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Sherif Makram-Ebeid, P. Boher. Defect pairs and clusters related to the EL2 centre in GaAs. *Revue de Physique Appliquée*, 1988, 23 (5), pp.847-862. 10.1051/rphysap:01988002305084700 . jpa-00245888

HAL Id: jpa-00245888

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Submitted on 1 Jan 1988

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Classification

Physics Abstracts

71.50 — 71.38 — 61.80 — 73.40G — 72.80E

Defect pairs and clusters related to the EL2 centre in GaAs

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(Reçu le 15 septembre 1987, accepté le 16 novembre 1987)

Résumé. — Dans cet article, nous proposons des interprétations cohérentes des données expérimentales sur l'As_{Ga} irradié obtenues par des études de spectroscopie de transitoires de niveaux profonds (DLTS), de résonance paramagnétique électronique et de conductivité électrique. Notre analyse révèle un niveau donneur simple (MG) situé au milieu de la bande interdite et apparenté à l'antisite As_{Ga}. Nous fournissons des arguments permettant d'identifier le niveau MG avec celui du centre EL2 natif du matériau massif. Nous nous servons d'un modèle physique récemment mis au point pour le calcul des taux de transition électronique tunnel assisté phonon entre défauts. Dans les matériaux irradiés à forte dose on peut attribuer la conductivité électrique à des sauts d'électrons entre défauts MG. Nos calculs sont en parfait accord avec les résultats expérimentaux de Deng *et al.* pour la conductivité en courant continu de l'As_{Ga} induite par un bombardement aux ions d'argon et ceci pour une gamme de températures allant de 20 K environ à 500 K. En cherchant un accord entre calculs et observations, on trouve une énergie de phonon ($\hbar\omega = 20 \pm 2$ meV) et une énergie Franck-Condon ($S\hbar\omega = 145 \pm 10$ meV) pour MG qui sont pratiquement identiques à celles déterminées au préalable pour EL2. La conductivité pour courants alternatifs a aussi été calculée et se trouve en accord avec les résultats expérimentaux de Mareš *et al.* pour l'As_{Ga} semi-isolant de haute pureté. A basses fréquences, nous pouvons attribuer complètement cette conductivité à une répartition homogène et aléatoire de défauts EL2 dans le volume. Pour rendre compte des résultats DLTS, nous sommes conduits à invoquer le niveau MG (identifiable à celui de EL2). Pour l'As_{Ga} de type n irradié aux électrons rapides, les pics E4 et E5 apparaissant vers les hautes températures des spectres DLTS sont attribués à deux paires de défauts comprenant chacune un niveau (MG). Pour les matériaux As_{Ga} de type n irradiés aux particules lourdes, des amas de défauts rendent compte des spectres DLTS. Nos simulations pour ces paires et amas prévoient correctement les positions des pics DLTS et leur dépendance du champ électrique.

Abstract. — In this article, we attempt to consistently interpret Deep Level Transient Spectroscopy (DLTS), Electron Paramagnetic Resonance (EPR) and electrical conductivity experimental data for irradiated GaAs. Our analysis reveals the occurrence of an irradiation-induced single donor mid-gap level (MG) related to the As_{Ga} antisite defect. We give evidence that MG can be identified with the deep level associated to the native bulk centre EL2. We make use of a model we have recently developed for the calculation of inter-defect phonon-assisted tunnelling rates. We calculate the nearest neighbour defect-induced hopping conductivities. In heavy dose irradiated GaAs, the DC conductivity is attributed to hopping between MG defects. Our calculations provide extremely good fits to the experimental results of Deng *et al.* for the DC electrical conductivity in GaAs induced by argon ion bombardment for temperatures ranging from around 20 K to 500 K. The phonon energy $\hbar\omega$ (20 ± 2 meV) and Franck-Condon shift $S\hbar\omega$ (145 ± 10 meV) of MG needed to achieve this fit are in very good agreement with the $\hbar\omega$ and $S\hbar\omega$ values earlier determined for the native EL2 defect. The bulk AC hopping conductivity has also been calculated and found to agree well with experimental results of Mareš *et al.* for high purity semi-insulating GaAs. The corresponding low-frequency AC conductivity is attributed entirely to a homogeneous random distribution of native mid-gap donor defects EL2. We are also led to invoke the mid-gap level MG (identifiable with that of EL2) in order to account for DLTS results. In fast-electron irradiated n-GaAs, the two high temperature DLTS peaks E4 and E5 are both accounted for by two defect pairs each including an MG level component. In heavy-particle bombarded n-GaAs damage clusters including MG defects account for the experimentally recorded high temperature DLTS peak. For these defect pairs and clusters, our DLTS simulations correctly predict the observed peak positions and their dependence on the electric field.

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Introduction.

The EL2 deep-level defect in GaAs is of great practical importance because it is essential in pinning the Fermi level near mid-gap in high purity and in indium-doped semi-insulating substrates. This has stimulated an abundant literature over the properties of EL2 [1, 2] and over its identification (see e.g. Refs. [1-5]). The symmetry and paramagnetic — optically monitored — resonance behaviour indicate that it is a complex including the antisite defect As_{Ga} . Recent publications [5] support the attribution of EL2 to a second-neighbour complex ($\text{As}_{\text{Ga}}\text{As}_i$) with an arsenic interstitial atom as earlier suggested by von Bardeleben *et al.* [4].

The Fermi-level has been reported to be pinned near mid-gap in GaAs materials after a large dose of fast-electron [4] or heavy-particle (fast-neutron or ion) [6, 7] bombardment. A similar Fermi-level pinning is also observed near real GaAs surfaces [8] irrespective of the surface treatment or dielectric deposition used. In all these cases, a defect compensation mechanism including a mid-gap level is responsible for the Fermi-level pinning. This is very similar to the compensation occurring in undoped or indium doped semi-insulating GaAs substrates and where EL2 is involved.

In this article we attempt to decide whether the mid-gap level induced by electron or heavy-particle irradiation is related to the native EL2 level. As will be seen later, this irradiation-induced mid-gap level systematically appears to be part of a close defect pair or of a dense damage cluster. Electron hopping probabilities between defects in these pairs and clusters cannot be neglected and prevent a straightforward interpretation of the electrical properties of irradiated GaAs.

In order to gain insight into these problems, we make use of our newly developed theory for the practical calculation of multiphonon tunnelling transition rates between deep level defect states in a semiconductor [9]. The fact that multiphonon effects may assist the ionization of isolated defects in such materials has earlier been demonstrated [10, 11]. We use our theory for predicting the defect-induced DC and AC electrical conductivities as well as the DLTS behaviour. We compare our theoretical simulations with experimental results.

1. Evaluation of multiphonon hopping rates.

In this section we describe the method we adopted for the evaluation of the inter-defect multiphonon tunnelling rates. The corresponding theory was recently developed [9].

Two defects labelled $i = 1$ and 2 are assumed to interact and their centroids to be a distance r_{12} apart. An electric field of intensity F acts at an angle θ with the line joining the defect centroids. We calculate

the electronic terms by making use of a Quantum Defect Model (QDM) [12]. In such a model, the potential of defect i at distances larger than a value a_i from its centroid is simply taken to be the long range Coulomb potential $\varphi_i(\mathbf{r})$ given by

$$\varphi_i(\mathbf{r}) = - \frac{\alpha_i}{|\mathbf{r} - \mathbf{r}_i|}$$

with

$$\alpha_i = q^2 Z_i / (4 \pi \epsilon_0 \epsilon_r)$$

where $\mathbf{r}_i$ is the positional radius vector for the centroid of defect i , $\mathbf{r}$ is the positional vector of an arbitrary point in the semiconductor and a_i . $Z_i q$ stands for the total charge of the ionized defect, q is the elementary charge and $\epsilon_0 \epsilon_r$ the dielectric constant of the semiconductor. The numerical value of α_i for GaAs ($\epsilon_r = 12.53$) is about $1.15 \text{ eV } \text{\AA}$ for a single donor.

