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Optical absorption on localized levels in gallium arsenide*

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The extrinsic optical absorption associated with defects in GaAs has been studied between 4 and 300 °K in the range from 0.6 to 1.5 eV. Two bands in particular are investigated: the first located around 0.9 eV is associated with chromium; the second at 1.2 eV, present in all materials, is probably related to some native defects such as gallium vacancies. The variations of the energy and of the shape of these two bands versus temperature demonstrate that they cannot come from transitions between extrinsic levels and the energy bands of the perfect crystal. The absorption curves of each line appear to be Gaussian at every temperature. As a consequence of lattice coupling, the width of these bands increases greatly with temperature according to a law: $W(T) = W(0)\,[\coth(h\nu g/2kT)]^{1/2}$. Finally, it is shown that a configurational-coordinate diagram may be applied to these two centers. On this basis, we give the values of the quantum energy of vibration of the centers in their ground states $h\nu g$: 13 meV for the chromium center, and 15 meV for the center at 1.2 eV. For this last one, we propose a configurational-coordinate diagram assuming the parabolic approximation to be valid. These results are discussed and compared with those obtained by photoconductivity or photoluminescence in GaAs, taking into account the important Stokes shift resulting from the lattice coupling we mentionned above. In particular, it is shown that the center absorbing at 1.2 eV is quite different of that emitting at 1.2 eV, i.e., the V_{Ga}:D complex for which Williams has already proposed a configurational-coordinate diagram.

I. INTRODUCTION

Electronic transitions leading to photon absorption in semiconducting materials are of three kinds: the ones involving free carriers, the ones arising between two bands (particularly between valence and conduction bands) or involving near band states, and the transitions associated with localized defects. In GaAs, as in most usual semiconductors, the first two mechanisms have been much investigated, but the last one is not yet well known. That is because the optical absorption associated with these deep-level transitions is generally very weak,[1] especially in the pure materials which are now of common interest. However, we have previously shown[2] that the extrinsic absorption between 0.6 and 1.5 eV can be measured even in nonintentionally doped materials. This extrinsic absorption is isolated after subtracting the contribution of the free-carrier absorption when not negligible, namely, above 10^{16} electrons per cm^3. Band-to-band transitions, even with band-tailing effects, induce very low absorption as soon as the photon energy is sufficiently smaller than the band-gap energy; for instance, at 4 °K, this is always right for $\hbar\nu < 1.4$ eV.

It is the purpose of this paper to report quantitative absorption studies of the extrinsic transitions in n-GaAs. Our aim was to determine the mechanisms of the transitions involving deep levels in this material. As is well known, three processes have to be considered: (i) transitions between localized levels and bands as generally observed in germanium and silicon, (ii) transitions involving two levels localized around the same center, which is the case for ionic crystals, and (iii) transitions between levels localized on different centers (pair transitions).

Till now, the studies on these deep-level transitions are chiefly from luminescence or photoconductivity measurements. But these last measurements are generally restricted to semiinsulating materials, for instance, chromium-doped GaAs,[3] while luminescence studies of deep levels[4–6] are difficult because the corresponding infrared emissions are out of the spectral range of photomultipliers so reducing greatly the measurements' accuracy. Consequently, very few studies in that field are quantitative, they often only give the energies of the line and no information is given on their shape. The only cases which have been extensively studied are that of the complex centers $V_{\mathrm{Ga}}:D$ by Williams and Elliott[7–9] and $V_{\mathrm{As}}:\mathrm{Acc}$ by Hwang,[10] which emissions are located, respectively, around 1.2 and 1.3 eV (or 1.45 eV); using these luminescence studies, it has been shown by the above-cited authors that configurational-coordinate diagrams describe well the lattice relaxation for these complexes. In this paper, the coupling of the transitions with the lattice is analyzed by means of absorption measurements versus temperature, as we have already done for excitonic[11] and free-carrier[12] transitions. It is shown that configurational-coordinate diagrams may also be applied for two other centers in GaAs: (i) for the center associated with chromium, whose absorption arises around 0.9 eV and (ii) for a new center we identify, whose absorption is located around

1.2 eV. This center seems to be "intrinsic," i.e., involving only native defects and no impurity for it appears in all the materials we investigated.

