the τ-mode coupling. Davies and Steele[32] were able to estimate the relaxation associated with the a-mode coupling and found it be much smaller than Baraff's maximum estimate. They concluded that the temperature dependence of the ZPL intensity was consistent with an overall weak lattice coupling, i.e., with a small energy separation between the vertical transition and the zero-phonon line. Taken together, these last studies[30–32] suggest either that (i) there may be a lattice-broadened transition which does give rise to a zero-phonon line, but for which the vertical transition is at a lower energy than the 1.18-eV peak, or (ii) the vertical transition is at 1.18 eV, with small lattice broadening which is masked by some purely electronic aspects of the transition. In the former case, there is a need to identify the source of the broad absorption peak at 1.18 eV that masks the lower-energy vertical transition. In the latter case, there is a need to explain the existence of the zero-phonon line.

Considering both Lannoo's argument that the "ZPL" is really a transition to a hydrogenic state,[27] and our calculation that purely electronic broadening of the T_2 resonance (see Fig. 7) gives more or less the correct overall shape of the absorption, one might conclude that there is no need to invoke lattice relaxation at all for these features of the spectrum. That conclusion cannot be totally correct either, because of the existence of the intracenter transition. Experimentally, the intracenter transition extends over an energy range where the electron is excited from the A_1 state to the conduction band. An electron placed in the conduction band will move away from the defect and eventually contribute to the photocurrent, and not to an intracenter transition. Even if this electron were excited into the electronically broadened T_2 resonance, it would still eventually leak away from the defect unless the lifetime of the resonance were long compared to the lifetime against deexcitation. This latter occurs only if the resonance is sharper than the natural line width, which is never the case. Thus, in order for an intracenter transition to occur, there must be some energy-loss mechanism operating (e.g., lattice relaxation via multiphonon emission) that can reduce the energy of the electron sufficiently to where it cannot leak away from the defect before deexcitation takes place. Although we have proposed one purely electronic mechanism that could allow an intracenter transition to occur,[30] there is no experimental evidence yet to confirm that proposal.

On balance then, the shape of the intracenter cross section does suggest that lattice broadening of the T_2 level exists as was correctly proposed by Kaminska *et al.*[6] even though there is inherently electronic broadening superposed over it. This vastly complicates the analysis. It could explain how the ZPL, under pressure,[26] rides up over the lower limit of the broadened absorption, since the part over which it rides could well be the electronically broadened part. On the other hand, Lannoo's argument that the "ZPL" is really a hydrogenic state attached to the L minima perhaps provides an explanation for the same effect, because the position of the hydrogenic state is not connected to the amount of lattice relaxation. Lannoo's presentation[27] is interesting in that it leads to a Hamiltonian virtually identical with the one under which the stress dependence of the ZPL was analyzed. This situation challenges all analyses of lattice-relaxation broadening of the T_2 level since they all were based on the validity of the ZPL being associated with a dynamic Jahn-Teller effect in a $\tau \times T_2$ system.[22,30–32] Clearly, a resolution of this point is of utmost importance. Very recent experimental evidence[33,34] tends to support Lannoo's suggestion.

Finally, we turn to the question of the discrepancy between the calculated and measured σ_{n2}^0 cross sections for transitions whose final state is in the Γ valley. High-precision studies of the emission from $EL2$[4,18] indicate that some of the emission originates from A_1-symmetry effective-mass-like state attached to the Γ minimum. The evidence for this is to be found in that part of the emission spectrum where the A_1 midgap level is the final state. What is seen is nondegeneracy of the initial state, a very small zero-phonon line, and a very strong intensity of the one-phonon LO peak. In other words, a LO phonon of T_2 symmetry enables this otherwise-forbidden $A_1 \rightarrow A_1$ transition to occur. The mechanism by which this occurs is exactly the same as the one by which a phonon supplies the momentum needed for band-to-band optical recombination an indirect band-gap semiconductor. The difference in detail is that here, there is no $\mathbf{k}$-conservation rule because of the localized nature of the final state. Instead, the phonon supplies the needed change in symmetry to the initial A_1-symmetry hydrogenic electronic state. It should be particularly easy for the phonon to do so because of the high density of nearby electronic states of T_2 symmetry from which it can borrow strength.

It is reasonable that this effect will also be strong in the A_1-to-Γ-valley absorption: the same physics is involved. In this case, the phonon borrows amplitude from the nearby states of T_2 symmetry and supplies it to the final states of A_1 symmetry in the Γ valley. Since the occupation of the enabling phonon is temperature dependent, the cross section for this transition should also be temperature dependent. Temperature dependence of this part of σ_{n2} has been measured,[17] but the interpretation of this measurement was that an electronically allowed transition is broadened in the usual way via lattice relaxation. This interpretation is suspect, because the transitions should be electronically forbidden. The question of the spectral shape and temperature dependence for the $A_1 \rightarrow (\Gamma +$ LO phonon) transition, and whether such a transition is in accord with what has been measured, is under study and will be reported elsewhere.[35]

VI. SUMMARY AND CONCLUSIONS

We have calculated the purely electronic part of the four cross sections σ_{n1}, σ_{p1}, σ_{n2}, and σ_{p2} for the isolated As_{Ga} defect. The two calculated electron cross sections were generically similar, as were the two calculated hole cross sections. The differences between the two members of each pair could be understood mainly on the basis of the energy difference between E_1 and E_2, the two localized levels involved. Although the experimental results on the two hole cross sections show them to differ in shape, we argued that the conditions under which σ_{p2} had supposedly been measured were such that, at best, it was $\sigma_{p2}-\sigma_{n1}$ that had been obtained. Therefore, comparison between the two published experimental hole cross sections is invalid.