The above long-range potential is assumed to hold in a region outside a sphere defined by $|\mathbf{r} - \mathbf{r}_i| \geq a_i$. In this region, the semiconductor's energy-momentum relationship is used to describe the electronic wave-function. Inside the sphere $|\mathbf{r} - \mathbf{r}_i| < a_i$ another (localized) Coulomb potential and a different electron effective mass have to be assumed and these are heuristically adjusted to agree with experimentally observed data of the defects. The radii a_i are of the order of one or two lattice spacings.

In describing the long-range electron wave-functions (for $|\mathbf{r} - \mathbf{r}_i| > a_i$), we make use of Franz-Kane relationship [13] $K(\Delta)$ between the wave-function attenuation factor K and the electronic energy Δ measured from the bottom of the conduction band. The electron wave function can thus be written as [10]

$$\psi_i(\mathbf{r}) = \eta_i \cdot \frac{(2 K_i)^{3/2}}{(4 \pi \Gamma(2 p_i + 1))^{1/2}} \cdot \frac{e^{-A_i(\mathbf{r})/2}}{(2 K_i |\mathbf{r} - \mathbf{r}_i|)^{1-p_i}} \quad \text{for } |\mathbf{r} - \mathbf{r}_i| > a_i \quad (1)$$

$$\text{with } K_i = K(\Delta_i), \quad p_i = \alpha_i \left. \frac{dK(\Delta)}{d\Delta} \right|_{\Delta=\Delta_i}$$

and

$$A_i(\mathbf{r}) = 2 \cdot \int_0^1 K(\Delta_i - q\mathbf{F} \cdot (\mathbf{r} - \mathbf{r}_i) \zeta) |\mathbf{r} - \mathbf{r}_i| d\zeta$$

where we have assumed spherically symmetrical (s-state) wave functions, $\Gamma(x)$ stands for the Gamma function [14], $\mathbf{F}$ is the electric field vector and Δ_i the energy of the localized electron measured below the conduction band. One recognizes the WKB expression $A_i(\mathbf{r})$ for the wave function attenuation. The numerical prefactor η_i is such that $(1 - \eta_i^2)$ is approximately the probability of finding the electron in the region ($|\mathbf{r} - \mathbf{r}_i| \leq a_i$). For the deep-levels we are dealing with here, one expects a

near unity probability for finding the electron inside the sphere ($|\mathbf{r} - \mathbf{r}_i| \leq a_i$) and a hence small value of η_i . Such a strong localization of deep level wave functions had to be assumed both in reference [10], to account for electric field ionization of defects, and by Burt [15] to account for deep level photo-ionization cross-sections in GaAs.

In order for an electron to hop from one defect site to another, multi-phonon energy has to be exchanged with lattice-vibration modes. The defect labelled i is assumed to be linearly coupled to a localized phonon mode of energy $\hbar\omega_i$ with a Huang-Rhys coupling constant S_i . One can then write the inter-defect hopping rate R_{12} as an integral over all energies E in the band-gap and for deep level defects, this takes the form [9]

$$R_{12} = \int_E P(E) \cdot D_1(E - E_{T1}) \cdot D_2(E_{T2} - E) \cdot dE \quad (2)$$

where

$$P(E) \approx \frac{256 \pi}{\hbar} \cdot \frac{(m^*)^{3/2}}{(m_{d1} m_{d2})^{3/4}} \times \eta_1 \eta_2 \left(\frac{E_{co} - E}{A(E)} \right)^2 e^{-A(E)}$$

with

$$A(E) = 2 \int_{-1}^{+1} K \left(E_{co} - E - qF \cdot \cos \theta \cdot \frac{r_{12}}{2} \cdot \zeta \right) \times r_{12} \cdot d\zeta$$

where E_{co} is the conduction-band energy mid-way between the two defects, $K(\Delta)$ stands for the Franz-Kane dispersion relation m^* and m_{di} are the effective mass in the conduction band and near the defect centroids respectively, E_{T1} and E_{T2} are the total (electron + lattice) free energy before and after the hopping transition respectively. The function $D_i(E_p)$ represents the probability density (per unit energy) that an electron trapped in defect i will absorb a multiphonon energy E_p . Negative E_p values imply multiphonon emission. These functions (for $i = 1$ and 2) are defined by

$$D_i(E_p) = \exp \left(-\frac{E_p}{2kT} - S_i \cdot \coth \left(\frac{\hbar\omega_i}{kT} \right) \right) \times I_m \left(\frac{S_i}{\sinh(\hbar\omega_i/2kT)} \right) / \hbar\omega_i \quad (3)$$

where I_m is the modified Bessel function [14] of order m and $m = -E_p/\hbar\omega_i$.

Reversing the roles of defects (1) and (2), the reverse tunnelling rate R_{21} can be deduced. From the above results, it can be shown that

$$R_{21} = R_{12} \cdot \exp \left(-\frac{E_{T1} - E_{T2}}{kT} \right) \quad (4)$$

This can be also obtained as a result of the Fermi-Dirac statistics from the principle of detailed balance.

In the above expression, when calculating the difference ($E_{T1} - E_{T2}$) in total energy of the defects, one should, in general, include the effects of both the semiconductor electric field F and those of the long-range Coulomb potentials of the defects themselves. We then have

$$E_{T1} - E_{T2} = \Delta_{T2} - \Delta_{T1} + qF \cdot r_{12} \cos \theta + \frac{\alpha_1 - \alpha_2}{r_{12}}, \quad (5)$$

Δ_{T1} and Δ_{T2} being the ionization energies for isolated defects 1 and 2 respectively.

2. Analysis of irradiation-induced defects in GaAs.

In this and the following sections, we make use of the above results as a tool for interpreting experimental data related to the defects induced by fast electron, fast neutron irradiation and by ion implantation of GaAs.

Lang [16] has reported a comparison (made by Kimerling *et al.* at Bell Laboratories) between DLTS spectra obtained for n-GaAs samples which have been previously bombarded by high energy particles of different types. The largest differences between these spectra appeared to be due to the deepest level (nearest to mid-gap). The corresponding DLTS peak becomes progressively wider when one goes from electron to proton, to He^+ and to O^+ irradiation. These authors attributed the difference in the spectra to the formation of defect clusters when heavier particles are used for bombarding the material. In contrast, electron bombardment is expected to produce simpler defects such as single vacancies, interstitials and Frenkel defect pairs. Physically, this is related to the fact that the mass of heavier ions is better matched than the mass of electrons to the lattice atoms. Hence, each impinging heavy-ion can impart a larger portion of its kinetic energy to lattice atoms. An initial interaction between an impinging ion and a lattice atom is referred to as a Primary Knock-On (PKO) event [17]. The lattice atom displaced during such an event can have considerable kinetic energy and is capable, in turn, of generating a cascade of other defects all localized within a small volume of the bombarded crystal. The geometry of the resulting damage clusters can be theoretically estimated [18] and is related to deposited energy data [19]. In the cases investigated here, the clusters are expected to have sizes of the order of 500 Å. When comparing DLTS results, fast-neutron-irradiated samples [20] are found to have spectra closer to those of heavy-ion implanted samples than to proton-bombarded samples [16]. This may seem surprising since protons and neutrons have practi-

cally equal masses. It is, however, recalled that unlike protons, the interaction of neutrons with lattice atoms occurs exclusively through nuclear collisions (no electronic stopping) and hence neutrons generate clusters more efficiently than protons.

2.1 INDIVIDUAL DEFECTS INVOLVED. — We start by reviewing the defects observed in n-GaAs after fast electron or gamma irradiation. The defects introduced by heavier particle bombardment are more difficult to analyse because of the occurrence of damage clusters as mentioned above.