II. EXPERIMENTAL RESULTS AND INTERPRETATION

The experimental process has been described previously.[2] The apparatus includes a double-pass single-beam monochromator (Perkin Elmer 112 G), a set of detectors (thermocouples and photomultipliers) followed by a synchronous detection, and a liquid-helium cryostat.[13] Samples are immersed in gaseous helium to prevent condensation on their surfaces and to assure their cooling down to 4.5 °K. The temperature is checked with a carbon resistor. For each sample the reflectivity is measured; its variation versus photon energy $h\nu$ is also taken into account in calculating the absorption coefficient K. Using sample thicknesses of about 1 cm, the uncertainty on the absolute value of K is around 10^{-2} cm^{-1}, and the dispersion of the experimental data is less than 5×10^{-3} cm^{-1}.

Studying a set of nonintentionally doped GaAs single crystals from various origins (Radiotechnique, Monsanto, Battelle), we have previously shown the existence of four absorption bands (A, B, D, E) located at 4 °K around 1.40, 1.20, 0.78, and 0.66 eV, respectively. Another band (C) appears at 0.9 eV in chromium-doped GaAs. The study of the transition processes described in the following has been carried out with bands B and C, which are the best resolved ones.

A. *C* band (0.9 eV)

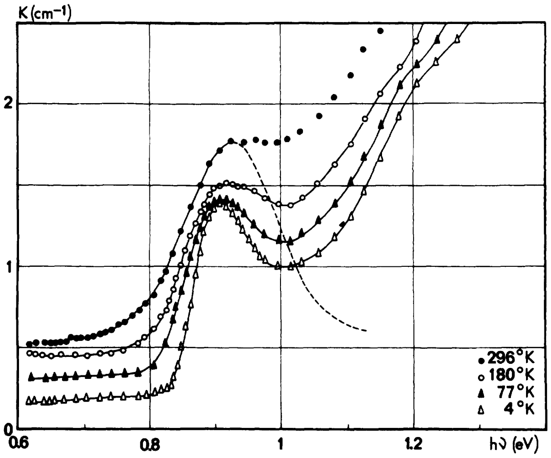

FIG. 1. Absorption curves of a chromium-doped GaAs (n) sample for T between 4 and 296 °K.

Figure 1 shows the absorption curves $K(h\nu)$ of a chromium-doped sample for temperatures between 4 and 296 °K. Two bands appear: C at 0.9 eV and B, which is partially unresolved here, around 1.20 eV. First, let us look at the transition mechanism responsible for the band C. It can be seen on the curves that the maximum of the C band moves very little as the temperature increases. Besides, the observed displacement from 0.905 eV at 4 °K to 0.92 eV at 293 °K is not very significant because, when the temperature increases, the bands C and B overlap more, giving rise to an apparent shift of the C maximum towards higher energies. This overlapping may then explain a part of the experimentally observed displacement. Nevertheless, it remains that band C does not move towards higher energy as the temperature is lowered, as might be expected for transitions from a deep-lying level to the conduction band. It is to be noted that the sample investigated here is n type, so transitions from valence band to deep levels are unlikely; in any case, for this last kind of transition, the absorption band should also move towards higher energy when the temperature is lowered. Moreover, for transitions involving the conduction band (or the valence band), the absorption bandwidth ΔE is directly connected to the extent of the localized electron wave function in k space, Δk, because of the wave-number-conservation rule. If Δr is the spatial extent of this wave function, using uncertainty relations, we get $\Delta k \simeq 1/\Delta r$. Then assuming parabolic bands, ΔE may be estimated in a very simple way, that is,

$$\Delta E \simeq \hbar^2/2m^*(\Delta r)^2 \quad ,$$

m^* is the effective mass in the band where transitions take place. Since the conduction band is involved here, we have to use the electron effective mass m_e^*. Experimentally, taking into account the overlap of C and B appearing in Fig. 1, the absorption band C may be, in a first approximation, looked at as symmetrical; its half-width is then about 170 meV at 4 °K. Using this value for ΔE, we obtain $\Delta r \simeq 25$ Å. With such a value it seems that the effective mass and the dielectric-constant approximation would still apply to this center[14]; the depth (0.9 eV) of the associated level would then be difficult to understand. Besides, the same band is observed in n- and p-type materials; this cannot be understood with the above model. Finally, we must consider that the band C does not arise from transitions between a level and a band but probably from transitions between two electronic levels localized on the same center. For pair transitions, the C maximum should move with temperature, and the behavior of the whole band would be different in n- or p-type materials. On the other hand, with the proposed model the variations of C do not follow those of the gap, and the Fermi-level location in the forbidden band has no influence as soon as the center is occupied.

