Symmetry of the $EL2$ defect in GaAs

T. Figielski* and T. Wosinski*
IV Physikalisches Institut der Universität Göttingen and Sonderforschungsbereich 126, Bunsenstrasse 11-15, D-3400 Göttingen, Federal Republic of Germany
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From experiments on the stress-induced splitting of the zero-phonon line associated with the optical-absorption band originating from photoexcitation of the $EL2$ center in GaAs, Kaminska *et al.* concluded that this center has tetrahedral symmetry, which would account for its simple point-defect structure. An alternative explanation of the observed splitting pattern, which involves an orthorhombic center of C_{2v} symmetry, is discussed in this paper. This would account for both the recently revealed complex structure of $EL2$ and its apparent high symmetry.

The nature of the technologically important midgap level in GaAs, called $EL2$, still has not been definitely determined despite a great effort made toward its identification. The principal and now well-documented discovery is that the As_{Ga} antisite defect is involved in the $EL2$ center (see, e.g., Ref. 1). An important step was made by Kaminska *et al.*[2] who discovered the zero-phonon line (ZPL) at the onset of the optical absorption band associated with internal photoexcitation of $EL2$. The latter finding allowed one to study the splitting of this ZPL under uniaxial stress applied to the sample and thus to obtain some information on the symmetry of $EL2$. Such piezospectroscopic experiments were performed by Kaminska *et al.*[3] who concluded that their results unambiguously show evidence of the $A_1 \rightarrow T_2$ electric dipole transition within a center of T_d symmetry being in the spin-singlet state. This would indicate that the isolated As_{Ga} antisite is the defect responsible for $EL2$. Later on we suggested the $(As_{Ga})_2$ dimer as a candidate for $EL2$ and argued that it would yield a splitting pattern similar to that found experimentally.[4]

The situation changed dramatically when Meyer *et al.*[5] reinterpreted their results obtained with the optically detected electron-nuclear double-resonance (ENDOR) technique. They demonstrated that the As_{Ga} antisite defect involved in $EL2$ has, besides its four nearest-neighbor As atoms at the regular lattice sites, also a fifth As atom neighbor probably placed at the second-neighbor tetrahedral interstitial site. This finding strongly suggested that $EL2$ represents a complex defect composed of an As_{Ga} antisite defect plus an As_i interstitial defect, which was in accordance with a similar conclusion drawn by Bardeleben *et al.*[6] from a study of the thermal evolution of $EL2$ and As_{Ga} species in GaAs. Such a conclusion, however, is in conflict with the results of piezospectroscopic measurements, which point out a high symmetry of the $EL2$ defect.

A compromise model was proposed recently[7] according to which $EL2$ is composed of the $(As_{Ga})_2$ dimer, where the two constituents are second neighbors along a $\langle 110 \rangle$ axis, plus an As_i interstitial in the position symmetric with respect to both. Such a complex represents an orthorhombic defect of C_{2v} symmetry, and reconciles the two apparently opposed findings: involvement of the As_i interstitial in $EL2$, and the appearance of a high symmetry of this center.

In the present paper we discuss in detail the expected characteristics of the piezospectroscopic splitting for an $\langle 110 \rangle$ orthorhombic center of C_{2v} symmetry. This discussion is aimed at the verification of whether a complex defect of this symmetry can account for the observed piezospectroscopic properties of $EL2$.

Characteristic of the stress-induced splittings of the spectral lines corresponding to all allowed transitions within both cubic and possible anisotropic centers in cubic crystals have been calculated by Kaplyanskii[8,9] with group-theoretical methods and perturbation theory. There are three basic characteristics of the splitting that are usually observed under uniaxial stress applied along $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ axes: the number of split components, their shifts from their positions in the unstressed crystal, and the intensity and polarization degree of the components.

Among the great variety of splitting patterns predicted for cubic crystals, there are only two cases displaying the identical number of split components, i.e., 2, 2, and 3 components for the stress applied along a $\langle 111 \rangle$, $\langle 100 \rangle$, and $\langle 110 \rangle$ axis, respectively, which just correspond to the splitting pattern observed for the $EL2$ ZPL in GaAs.[3] The first case corresponds to the $A_1 \rightarrow T_2$ electric dipole transition within a center of T_d symmetry, and results from removal of the threefold orbital degeneracy of the T_2 state by the applied stress. The second case corresponds to a transition within an orthorhombic defect of C_{2v} symmetry aligned along a $\langle 110 \rangle$ axis, and results from removal of the sixfold orientational degeneracy (any orbital degeneracy in the C_{2v} point group is lifted by the crystal field). Accordingly, there are two possible ways of interpreting the splitting pattern for the $EL2$ zero-phonon absorption line in GaAs. The first mentioned case (tetrahedral-center model) has been invoked by Kaminska *et al.*,[3] while the second one (orthorhombic-complex model) has been suggested by the present authors.[4]