2.1.1 Defects in fast-electron-irradiated n-GaAs. — The main electron trapping levels observed for fast-electron irradiation have been labelled [16, 21] E1 ($E_c - 0.045$ eV), E2 ($E_c - 0.14$ eV) and E3 ($E_c - 0.310$ eV). These levels are the most extensively studied. Convincing evidence exists that they are all due to arsenic atom displacements and that E1 and E2 are related to two charge states of the same defect [21] (i.e. $E1 = E2 + \text{electron}$). Two other wide DLTS electron peaks labelled E4 and E5 are also observed with appreciable amplitudes. The introduction rates of E1, E2, E3, E4 and E5 in n-GaAs for 1 MeV electron irradiation have been reported [21] to be 1.5, 1.5, 0.4, 0.08 and 0.1 cm^{-1} respectively. The E4 and E5 peaks are not completely resolved from each other in the as-irradiated material. Their apparent ionization activation energies are 0.72 ± 0.03 eV and 0.88 ± 0.08 eV respectively. It was recently shown that recombination annealing during current injection in a p-n junction diode can significantly reduce the E5 DLTS signal amplitude without affecting that of E4 [22]. This allows the separate observation of the E4 DLTS peak which proved to be much wider than is expected for an isolated defect level. Moreover, we have studied E5 with the help of the Differential DLTS (DDLTS) technique [23] in order to determine its electric-field sensitivity. The E5 DDLTS peaks were found to be extremely sensitive to electric fields as low as 100 kV/cm. Neither a Poole-Frenkel effect nor a multiphonon-assisted field ionization of an isolated defect with a near mid-gap level can account for this abnormal electric field sensitivity of E5.

The above observations rule out the attribution of E4 or E5 to isolated point defects. Instead, we are led to attribute each of E4 and E5 to a distant defect pair, one defect having a near mid-gap level while the other has a level nearer to the conduction band. For such a pair and at low temperatures, the emission rate of a single captured electron will be very slow and a second electron can be captured and has to occupy the shallower level (by virtue of Pauli's exclusion principle). The trapping and subsequent ionization of this second electron should thus be seen as a low-temperature DLTS peak corresponding

to the shallower level. Thus, the shallower level component in these defect pairs should be directly observable by DLTS and can only be E2 or E3. The low-field ionization kinetics of E2 and E3 are exponential as evidenced by their narrow DLTS peaks [21]. This indicates that the mid-gap level component of the E4 and E5 pairs should be a single donor; otherwise, when occupied by an electron, its Coulomb potential could introduce an observable random fluctuation in the ionization energies of E2 and E3.

We are thus led to postulate the occurrence of a Mid-Gap level defect which we represent by the symbol MG in this article. Independent evidence for such an irradiation-induced mid-gap level comes in fact from EPR, Hall effect and hopping conductivity measurements as discussed below.

2.1.2 Irradiation-induced mid-gap levels in GaAs. — An Electron Paramagnetic Resonance (EPR) quadruplet structure attributed to the antisite As_{Ga}^+ can be obtained in concentrations up to 10^{18} cm^{-3} by electron irradiation [24, 25]. Similar EPR spectra are observed after plastic deformation or fast neutron irradiation [3] of n- or p-GaAs. The photo-EPR response for plastically deformed materials shows that the EPR signal is related to a mid-gap single donor level. Electrical conductivity and Hall effect measurements show that the Fermi level is pinned near mid-gap after large doses of either fast electron [4] or fast neutron [6] irradiation. These observations suggest that the As_{Ga} defect is associated with the mid-gap single donor level MG that was postulated above for the interpretation of DLTS data.

The famous EL2 single donor, which is native in bulk and vapour phase epitaxial materials, is probably a complex including the As_{Ga} defect [1-6]. Identifying together the two As_{Ga} related mid-gap single donors MG and EL2 is still a matter of discussion. Our observations suggest that E4 and E5 are due to defect pairs each consisting of the As_{Ga} related mid-gap donor together with one of the acceptors E2 or E3, which are both believed to be associated with a V_{As} vacancy [21].

We shall demonstrate in a later section that large-dose irradiation gives rise to a nearest neighbour hopping DC conductivity through a mid-gap defect with practically the same lattice relaxation parameters $\hbar\omega$ and $S\hbar\omega$ as those of EL2.

2.1.3 Defects in heavy-particle bombarded GaAs. — Detailed DLTS data have been published [26] for boron ion implanted n-GaAs. The DLTS spectra observed, as can be seen in figure 1, consist of a wide high temperature peak, referred to as the U-peak, together with shallower levels. Experiments [27] show that the main observable shallow level in the implanted material is level E3 ($E_c - 0.32$ eV at 0 K). Both the observed peak position

Fig. 1. — DLTS spectra for 100 keV boron-ion implanted n-GaAs after 30 min isochronal annealing at different temperatures, from reference [26]. In the starting material, the free electron concentration was about 10^{17} cm^{-3} . Gold Schottky diodes were used. The reverse bias voltage and the filling bias pulse amplitude were both 2 V.

and its high electric field sensitivity [28] confirm that this defect is identical with defect level E3 generated in fast electron proton bombarded materials [17]. Other authors [16] also report a small DLTS signal related to level E2 ($E_c - 0.14 \text{ eV}$) in ion-implanted materials which is again identified with that observed in electron-irradiated materials.

As to the high temperature U-peak, we shall confirm in this article its attribution [26] to electronic interactions between the mid-gap defect level MG with the shallower defect E2 and E3.

The large defect density at the clusters' core solidly pins the Fermi level at mid-gap and, as will be discussed in section 6.2, only defects at the clusters outskirts can have an observable influence on DC electrical conductivity and DLTS results. The damage energy imparted per lattice atom at these outskirts is expected to be of the same order as that imparted during fast-electron irradiation and the same type of individual point defects should be created. Moreover, it will be shown in section 6 that the shallower defects can only be observed by DLTS when they are well away from the cluster cores. One therefore understands why the same isolated shallow traps (E2, E3) as in electron irradiated materials are observed. In the next sections we shall see that the experimental results for heavy-particle bombarded semi-insulating and n-GaAs can be explained by invoking the same defects (E2, E3, MG) as for fast-electron-irradiated materials with the same relative concentrations.

2.2 DATA USED IN OUR CALCULATIONS. — In our calculations we shall make use of the properties known for the above defects and listed in table I. An important input to our calculations is the donor or acceptor nature of the defects involved. This is because Coulomb potentials introduce an important term in the difference between interacting defect levels (see Eq. (5)).

The defect related electron effective masses m_{di} entering equation (2) are taken, in all cases, to be 0.25 in units of the free-electron mass. This value together with reasonable assumptions for the defect potential near the centroid (for $|\mathbf{r} - \mathbf{r}_i| < a_i$) lead, within our quantum defect model, to ionization energies comparable to those of table I. The numerical value of the square of the wave function pre-exponential factor η_i^2 is given in table I as deduced from the electric-field ionization data (in Tab. I of Ref. [10] this factor is represented by the symbol $3\hbar\gamma/2$). We can thus evaluate the product of the pre-exponential factors in the expression of $P(E)$ appearing in equation (2) within an uncertainty of about a factor of 3.

Apart from as-irradiated defects, we have also listed EL6 which is native in bulk GaAs and is probably identical to a defect P1 observed (in low concentrations) after fast-electron irradiation and annealing [32]. This defect is worth studying because it has an electron ionization activation energy almost identical with that of E3 and can be confused with it in DLTS experiments. EL6 can be differentiated from E3 because of the very different behaviour of their DDLTS peak position at different electric fields. E3 is known to be very sensitive to the electric field [28] whereas EL6 is practically insensitive to the field [27]. This difference in the electric-field behaviour of E3 and EL6 can be accounted for, according to the theory of reference [6], by the abnormally large lattice relaxation energy of EL6 [27, 33] ($S\hbar\omega \approx 600 \text{ meV}$).

In the following sections we shall refer, in our interpretations, mainly to the defects MG, E2 and E3. Experimental observations in irradiated GaAs will be shown to be a result of electronic interactions between these defects. As for E1, we recall that it is a second charge state of E2. In our notation, we shall reserve label $i = 1$ for the mid-gap defect MG.

In the heavily damaged regions of irradiated GaAs the Fermi level is, as already discussed, pinned on the mid-gap level MG. If f_0 is the average thermal equilibrium occupation ratio of this MG single donor level, the fraction $(1 - f_0)$ of these defects will be positively charged and the rest will be neutral. Since other defect levels, at all temperatures of interest, are many kT units above or below the Fermi energy, they can only introduce a temperature-independent charge density. Overall charge neutrality, therefore, implies a temperature-independent value of f_0 .