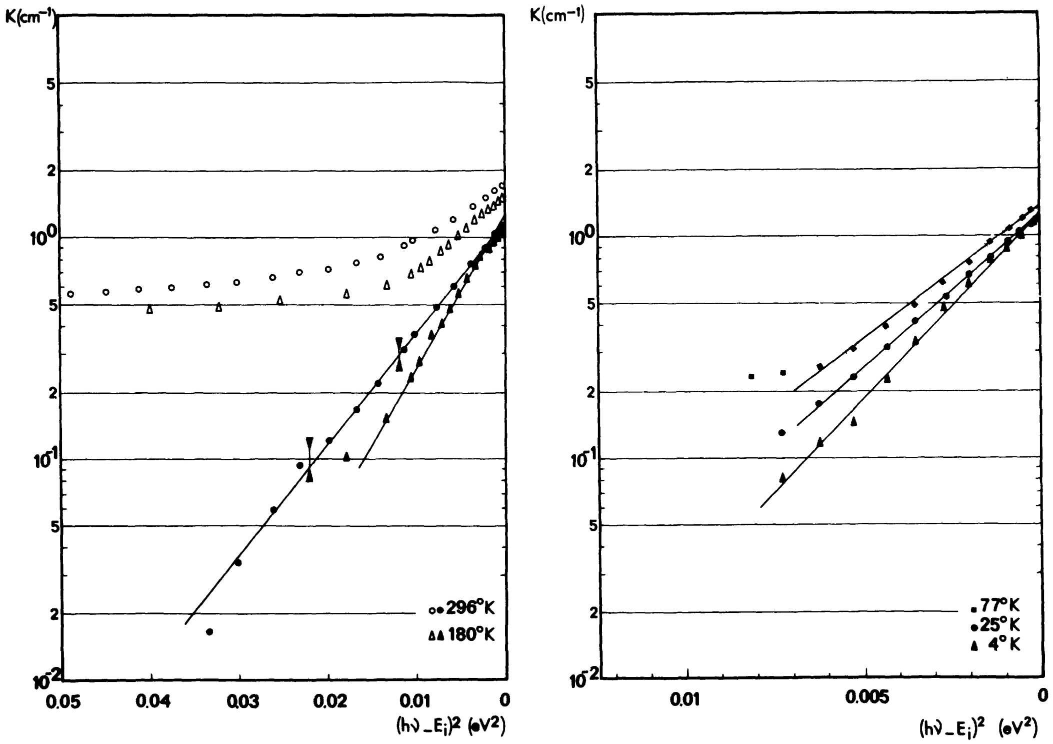

FIG. 2. Curves $\log_{10}K = f(h\nu - 0.9)^2$ from 4 to 296 °K for $h\nu \leq 0.9$ eV. The solid dots are for values obtained after subtracting free-carrier absorption from measured absorption (open dots).

Now let us turn to the lattice coupling effect. Figure 1 shows that the width of the *C* band increases with temperature; this indicates that these transitions are strongly coupled to the lattice as might be expected in GaAs, according to the behavior of more ionic crystals.[15,16] Using the adiabatic approximation (linear or semiclassical), it has been shown[17] that lattice coupling induces Gaussian absorption bands with half-width W varying versus temperature according to the law[18]

$$W(T) = W(0)\,[\coth(h\nu g/2kT)]^{1/2} \quad , \qquad (1)$$

here $h\nu g$ is the vibration quantum energy for the center in its ground state. The curves $\log_{10}K = f(h\nu - 0.9\text{ eV})^2$ for $h\nu < 0.9$ eV plotted in Fig. 2 show that the Gaussian approximation is, in fact, valid at all temperatures if we take into account the measurements' uncertainty. The slopes of the straight lines appearing in Fig. 2 give the values of W, which we have plotted in Fig. 3. It can be seen that the law (1) fits well the experimental values for $h\nu g = 13$ meV. The discrepancy between the experimental results and the theoretical curve does not exceed 5 meV, which is still in good agreement with the measurement uncertainty.