Our calculated cross sections do have the experimentally measured order of magnitude and do correspond in shape fairly well to σ_{n2} and σ_{p1}, the two cross sections that have been measured correctly. Some deviations from experiment are to be expected because these purely electronic calculations ignore the role of the lattice in affecting the spectral shape. The three most prominent differences are (i) the absence of the zero-phonon line; (ii) the absence of the phonon replicas (even if it should turn out that the zero-phonon line and phonon replicas are not lattice related but are, instead, hydrogenic states attached to the L-band minima,[27–29] they do not appear here because our calculation truncates the long range Coulomb potential needed to create them); (iii) the very small purely electronic cross section for transferring an electron from the A_1 localized state into the Γ valley of the conduction band.

We attributed the larger experimental cross section for optical transition between the A_1 state and the Γ valley to the effect of LO phonons. These can enable this otherwise forbidden transition to occur. We cited experimental evidence that makes this a likely explanation. If this should indeed be the explanation, then the lattice relaxation of the A_1 localized state (which has been measured via the temperature dependence of this optical cross section[17]) will have to be reevaluated. This is because the LO phonon will contribute its own temperature dependence to the cross section in this energy range.

The question of the relation of the vertical transition to the zero-phonon line could not be settled in a definitive way, primarily because of Lannoo's demonstration that a hydrogenic state attached to the L bands would be governed by the same Hamiltonian as had been used to analyze the zero-phonon line.[27] Nonetheless, we were able to show that the vertical transition is markedly broadened by electronic mixing with the background states of T_2 symmetry, and we demonstrated how that broadening depended on the exact position of the resonance relative to the L-band edge. We also argued that, in spite of an electronic broadening that seems to reproduce the shape of the cross section, the existence of an intracenter transition implies that there is still significant lattice relaxation also contributing to the broadening.

Initially, the purpose of these purely electronic calculations had been only to serve as input for a more complete calculation to investigate the effect of lattice relaxation and, in particular, its effect on the T_2 conduction-band resonance. In spite of this limited objective, the information derived from these calculations should be useful in filling in some gaps in the present understanding of the $EL2$ defect in GaAs.

Note added in proof: Equations (1.4) were previously given in Ref. 16. We have, unfortunately, reversed the definitions of states 1 and 2 from that used in Ref. 16, thereby adding an unnecessary complication to a comparison of the results.

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APPENDIX: k-DEPENDENT SCISSORS OPERATOR

The scissors operator is a name that has been given to the technique of adjusting the energy of the states of the perfect crystal prior to evaluating the Green's functions $G^0(E)$. Originally,[14] the adjustment raised all the conduction bands by the same constant energy Δ. Now, we want to raise $\varepsilon_c(\mathbf{k})$, the calculated energy of the lowest conduction band, by an amount $\Delta(k)$ such that $E_c(\mathbf{k})$, the lowest conduction-band energy used in evaluating G^0, will be

$$E_c(\mathbf{k})=\varepsilon_c(\mathbf{k})+\Delta(\mathbf{k}) \ . \tag{A1}$$

$E_c(\Gamma)$, $E_c(X)$, $E_c(L)$, and $\varepsilon_c(\mathbf{k})$ are known, either from experiment or from the LDA calculation.

The function $\Delta(k)$ has the full translational and rotational symmetry of the Brillouin zone. For this reason, it can be expanded in the form

$$\Delta(\mathbf{k})=\sum_{m=1} C_m A_m(\mathbf{k}) \ , \tag{A2}$$

where the individual functions $A_m(\mathbf{k})$ are symmetrized sums of plane waves. (See, for example, Ref. 36.)

For the fcc lattice appropriate to GaAs, the first three functions $A_m(\mathbf{k})$ are

$$A_1(\mathbf{k})=1 \ , \tag{A3a}$$

$$A_2(\mathbf{k})=\frac{1}{3}\left[\cos\left[\frac{x}{2}\right]\cos\left[\frac{y}{2}\right]+\cos\left[\frac{y}{2}\right]\cos\left[\frac{z}{2}\right]+\cos\left[\frac{z}{2}\right]\cos\left[\frac{x}{2}\right]\right] \ , \tag{A3b}$$

$$A_3(\mathbf{k})=\tfrac{1}{3}(\cos x+\cos y+\cos z) \ . \tag{A3c}$$

Experimental data on optical cross sections seemed at first[5] to exhibit thresholds at the three conduction-band minima. Therefore, in the calculation, it is especially important to place these minima at the correct energy and we use $\Delta(\mathbf{k})$ to do so. It is only necessary to guarantee that Eq. (A1) is satisfied at Γ, X, and L. For this reason, only three nonzero constants C_m are needed. They are given by

$$C_1=\frac{1}{8}[\Delta(\Gamma)+3\Delta(X)+4\Delta(L)]\ , \quad \text{(A4a)}$$

$$C_2=\frac{3}{4}[\Delta(\Gamma)-\Delta(X)]\ , \quad \text{(A4b)}$$

$$C_3=\frac{1}{8}[\Delta(\Gamma)+3\Delta(X)-4\Delta(L)]\ , \quad \text{(A4c)}$$

where $\Delta(\Gamma)$ is the correction needed for the energy of the Γ valley, etc. This choice places the valley minima at the correct energy while making the smoothest possible correction to the other energies in the lowest conduction band.

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