3. DC hopping conductivity in irradiated GaAs.

Deng *et al.* [34] have extensively studied the DC electrical conductivity induced in GaAs by heavy-particle (Ar^+) bombardment, which causes damage in a layer approximately $0.4 \mu\text{m}$ thick. Their conduc-

Table I. — *Physical parameters characteristic of the individual n-GaAs deep-level defects as assumed in the numerical evaluations. Our calculations proved tolerant to the indicated uncertainties in phonon energies $\hbar\omega$ and Franck-Condon shifts $S\hbar\omega$. The dimensionless constant η_i^2 is the square of the pre-exponential factor appearing in equation (1) for the trapped electron wave-function. It is deduced by comparing the experimental electric-field ionization with the predictions of the theory of reference [10]. The largest parameter uncertainty is that of η_i^2 and is related to experimental uncertainties in the electric fields. The ionization energy is assumed to depend on temperature according to a law similar to that of the GaAs band-gap (Ref. [29]), i.e.*

$$\Delta_T(T) = \Delta_T(0) - \gamma T^2 / (T + 200)$$

where the temperature coefficient γ is determined from the deep level electron capture and emission data (Ref. [30]). E1 has a large lattice relaxation. Its negative (repulsive) potential suggested by the small capture cross-section ($\approx 10^{-18} \text{ cm}^{-2}$ reported in Ref. [31]) is confirmed by the small experimentally determined value of η_i^2 . E2 has a large capture cross-section ($(1.3 \pm 0.3) \times 10^{-13} \text{ cm}^{-2}$ as shown in Ref. [31]). Since $E1 = E2 + \text{electron}$, E1 and E2 can only be double and single acceptor levels respectively. The data for EL6 are incomplete. Because of its very large Franck-Condon Shift, we have assumed that its electron capture cross-section has a small Arrhenius activation energy.

Defect label and type	Δ_T meV	γ meV/K	$\hbar\omega$ meV	$S\hbar\omega$ meV	η_i^2 dimensionless	References for data
E1 Double Acceptor	45	1	4 ± 2	60 ± 20	$(1.1 \pm 0.9) \times 0.0001$	This work using theory of Ref. [10] to fit experiments of Ref. [31] Confirmed by the temperature dependence of the electron capture rates
E2 Single Acceptor	140	0	4 ± 1	55 ± 5	0.02 ± 0.015	This work using theory of Ref. [10] to fit experiments of Ref. [31]
E3 Single Acceptor	310	0.17	10	100 ± 20	0.02 ± 0.005	Refs. [10, 11, 28]
EL6 = P1 Probably Single Acceptor	320 ± 30	0.2 ± 0.1	unknown, but assuming $\hbar\omega < kT$	600 ± 100	taken 0.02	Refs. [27, 33]
MG or EL2 Single Donor	735	0.27	20 ± 2	145 ± 10	0.08 ± 0.03	Refs. [10, 11]. Also using theory of section 4 of this work to fit experiments of Ref. [34].

tivity increased with ion dose but saturated at about a dose of $3 \times 10^{13} \text{ Ar}^+ \text{ cm}^{-2}$. Both the type of temperature dependence observed and the magnitude of thermo-power allow the attribution of this

conductivity to electron hopping. However, Deng *et al.* accounted for their experimental results with a variable range hopping model [35] and they had to assume a continuous defect density energy distri-

bution in the band-gap. This defect distribution is in clear conflict with DLTS and EPR observations. Furthermore, an essential condition for the occurrence of multiple range hopping is that first and second neighbour hopping probabilities should be comparable [35]. This, in fact, implies complete amorphization for large-dose heavy-particle bombardment, in contradiction with the X-ray diffraction data of Coates and Mitchell [36]. For the ion bombardment doses needed to approach the saturation hopping DC conductivity, the defect concentration can be roughly estimated by extrapolating DLTS data [26] to be of the order of 10^{19} cm^{-3} . An estimate is also obtained from EPR of fast-neutron-irradiated materials [6], in which case the onset of hopping conduction is observed when the As_{Ga}^+ defects are in a concentration of 10^{18} cm^{-3} [7]. For these concentrations, nearest neighbour hopping probabilities are expected to exceed those for second neighbour hopping by several orders of magnitude.

We have calculated the nearest neighbour hopping conductivity according to the theory of reference [9]. Our DC conductivity calculations are an extension of the Miller and Abrahams theory [37] for percolation conduction but include in addition multiphonon effects. The expression we use for DC hopping conductivity σ_{dc} between mid-gap level defects (labelled 1) can be written as

$$\sigma_{\text{dc}} = \frac{3 q^2 B_c^2}{8 \pi r_{11}^2 \kappa} \cdot \frac{f_0(1-f_0)}{kT} \cdot e^{-\epsilon_c/kT} \cdot R_{11}(r_{11}) \quad (6)$$

where $\kappa = \frac{1}{2} \cdot d(\ln(R_{11}))/dr_{11}$. B_c stands for the average number of above critical conductances emerging from each site at percolation threshold and can be taken to be 2.7 in accordance to Monte Carlo simulations for three-dimensional uniform random distribution of defects [38, 39]. The critical inter-defect distance r_{11} is related to the average mid-gap defect (MG) concentration n_{MG} by $\frac{4}{3} \pi r_{11}^3 n_{\text{MG}} = B_c$.

The hopping rate $R_{11}(r_{11})$ appearing in the above expression is calculated for zero electric fields (same initial and final energies) and for MG defects separated by a distance r_{11} . The activation energy ϵ_c corresponds to random fluctuations of the Coulomb potential in accordance to the theory of Miller and Abrahams [37]. Introducing this activation energy very considerably improves the agreement with experimental results as compared to our earlier calculations where we did not take it into account [40].

Figure 2 shows best fits of our theoretical results for σ_{dc} with the experimental results of Deng *et al.* for as-implanted samples. The high-temperature activation energy can be proven to be equal to

Fig. 2. — Comparison of theory and experiment for the low-temperature electrical conductivity. The experimental points are from Deng *et al.* in reference [34] for large dose Ar bombarded GaAs. The full circles correspond to as-bombarded samples while the full triangles correspond to a 400 °C annealed sample. The curves are calculated for hopping between MG defects. For both curves we have taken $f_0 = 1/2$.

$\epsilon_c + (S\hbar\omega - 3kT)/2$ so that the Franck-Condon shift $S\hbar\omega$ of MG is directly deduced. The value of the activation energy ϵ_c is deduced from the behaviour of σ_{dc} in the low temperature limit ($T < 50 \text{ K}$) where it is responsible for the observed activation energy. The phonon energy $\hbar\omega$ is deduced from the plot of $\log(\sigma_{\text{dc}})$ versus $1/T$ for intermediary temperatures ($200 > T > 100 \text{ K}$). It is remarked that the fit gives very good agreement with experimental results with a slight discrepancy only at the highest temperatures in the 400 °C annealed samples. This discrepancy can be completely attributed to hopping conduction through levels shallower than MG [9]. This shallow levels contribution is expected to be significant at high temperatures and when the defect densities are relatively low (as is the case after thermal annealing).

The phonon best-fit parameters deduced in the above manner are $\hbar\omega = 20 \pm 2 \text{ meV}$ and $S\hbar\omega = 145 \pm 10 \text{ meV}$, which are in excellent agreement with those reported [10, 11] for the native mid-gap level EL2 ($\hbar\omega = 20 \pm 5 \text{ meV}$ and $S\hbar\omega = 140 \pm 10 \text{ meV}$).

Miller and Abrahams [37] have tabulated the normalized theoretical values of the activation energy ϵ_c (in their article they used the symbol ϵ_3 in place of ϵ_c) for different compensation ratios. Our best-fit procedure yields $\epsilon_c = 19 \pm 2 \text{ meV}$ which agrees with the predictions of Miller and Abrahams theory for the mid-gap defect concentrations deduced from figure 2 provided we take a compensation ratio of $(1 - f_0) = 0.5 \pm 0.2$ for the as irradiated sample and $(1 - f_0) \approx 0.1$ for the annealed sample. We therefore see that the different

parameters needed for the fit are self-consistent. However, the above estimates of the compensation ratio $(1 - f_0)$ must be considered as rough because of the uncertainty in the estimated inter-defect separations (r_{11} values in Fig. 2).