B. *B* band (1.20 eV)

This band appears in all the investigated materials except in the most doped n-type ones, therefore it is probably related to some native defect. We think that gallium vacancies, which are always

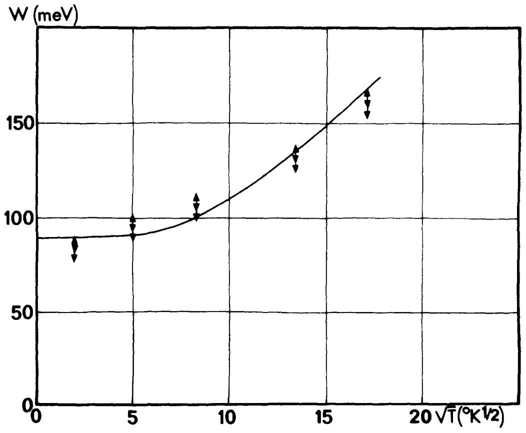

FIG. 3. Half-width W variations vs temperature T for *C* band. The continuous curve represents the function $W = 90[\coth(13/2kT)]^{1/2}$, with (kT) in meV.

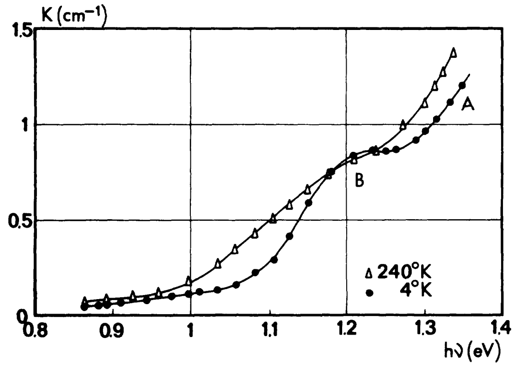

FIG. 4. Absorption band B at $T = 240$ and 4°K in a n-type undoped GaAs sample.

present in GaAs, may be responsible for this band. As it is known that gallium vacancies associate with donors to form the $V_{\mathrm{Ga}}:D$ complex, the disappearance of band B in n^+ materials may corroborate that hypothesis.

The preceding study referring to the C band can be carried out again for the B band, though it is impossible to observe the decrease of $K(h\nu)$ on the high-energy side of the absorption band, i.e., above 1.20 eV, because of the overlapping with A band (1.40 eV) as shown in Fig. 4. For instance, it can be seen that it does not move towards lower energies as T increases. We have also observed that this band is independent of whether the samples are n or p type. Finally, Fig. 5 shows that its half-width varies with temperature according to a law of type (1); the ground-state vibrational energy of the center involved is $h\nu g$: (15 ± 0.5) meV.

III. DISCUSSION

A transition between two energy states of a system may be characterized by its oscillator strength f, a quantity which is always less than unity. In a solid, if N_0 is the number of absorbing systems per unit volume, the integral of the absorption curve may be written in the following form[17]:

$$\int K(h\nu)\,d(h\nu) = \left[\frac{1}{n}\left(\frac{E_{\mathrm{eff}}}{E_0}\right)^2\right] N_0\,\frac{\pi e^2 h}{m_e^* c}\,f \quad . \qquad (2)$$

n is the refractive index of the material, e is the electron charge, and c is the velocity of light in vacuum. The ratio of the effective field E_{eff} to the applied field E_0 is different from unity for localized orbits; if Lorentz correction is supposed to be valid, one gets[17]:

$$E_{\mathrm{eff}}/E_0 = \tfrac{1}{3}(n^2 + 2) \quad .$$

Assuming symmetrical absorption bands as above, we find, from Fig. 4,

$$\int K(E)\,dE \simeq 0.07 \text{ eV cm}^{-1} \text{ for the } B \text{ band.}$$

As may be expected in this model, this value is roughly independent of temperature, and gives through Eq. (2)

$$N_0 f \simeq 10^{14}\ \mathrm{cm}^{-3} \quad .$$

In different bulk samples, we found this quantity varying from 10^{14} to 3×10^{14} cm^{-3}. This leads to a plausible value for the number of defects N_0, provided f is not much smaller than unity as is generally the case for similar transitions in ionic crystals.