4. AC hopping conductivity in GaAs.

A non-zero DC electron hopping conductivity σ_{dc} implies the availability of uninterrupted hopping paths between the electrodes. Another type of hopping-related conductivity can be observed and does not imply the occurrence of such continuous conduction paths. In the presence of an AC electric field, dielectric polarization losses [41] give rise to an additional AC conductivity component σ_{ac} , and thus the total electrical conductivity σ_{tot} should be expressed as a sum $\sigma_{tot} = \sigma_{dc} + \sigma_{ac}$. The AC electric field induces dielectric dipoles; a lag angle in the time-response of these induced dipoles with the field gives rise to power losses which can be expressed as a conductivity σ_{ac} .

Pollak and Geballe [42] made the corresponding calculations exclusively taking into account pairs of centres. This isolated defect pairs approximation is shown to be valid only for angular frequencies ω_s higher than the hopping rate $R_{12}(r_0)$ corresponding to the average separation r_0 between the centres [42]. The direct Kirchhoff's law numerical simulations of McInnes *et al.* [43] have later shown that the isolated defect pairs approximation gives indeed a good estimate of σ_{ac} for high frequencies ($\omega_s > R_{12}(r_0)$). At lower frequencies, this approximation fails but this is of little consequence since the AC conductivity has always to be added up to the DC conductivity and this swamps any erroneous evaluation. Making this simplifying isolated pairs assumption, the AC loss-conductivity σ_{ac} can be obtained by adding up the contributions of the defects having separations between $r_{12} = r$ and $r_{12} = r + dr$ from $r = 0$ to ∞ , thus

$$\sigma_{ac} = N_p \int_{r=0}^{\infty} (f_1(1 - f_2) + f_2(1 - f_1)) \times \frac{(qr)^2 \cdot \exp\left(\frac{E_{T2} - E_{T1}}{kT}\right)}{3 kT \left(1 + \exp\left(\frac{E_{T2} - E_{T1}}{kT}\right)\right)^2} \times \frac{\omega_s^2 \cdot R_{ss}}{\omega_s^2 + R_{ss}^2} \cdot \frac{dP(r)}{dr} \cdot dr \quad (7)$$

where $R_{ss} = R_{12} + R_{21}$ and N_p is the volume concentration of nearest-neighbour pairs. Only those pairs with one defect occupied with an electron and the other empty are effective. This accounts for the factor $(f_1(1 - f_2) + f_2(1 - f_1))$ appearing in the above expression; f_1 and f_2 being the steady-state

Fermi-Dirac occupation probabilities of levels 1 and 2 respectively. E_{T1} and E_{T2} are the total energies of the two centres involved. $P(r)$ is the portion of these pairs separated by distances smaller than r .

From equation (7), the defect levels most likely to contribute to the above AC conductivity prove to be those situated very near the Fermi level. For undoped semi-insulating or heavy dose irradiated GaAs, these defects can only be EL2 or MG respectively. In both cases, we may take for N_p half the total defect concentration N_T , and for $P(r)$ we take a Poisson distribution given by [44]

$$P(r) = 1 - \exp\left(-\left(\frac{r}{r_0}\right)^3\right),$$

$$\text{where } r_0 = \left(\frac{3}{4\pi N_T}\right)^{1/3}.$$

We have numerically evaluated the above integral expression for σ_{ac} . Our numerical results differ from those earlier published for shallow impurity-band AC conduction [42, 43] since our transfer rates include multi-phonon hopping effects.

Comparison with experimental results. — Figure 3 reports the loss part of the defect-related permittivity defined by $\varepsilon'' \equiv \frac{\sigma_{ac} + \sigma_{dc}}{\omega_s}$, calculated as a function

of the frequency $\frac{\omega_s}{2\pi}$ for different defect densities N_T corresponding to different average defect separations r_0 . The results are normalized to ε_∞ , which is the intrinsic dielectric permittivity of the medium in the absence of defects. In the calculations, we

Fig. 3. — $\varepsilon''/\varepsilon_\infty$ (practically equal to the dielectric loss tangent) at $T = 90$ K as a function of frequency for different average defect separations r_0 . The dashed parts of the curves for $r_0 = 25$ and 50 Å correspond to a dominant influence of the DC conductivity. The experimental points are from Mareš *et al.* in reference [45] for two high purity semi-insulating GaAs substrates. The results correspond to true homogeneous bulk dielectric losses (guard rings used and surface not heavily damaged).

assumed EL2 defects and we took for the compensation ratios $(1 - f_1) = (1 - f_2) = 1/2$.

Mareš *et al.* [45] have performed dielectric loss measurements in the frequency range from 10 Hz to 10 kHz for undoped semi-insulating GaAs. These authors showed that the experimental measurements are very sensitive to surface treatments and they showed that it is essential to use guard rings in order to obtain reliable results. For undoped GaAs, the EL2 native mid-gap defect concentration is a few 10^{16} cm^{-3} , thus corresponding to an average defect separation in the range of 150 to 250 Å. Our predictions (curves in Fig. 3) agree both in order of magnitude and in frequency dependence with the experimental results (empty and full circles in Fig. 3) of these authors.

The above calculations and experimental results refer to a temperature of 90 K. For the above mentioned EL2 concentrations and frequencies, our model predicts only slight changes in the AC dielectric losses when the temperature changes from 90 to 300 K, in agreement with the experimental observations of Mareš *et al.* For larger defect densities ($r_0 < 50 \text{ Å}$), the low-frequency 90 K dielectric loss is predicted to be mainly due to the DC conductivity σ_{dc} (dashed part of the curves for $r_0 = 25$ and 50 Å in Fig. 3). The corresponding ε'' tends to $\varepsilon'' \approx \frac{\sigma_{dc}}{\omega_s}$ which is inversely proportional to frequency and varies with temperature proportionally to σ_{dc} as was studied in the previous section.

For microwave frequencies (4 to 40 GHz) the dielectric loss tangent (nearly equal to $\varepsilon''/\varepsilon_\infty$) has been measured at and above room temperature for semi-insulating GaAs [46] and tends to increase with frequency. This behaviour cannot be reproduced by a model with a uniform random distribution of defects. Instead, one is led to suggest the occurrence of zones with highly localized defect concentrations. In these zones the DC conductivity can be locally high. The dielectric function of a semiconductor with such inclusions can be predicted from a standard formula for a mixture [45]. Only a very small fraction (of the order of 10^{-4}) of the semiconductor's volume with a high — but non-metallic — DC conductivity can account for the dielectric loss at microwave frequencies. Such microscopic high σ_{dc} regions may occur, for example, within a disturbed layer near the semiconductor's surface. The role of such a near-surface layer is confirmed by the observations of Mareš *et al.* who report a marked increase in ε'' which becomes nearly proportional to frequency (in the range of a few kHz) after a surface oxidation of semi-insulating GaAs.

5. Electron ionization rates of defect pairs.

We now predict the transient ionization behaviour of a defect pair consisting of a deep level defect

(labelled 1) and a shallower level (labelled 2). Assuming that a single electron is trapped in the defect pair, it will occupy level 2 for a fraction f_2 of the trapping time. During the remaining fraction $(1 - f_2)$ of this time, the electron will occupy level 1. The value of f_2 can be determined from the quasi-equilibrium condition

$$f_2(e_2 + R_{21}) = (1 - f_2) R_{12}$$

$$\text{and thus } f_2 = \frac{R_{12}}{R_{21} + R_{12} + e_2},$$

where e_2 is the electron emission rate from level 2. The trapped electron can either be directly ionized from the ground level (1) at a rate e_1 or, indirectly through level (2), at a rate e_{ind} given by

$$e_{ind} = f_2 e_2 = \frac{R_{12} e_2}{R_{21} + R_{12} + e_2}.$$

It must be pointed out that each of the direct ionization rates e_1 and e_2 from defects 1 and 2 differs from that of an isolated defect since the Coulomb potential of the neighbouring defect changes its ionization energy. Taking this potential term into account amounts to changing the ionization energies of defects 1 and 2 from Δ_{T1} and Δ_{T2} to $\Delta_{T1} + \frac{\alpha_2}{r_{12}}$ and $\Delta_{T2} + \frac{\alpha_1}{r_{12}}$ respectively. We deduce the emission rate e_i from e_{i0} of the isolated defect from the relationship

$$e_i = e_{i0} \frac{D_i \left(\Delta_{Ti} + \frac{\alpha_j}{r_{12}} \right)}{D_i(\Delta_{Ti})}$$

where $i \neq j$, and it is recalled that $D_i(E_p)$ represents the probability that an electron trapped in defect i will absorb a multiphonon energy E_p (Eq. (3)).

In the above treatment, the indirect ionization rate e_{ind} was written as $f_2 e_2$ which is a « quasi-static occupation ratio » approximation. A more exact treatment by Rees *et al.* [47] gives practically identical results provided the energy difference between the two levels is large enough to guarantee the inequality $R_{12} \ll R_{21}$. This condition is largely met for the defect pairs we are dealing with. Adding up direct and indirect components, we obtain for the total electron ionization rate e_n :

$$e_n = e_1 + \frac{R_{12} e_2}{R_{21} + e_2}. \quad (8)$$

The above emission rate e_n is a function of the electric field since the hopping rates R_{12} and R_{21} as well as the individual defect ionization rates e_1 and e_2 are all field-dependent. The field dependence of the ionization rates of all the levels involved

in our present study is known from previous work [10, 26, 27, 31]. The field dependence of the rates R_{12} and R_{21} comes mainly from the contribution $q \cdot F \cdot r_{12} \cos(\theta)$ to the difference in the energy levels (see Eq. (5)). Two extreme cases can be recognized with equation (8) :

i) If the inequality $R_{21} \gg e_2$ holds (level 2 not too shallow), equations (4), (8) yield

$$e_n = e_1 + \exp\left(\frac{E_{T1} - E_{T2}}{kT}\right) \cdot e_2. \quad (9a)$$

ii) If the reverse inequality $R_{21} \ll e_2$ holds (level 2 is shallow), we have

$$e_n = e_1 + R_{12}. \quad (9b)$$

and the indirect electron emission rate is governed by the internal transition rate R_{12} .

The above results can be used to make computer simulations of the DLTS response of defect pairs. We use equation (8) to calculate the apparent electron-emission rate e_n which must, in general, be treated as a function of the junction electric field F and of the angle θ between the electric field and the line joining the defect centroids. The transient occupation ratio $Y(t, \theta)$ for a defect pair filled at time $t = 0$ with an electron will be

$$Y(t, \theta) = \exp(-e_n(\theta, F) \cdot t).$$

Averaging over a random distribution of θ (equivalent to integrating over a 4π steradians solid angle), we get

$$\bar{Y}(t) = \frac{1}{2} \int_{-\pi}^{+\pi} \exp(-e_n(\theta, F) \cdot t) \cdot \sin \theta \, d\theta, \quad (10)$$

where we have assumed a constant inter-defect separation r_{12} . Calculating the DLTS response for a defect pair would amount to replacing the usual exponential ionization kinetics with equation (10). For the other more conventional aspects of DLTS simulation, the reader is referred to references [48, 49].

6. Electron ionization rates for densely packed defects.

We extend the above treatment to a large number of densely packed defects. This case is quite distinct from that of isolated point defects or defect pairs. In our DLTS experiments, the defects are situated in the depleted region of a reverse-biased Schottky diodes fabricated on n-GaAs. The individual defects are initially filled with electrons by means of a filling bias pulse during which the diode depleted region is reduced. The defect density is usually larger than the initial electron concentration. We thus expect that

only a small fraction of the defects will capture electrons during the filling pulse. Consequently, the DLTS peak amplitudes cannot be used to reliably estimate the defect concentrations. Furthermore, shallower defects with energies well above the Fermi-level will undergo very small changes in their electron occupation rates and will be more difficult to see than the defects with energies near to the Fermi-level. We therefore concentrate in the following treatment on the indirect emission through shallower levels of electrons previously trapped in the defect nearest to the Fermi-level.

Densely packed defects can occur in many situations. For example, a large dose of fast-electron, fast-neutron or fast-ion irradiation would lead to a high density of uniformly and randomly distributed defects. Another case of interest is that of defect grouped in clusters as could be generated by a moderate dose of heavy-particle bombardment. In the following, we first deal with the extreme case of uniformly distributed defects and we then deal with the opposite extreme case of defects grouped in well defined clusters.

6.1 UNIFORMLY DISTRIBUTED DENSELY PACKED DEFECTS. — To simplify the notation, we assume the occurrence of three electron trap types (1, 2 and 3) with label 1 referring to the mid-gap defect (MG). In fact, the generalization to any number of defects with energy levels in the band-gap is straightforward. We can see from section 3 that the transition rates between defects of the same energy level can be extremely large (much larger than any of the ionization rates) even for separations as large as $100 \text{ \AA}$ corresponding to concentrations around $2.5 \times 10^{17} \text{ cm}^{-3}$. One can therefore treat the three levels ($i = 1, 2$ and 3) as three bands with N_1, N_2, N_3 available electronic states respectively.

To calculate the ionization kinetics of the combination, we generalize the treatment of section 5 in order to determine the quasistatic electron occupation probabilities f_2 and f_3 of levels 2 and 3 in terms of f_1 of the deepest level. For any permutation i, j, k of the three labels 1, 2, 3, one should have :

$$\begin{aligned} N_i N_j [f_i(1 - f_j) R_{ij} - f_j(1 - f_i) R_{ji}] + \\ + N_k N_j [f_k(1 - f_j) R_{kj} - f_j(1 - f_k) R_{jk}] - \\ - N_j f_j e_j = 0 \quad (11) \end{aligned}$$

where the symbols e_j represent as before the emission rates from the different individual defects. R_{ij} stands, in general, for the average electron tunnelling rate between defect levels i and j . For densely packed defects, the term $N_j f_j e_j$ can be neglected compared to the others in equation (11). Within this approximation, and making use of the detailed balance equation (Eq. (4)), we obtain for $i = 2$ or $i = 3$

$$f_i = \frac{1}{1 + \frac{1-f_1}{f_1} \exp\left(\frac{E_{Ti} - E_{T1}}{kT}\right)} \approx \frac{f_1}{1-f_1} \exp\left(\frac{E_{T1} - E_{Ti}}{kT}\right) \quad (12)$$

which is thus seen to follow a Fermi-Dirac distribution. More general solutions to equation (11) can be obtained for cases where, in contrast to the above treatment, the terms $N_j f_j e_j$ cannot be neglected. Since one expects $f_2 \ll 1$ and $f_3 \ll 1$, equation (11) for $j = 2$ and $j = 3$ yields simply a set of two linear equations in two unknowns. When this is done, we obtain results practically identical with equation (12) provided the following inequalities hold :

$$e_2 \ll N_1 R_{21}(1-f_1) + N_3 R_{23}$$

$$\text{and } e_3 \ll N_1 R_{31}(1-f_1) + N_2 R_{32}. \quad (13)$$

Having determined $\frac{f_2}{f_1}$ and $\frac{f_3}{f_1}$, the ionization kinetics of the closely packed defects can be predicted from

$$N_1 \left(\frac{df_1}{dt} \right) = N_1 f_1 e_1 + N_2 f_2 e_2 + N_3 f_3 e_3.$$

Thus, provided inequalities (13) hold, the corresponding effective electron emission rate can be written as

$$e_n = e_1 + \frac{N_2}{N_1^*} \exp\left(\frac{E_{T1} - E_{T2}}{kT}\right) e_2 + \frac{N_3}{N_1^*} \exp\left(\frac{E_{T1} - E_{T3}}{kT}\right) e_3 \quad (14)$$

where

$$N_1^* = (1-f_1) N_1.$$

As can be seen from equation (14), the emission kinetics of the defect collection cannot, strictly speaking, be described by a linear differential equation because of the occurrence of the term $(1-f_1)$. We can, however, approximate $(1-f_1)$ to a constant because the quasi-Fermi level of the closely packed defects is expected to change only slightly during the ionization transient.