In the adiabatic linear approximation, the intensity of the coupling between phonons and localized electrons may be characterized by one parameter S which is the average number of emitted or absorbed phonons during the transition.[19] Hopfield calculated this parameter for optical phonons,[20] typical values obtained with his model are between 0.02 for silicon on As site to 0.5 for copper.[21] In our case, from the experimentally determined quantities $h\nu g$ and $W(0\ {}^\circ\mathrm{K})$, we find

$$S = 7 \text{ for } C \text{ band}$$

and

$$S = 8.6 \text{ for } B \text{ band} \quad .$$

Such values are much too high to be explained with Hopfield's model. So it turns out that coupling occurs more likely with localized vibrating modes as has already been supposed by Williams[7] and Hwang[10] for the particular cases of vacancy-impurity complexes. In this model, the atomic binding strengths vary with the radius of the electron orbit so the localized phonons energies are generally different for the ground and excited states of the center.

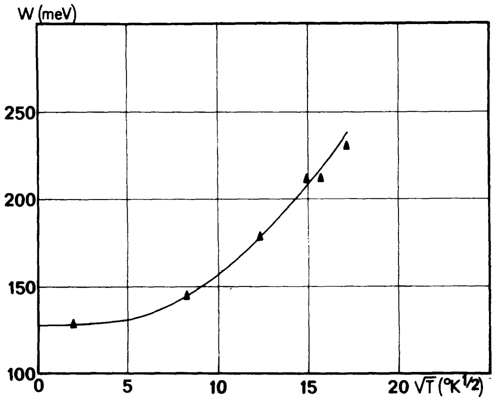

FIG. 5. Half-width W variations vs temperature T for B band. The continuous curve represents the function $W = 128[\coth(15/2kT)]^{1/2}$, with (kT) in meV.

This implies that a linear approximation is no longer valid; therefore the description of the center energy states has to be done using a configurational-coordinate diagram. To determine such diagrams, it is necessary to know both absorption and emission curves corresponding to each center. As strong lattice coupling has been pointed out, an important Stokes shift of emission towards low energies referring to absorption is to be expected. This makes the absorption and emission bands difficult to identify. For instance, absorption band B around 1.2 eV cannot be attributed to the $V_{\mathrm{Ga}}:D$ complex whose emission also arises around 1.2 eV (which may be confusing); as has been clearly demonstrated by Williams,[8] the absorption band of this complex must peak around 1.50 eV. Still, looking at a configurational-coordinate diagram, one easily sees that Stokes shift always exceeds the half-width of the absorption band at high temperature. So, for the band B, referring to room-temperature absorption measurements, we can assert that the Stokes shift is larger than 150 meV; the emission corresponding to B must then lie at an energy lower than 1.05 eV. Several authors[5,22–24] have reported on an emission band in undoped GaAs located between 0.9 and 1 eV. In particular, Sugiyama,[23] who made an extensive study of this band, found that it is probably related to gallium vacancies. Therefore, we may assume that this is the emission associated with B. According to this hypothesis, we have determined a possible configurational-coordinate diagram for the center B; it is shown in Fig. 6. We have supposed the curves to be parabolic in the whole range considered here; such an approximation is certainly far from the real case but gives a first approach of the problem. The activation energy $\Delta E = 0.46$ eV has been calculated using the luminescence-intensity-versus-temperature curves given by Sugiyama. Finally, the vibrating energy of the excited state $h\nu_e$ is found to be about 9 meV.

It is easier to find the emission band corresponding to C because it only appears when chromium is present. In similarly doped materials, Allen,[3] using cathodoluminescence measurements, and Gorelenko,[25] using photoluminescence, both find an emission band around 0.80 eV. So, in this case, the Stokes shift is unambiguously about 100 meV. Unfortunately, these authors do not give enough results to permit even a rough calculation of the configurational curves for this center. Nevertheless, the just-found Stokes shift explains the difficulties encountered in relating photoconductivity to photoluminescence measurements on chromium-doped crystals, for it is generally neglected. The photoconductivity curves reported, in particular, by Nasledov,[26] show a maximum at about 0.9 eV. These curves behave exactly like the C absorption curves shown in Fig. 1; this is to be expected since the two phenomena are closely related. First, we may assert that the decrease of photoconductivity response above 0.9 eV does not come from a quenching effect or from a negative photoconductivity mechanism, as it has been assumed in the past[26,27]; this decrease simply follows that of the absorption in the same energy range. Furthermore, the localized nature of the transition implies that photoconductivity occurs via a two-stage process: first the excitation of the center, then its ionization. Let us note that Nasledov previously suggested such a process may explain the kinetics of the photoconductivity associated to chromium.

IV. CONCLUSION

First, this study gives evidence for an important defect center in GaAs (referred as B in this paper) in which optical absorption arises around 1.2 eV. It also appears in some previous experimental works, for instance, in the absorption curve given by Sturge[1] or in photocapacitance studies,[28,29] but these results have been interpreted in a quite different way. In particular, it has been confused with the $V_{\mathrm{Ga}}:D$ complex as far as Stokes shift was neglected. More extensive studies will have to be done to exactly assert its origin. Still, till now we have found it in all the bulk GaAs samples we investigated and we give some evidence that gallium vacancies may be involved. Of course, the absorption measurements cannot be carried out on epitaxial materials because epitaxial layers are too thin. However, similar studies can be performed using photocapacitance measurements because the transitions processes are rather similar. We have done such experiments[30,31]; the results

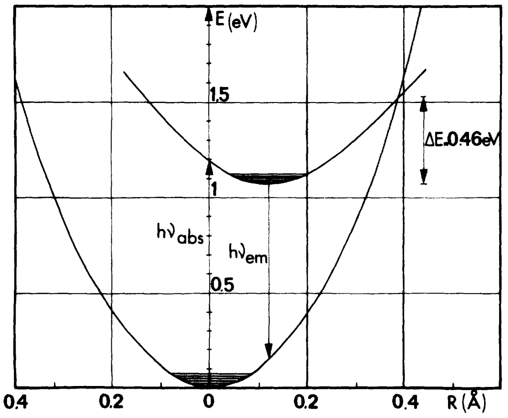

FIG. 6. Configurational-coordinate diagram proposed for center B. The two curves are supposed parabolic. For the fundamental state, $h\nu g = 15$ meV; for the excited state $h\nu_e = 9$ meV; $h\nu_{\mathrm{abs}} = 1.2$ eV and $h\nu_{em} = 0.95$ eV.

we obtain show that the same center is present in high-purity materials grown either by vapor-phase or by liquid-phase epitaxy. However, it appears that the liquid-phase technique leads to a density of centers about a tenth of that produced with the vapor phase. As in liquid-phase layers, the density of gallium vacancies is probably less than in vapor-phase-growth layers, this observation corroborates the assignment of the center B to gallium vacancies. For technical purposes, it would be useful to determine how this center may affect the electronic properties, such as the mobility or the minority carriers lifetime, of GaAs. The same work have also to be carried out in other III-V compounds; for instance, we found quite similar effects in indium phosphide.

~~-~~Besides, two conclusions can be drawn out concerning the transition processes. (i) The transitions responsible for the optical absorption of both the bands B and C seem to involve localized electronic states either in their initial and final states. No quantitative studies have been carried out for the other absorption bands observed in the samples because they are too weak or unresolved. This behavior of the deep-level-associated transitions in GaAs is rather similar to what happens in more ionic crystals (II-VI or I-VII compounds). (ii) This similarity also appears in the strong coupling of both transitions with localized vibrational modes we have pointed out. We got the energies of these modes for each center, i.e.: $h\nu g = 13$ meV for C, and $h\nu g = 15$ meV for B. This model used configurational-coordinate diagrams to describe the behavior of the center. We have shown that the absorption curves may be interpreted in such a way with a good accuracy for the two centers we have studied. Williams and Hwang have previously used the same model to explain the luminescence behavior of the complexes centers $V_{\mathrm{Ga}}:D$ and $V_{\mathrm{As}}:\mathrm{Acc}$, but no work had been done concerning absorption. Moreover, our results show that the configuration-coordinate model may apply for two other centers in GaAs. To completely determine the configurational-coordinate model of a center, it is necessary to know both the absorption and emission of this center. We have shown that, using the infrared-luminescence results found in the literature, it is possible to give a first approximation of the configuration-coordinate diagram for the B center. This supposes that the 1-eV emission band generally observed in GaAs is related to the absorption band at 1.2 eV.

Finally, it appears that the center B is of particular interest for studying the problem of configurational-coordinate model in GaAs. In fact, we have shown that absorption and luminescence can be studied in a quantitative way. For the $V_{\mathrm{Ga}}:D$ and $V_{\mathrm{As}}:\mathrm{Acc}$, the study of luminescence is easy but absorption cannot be measured because it is masked by edge absorption. What is now needed to enhance the accuracy of the determination of the configurational-coordinate B and C is a careful study of their luminescence properties. We are now engaged in that work. The first results confirm that the 1-eV emission line is really related to the 1.2-eV absorption band.

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