It should be noted that the electron emission rate of equation (14) is sensitive to the defect concentration ratio $\frac{N_i}{N_1}$. This ratio represents the number of

different paths through which an electron trapped in the deepest level 1 can be ionized *via* level i . We also note the sensitivity of the emission rate to $(1-f_1)$ and thus to the compensation ratio or quasi-Fermi level of the mid-gap defects.

6.2 DEFECTS GROUPED IN WELL DEFINED CLUSTERS. — We now deal with the other extreme case of defect densely pack in well defined clusters. In view of the appreciable hopping conductivity, demonstrated in section 3, the clusters can be considered as conductors. For example, in the core of the clusters generated by boron-ion bombarded in n-GaAs, the defect density can be roughly estimated [9] to be of the order of 10^{19} cm^{-3} . From elementary electrostatic considerations, it can be seen that the space charge can only be altered at the outskirts of these clusters during the DLTS bias sequence. Any variation in the junction field will only change the electron occupation of MG defects in their first layer around the clusters provided the inequality $\frac{q f_1}{r_{11}^2} >$

$q \epsilon_0 \epsilon_r F$ holds. For fields F around 200 kV cm^{-1} and with $f_1 = 0.5$, this inequality will hold provided the MG defect separation r_{11} is smaller than $60 \text{ \AA}$ (i.e. for MG densities larger than $3.0 \times 10^{18} \text{ cm}^{-3}$). From the discussion in section 2, we expect the Fermi level at the clusters' core to be strongly pinned at mid-gap by the defects themselves and we, moreover, expect average charge neutrality there. Hence a DLTS experiment can only reveal those defects situated at the clusters' periphery where their density is of the order of 10^{18} cm^{-3} (much smaller than at the cores). Furthermore, within or in the immediate vicinity of clusters, shallow electron trapping levels cannot be filled with electrons because of the near mid-gap position of the Fermi level. In particular, it is seen from figure 4 that shallow level defects have to be separated by a minimum distance W from the clusters to be observable by DLTS.

Fig. 4. — Energy band diagram across a damage cluster situated in the neutral region of heavy particle bombarded n-GaAs. The electrical properties of the defects at the cluster's core are masked because of electrostatic screening effects and because the Fermi level is strongly pinned at mid-gap there. Shallow levels at distances less than W from the clusters will remain empty and will not be detected by DLTS.

We define the inside of a cluster as the region where the inter-defect hopping rates are larger than the rates observable through the DLTS rate window.

The « well defined clusters » situation is that in which the inter-defect hopping rates decrease when one moves away from the clusters within a transition region much smaller than the cluster size. Such a situation can be assumed for our low-dose implanted samples which have not been subject to any annealing treatment. In these samples, the clusters do not overlap and the diode depleted regions are much larger than the clusters sizes. In this context and for simplicity reasons, we treat the cluster as a spherical conductor in a uniform external junction field F . From elementary electrostatics, one can evaluate the electric field $F_s(\theta)$ experienced by a defect at the cluster's periphery as a function of the angle θ between the external field and the radius-vector of the sphere. One gets

$$F_s(\theta) = 3 F \cos(\theta).$$

The electron emission rate $e_n(F_s)$ from a given point at the clusters outskirts can now be deduced from equation (14). The effective clusters emission rate e_n^* is obtained by averaging over the surface of the spherical cluster and hence

$$e_n^* = \frac{1}{2} \int_{\theta=-\pi}^{+\pi} e_n(3 F \cos(\theta)) \cdot \sin \theta d\theta, \quad (15)$$

7. Interpretation of DLTS data in fast electron irradiated GaAs.

As was discussed in section 2, one is led to attribute the E4 and E5 fast-electron irradiation DLTS peaks to the defect pairs (MG + E2) and (MG + E3). In order to verify this interpretation of E4 and E5, we have made computer simulations for the Differential DLTS (DDLTS) behaviour of the defect pairs (MG + E2) and (MG + E3). The results of section 3 allow us to take the MG phonon parameters equal to those of the EL2 native defect. Our model proved, however, to be insensitive to those MG phonon parameters. In contrast, the simulations proved extremely sensitive to variations of the phonon parameters of E2 and E3 around their experimentally known values (Tab. I). Another parameter to which our model is sensitive is, of course, the energy level of MG. Agreement with observations is obtained only if the MG level is taken within 10 meV of that of EL2.

In figure 5, the E4 DDLTS peaks are seen to have a behaviour consistent with that predicted for (MG + E2) pairs. If the defect centroids separation r_{12} is larger than 30 Å, the model predicts, for such pairs, an ionization rate practically equal to the internal electron hopping rate R_{12} between MG and E2 (Eq. (9b)). This behaviour is related to the very high electron emission rate of E2 (see Eqs. (8) and (9b) and the discussion around them). Furthermore, R_{12} varies quickly with the interdefect separation

r_{12} , but is insensitive to the electric field. Thus, the wide DDLTS peaks observed for E4 are explained by random variations of r_{12} around 30 Å while their insensitivity to the field is as expected for R_{12} . The uncertainties in the pre-exponential factors used in our model, as defined in section 2.2, directly influence our evaluation of R_{12} . This leads to an uncertainty about ± 10 K in the calculated DDLTS peak positions. The agreement of the model for $r_{12} \approx 30$ Å with the experimental results for E4 is well within this uncertainty. It is noteworthy that, in (MG + E2) pairs for which $r_{12} < 30$ Å, E2 does not behave like a shallow level defect anymore because the Coulomb potential of MG appreciably increases the effective ionization energy of E2. This explains the occurrence of a minimum in the calculated DDLTS peak temperatures of (MG + E2) pairs for $r_{12} = 30$ Å.

Fig. 5. — Model simulation for the Differential DLTS (DDLTS) peak position as a function of electric field for two types of defect-pair. The theory is compared with our own (LEP) DDLTS experimental results for the electron-bombardment defects E4 and E5. The most significant uncertainty of the model is that of the DDLTS peak position predicted for the (MG + E2) pairs and is about ± 10 K. For this pair, a minimum DDLTS peak temperature is predicted for $r_{12} \approx 30$ Å.

Different predictions are made for the pair (MG + E3) because E3 has a deeper level than that of E2 and equation (9a) gives a good approximation to the pair's electron emission rate. In figure 5, we see that the DDLTS peak position of E5 and its high sensitivity to the electric field agree with those expected for the (MG + E3) pair. For this pair, the ionization rate e_n obtained from equation (9a), is proportional — at different electric fields — to that e_2 of E3 which is known to be very sensitive to the electric field [28]. In contrast to the simulations for (MG + E2), those for (MG + E3) pairs proved practically insensitive to the pre-exponential factors of the model.

8. Interpretation of DLTS data in heavy-particle bombarded GaAs.

We now make use of section 6 to interpret our DDLTS results for boron-ion implanted n-GaAs. We assume the densely packed defects to be MG, E3 and E2. The dotted curve in figure 6 corresponds to the well defined clusters approximation (Eq. (15)) with the same deep-level concentration ratio as for electron-irradiated materials $N_1 : N_2 : N_3 = [\text{MG}] : [\text{E3}] : [\text{E2}] = 1 : 2 : 8$. The compensation ratio $(1 - f_1)$ which enters equation (14) has been taken to be 0.5 in accordance with section 3. Without any further parameter adjustment, the model predicts very well the observed DDLTS peak positions and their electric field dependence for the non-annealed samples.

The dashed curve of figure 6 corresponds to a simulation for uniformly and densely packed defects (Eq. (14)) with $N_1 : N_2 : N_3 = [\text{MG}] : [\text{E3}] : [\text{E2}] = 1 : 1 : 1$. This is seen to agree very well with experimental results for the sample annealed at 450 °C.

More generally, for the samples annealed at increasingly higher temperatures, good agreement with experimental results is obtained if one introduces the two following assumptions in our computer simulations :

- i) That the defects tend to be more uniformly distributed as the annealing temperature increases.
- ii) That the ratio of shallow to deep level concen-

tration decreases with increasing annealing temperature.

Inside a cluster, one expects a higher annealing rate than at its periphery since we know from earlier studies that long range recombination between implantation defects have an important influence [50]. Hence the defects will tend to become uniformly distributed in accordance to assumption (i). Assumption (ii) is confirmed by the fact that after ion implantation and annealing at 600 °C, the only surviving irradiation induced electron-trap DLTS peak can be identified with the native mid-gap level EL2 [1, 51]. Both this level and EL2 are insensitive to the electric field in the range reported in figure 6. One thus deduces that the MG defects anneal less quickly than E2 or E3 at temperatures up to 600 °C.

Our DLTS measurements indicate that the peak E3 (see Fig. 1) survives 30 min annealing steps up to 450 °C. There is an apparent increase in the ratio of shallow to deep level concentrations which must be attributed to the reduction of the defect packing density (Fermi level not pinned anymore as in Fig. 4). In contrast, the annealing of E3 occurs at much lower temperatures in electron-irradiated n-GaAs. One reason for the E3 survival at higher anneal temperatures could be the charge state dependence of its annealing rate. Pons [52] has demonstrated that the annealing rate of an ionized E3 defects is much smaller than for those occupied with electrons. Using the data of this author, one can extrapolate the annealing rates up to temperatures in the vicinity of 400 °C for unoccupied E3 defects (as expected near a defect cluster in Fig. 4). This would predict an annealing stage for E3 near to 350 °C (instead of above 400 °C). The discrepancy between expected and observed annealing is probably due to defect-induced changes in the Debye temperature of the material. The level E2 in electron-irradiated material has a more reduced charge-state dependence than E3 for its thermal annealing rate [52] so one may assume that the E2 concentration in the clusters decreases faster than that of E3 after annealing. In samples annealed above 450 °C the defect density decreases to such an extent that inequalities (13) are expected to fail. It is therefore understandable why the DDLTS peaks behave as a mixture of densely packed defects combined with isolated (MG + E2) and (MG + E3) pairs.

In the framework of our computer simulations, the observed behaviour of the DDLTS peaks for different electric fields and annealing treatments is consistent with the above-reviewed annealing properties of the E2, E3 and MG defects.

9. Nature of the irradiation-induced defects.

As discussed in sections 2.1, experimental evidence for electron-irradiated n-GaAs leads us to attribute

Fig. 6. — DDLTS peak positions *versus* junction electric-field. The dotted curve correspond to DDLTS model simulation for defects grouped in well defined clusters with $f_1 = 1/2$ and $N_1 : N_2 : N_3 = 1 : 2 : 8$. The dashed curve correspond to DDLTS model simulation for uniformly distributed densely packed defects with $f_1 = 1/2$ and $N_1 : N_2 : N_3 = 1 : 1 : 1$. The upper continuous curves correspond to isolated MG defects with parameters taken identical to those of EL2. The lower continuous curve corresponds to a combination in equal concentrations of the defect pairs MG + E2 and MG + E3. The experimental points correspond to ion-implantation defects for different 30 min isochronal annealing temperatures from reference [26].

the high-temperature DLTS peaks E4 and E5 to the defect pairs (MG + E2) and (MG + E3) respectively. As was shown in section 7, our calculations for such pairs confirm these attributions. Furthermore, identifying E5 with the pair (MG + E3) is consistent with the fact that E5 and E3 are observed to show very similar thermal [21] and recombination enhanced [22] annealing behaviour over a wide temperature range.

Both E2 and E3 are very probably associated with an As vacancy [53]. This suggests that E4 and E5 may be viewed as the result of the initial formation of the defect pair $V_{Ga} - Ga_i$ as part of a primary Frenkel defect. This pair is believed to be unstable [21, 54, 55]; it may either recombine or else a nearest neighbour As lattice atom can move into the Ga vacancy, thus producing two stable defects As_{Ga} and V_{As} which may subsequently diffuse apart. The observation by EPR of the corresponding « precursor » defect complex ($As_{Ga}V_{As}$) has been recently reported by von Bardeleben *et al.* [54, 55]. The electron irradiating beam does not only induce lattice ion displacements, it is also expected to have a strong ionizing influence and to liberate considerable amounts of phonon energy. As a consequence, one expects the mobility of the crystal's As and Ga interstitial atoms to be greatly enhanced during irradiation [21]. These diffusing interstitial atoms can then be preferentially trapped at V_{As} or As_{Ga} related interstitial sites. Details of this defect creation process remain to be established by further studies.

In interpreting the electrical conductivity observations in bombarded GaAs in sections 2 and 3 it appeared unavoidable to invoke a mid-gap irradiation-induced defect (MG). In samples annealed below 600 °C, this MG level is not directly observable by DLTS. In sections 5 to 8 the observed high-temperature peaks were, however, accounted for either by defect pairs including MG together with a shallower defect (in fast-electron-irradiated n-GaAs) or by damage clusters including MG, E2 and E3 defects (in heavy-particle bombarded n-GaAs). For heavy-particle bombardment, we showed in section 6.2, that only the defects at the clusters' outskirts have an appreciable influence on DC electrical conductivity and DLTS observations. The ion bombardment damage energy at these outskirts is comparable to the damage energy due to fast-electron irradiation. This explains why we were able to attribute results in heavy-particle and electron-irradiated materials to the same types of individual point defects.

The MG defect (irradiation induced) and the EL2 defect (native in bulk GaAs) share the properties of both being single donors, having mid-gap energy levels and being associated with the As_{Ga} defect. Furthermore, we have shown in section 3 that the

lattice relaxation parameters $\hbar\omega$ and $S\hbar\omega$ for the two defects are similar. One is thus led to identify MG with the deep level associated to EL2.

A widely accepted signature revealing the presence of EL2 defects is the « quenching » behaviour observed in the photo-capacitance transients corresponding to sub-band-gap illumination [1, 51]. The occurrence of this behaviour in heavy-ion bombarded materials subsequently annealed above 600 °C gives clear evidence for the creation of EL2 [51, 1]. For samples annealed below 600 °C, the absence of the « quenching » behaviour is often used as an argument to demonstrate that EL2 is not created during ion bombardment [25]. In our present work we were led to believe that all the irradiation-induced defects MG are part of defect pairs or dense damage clusters for samples annealed below 600 °C. Consequently, although MG and EL2 are probably identical, it is easy to understand the observed departure of the photocapacitance transients of MG defects from the transients typical of isolated EL2 defects.

10. Summary and conclusions.

Making use of a recently developed theory, we have studied the multi-phonon assisted hopping DC conductivity in GaAs induced by heavy particle bombardment. From our best-fit procedure, we deduced that the irradiation induced mid-gap (MG) level can be identified with that of the native EL2 centre.

We have also mathematically simulated the Deep Level Transient Spectroscopy (DLTS) response of defect pairs and clusters taking in account the hopping of electrons between the individual defects involved. We attributed each of the high-temperature DLTS peaks E4 and E5 in fast-electron bombarded n-GaAs to distant defect-pairs involving the As_{Ga} anti-site related donor level MG together with shallower V_{As} related acceptor defects. The high-temperature DLTS peak in heavy-particle bombarded materials is accounted for by our simulations for defect clusters. For defect pairs as well as clusters, we account for the observed wide DLTS peaks, together with their often high sensitivity to the electric field. Our DLTS studies confirm that EL2 and MG are related.

Acknowledgments.

The theoretical background to this work has been partly developed in collaboration with M. Lannoo. The authors wish to thank P. Langlade who has performed part of the electrical measurements. Thanks are also due to H. J. von Bardeleben, H. M. J. Boots, J. C. Bourgoin, R. Eppenga, L. F. Feiner, A. Goltzene, F. J. A. Greidanus, J. C. M. Henning, S. Kalbitzer, H. W. van Kesteren,

E. Montie, D. Pons, A. Roizes, M. F. H. Schuurmans and D. Stievenard for fruitful discussions. We

acknowledge skilful technical assistance from E. Boucherez and M. Auger.

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