Since the number of split components alone does not allow one to decide which of the two models operates in the case of $EL2$, we have to appeal to the second characteris-

tic of the piezospectroscopic splitting: the amount of shift of the split lines as a function of the stress value. Inspecting the experimental results, indicated by points in Fig. 1, we see that two of the split components (the lower one for the [111] and the central one for the [110] stress direction) exhibit a nonlinear stress dependence, and hence they cannot be explained on the grounds of the linear approximation of Kaplyanskii, i.e., by the static crystal-field model. Therefore, Kaminska *et al.*,[3] interpreting their results in the framework of the tetrahedral-center model, claimed a Jahn-Teller (JT) coupling of the T_2 term to the τ mode of lattice vibration.

Remaining in the framework of the orthorhombic-complex model we notice that the observed nonlinearities may arise from the centers which are oriented in such a way that their symmetry is reduced to C_s under the applied stress. This suggests that the center responsible for the ZPL is subjected to a JT distortion and that the nonlinearity follows from a coupling of this spontaneous distortion to that due to the external stress. In fact, a pseudo-JT effect, of the type $(A+B)\otimes\beta$ in the notation of Englman,[10] is expected for an orthorhombic complex containing two identical weakly linked entities. In such a complex, as a result of the pseudo JT effect, the electronic near-degeneracy is replaced by the vibronic twofold degeneracy, and the system may be located in one of the two potential minima. The height of the barrier above the minima may be much lower than the JT energy, and then one expects the defect to go over from one potential minimum to another by quantum-mechanical tunneling. This results in the tunneling splitting of the lowest vibronic level into two components separated by Δ; the lower component transforms now according to the B_2 irreducible representation of the C_{2v} point group.[11] This is presumably the terminal state of the zero-phonon transition. The ground state of the two-electron system, $^1A_1$, and its nearest state, $^3B_2$ do not couple through interaction with any of the lattice vibration modes and thus are stable against the JT distortion.

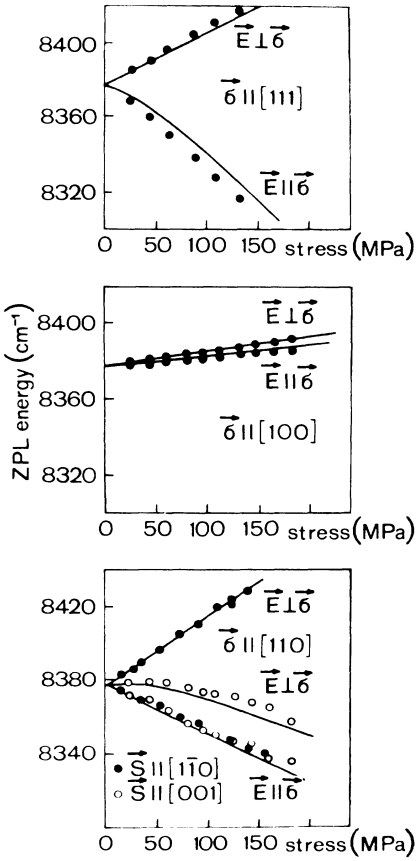

FIG. 1. Splitting pattern of the *EL*2 zero-phonon line under uniaxial stress. The experimental points are due to Kaminska *et al.* (Ref. 3). The solid lines represent theoretical curves fitted in the framework of the orthorhombic complex model.

Formally, the above may be taken into account by adding to the linear approximation of Kaplyanskii[8] additional nonlinear terms in each case when the external stress lowers the symmetry of the defect. The nonlinear terms contain the parameter Δ and a new stress coefficient b which is closely related to the JT coupling coefficient. Thus the following formulas for the dependence of the energy shift of the split components δE on stress σ are used (they are written in the sequence of their appearance in Fig. 1, beginning from the top).

For $\sigma \| [111]$:

$$\delta E_1 = \tfrac{1}{3}(a_1 + 2a_2 - 2a_3)\sigma ,$$

$$\delta E_2 = \tfrac{1}{3}(a_1 + 2a_2 + 2a_3)\sigma + \tfrac{1}{2}\Delta - \tfrac{1}{2}[\Delta^2 + 4(\tfrac{4}{3}b)^2\sigma^2]^{1/2} .$$

For $\sigma \| [100]$:

$$\delta E_3 = a_1\sigma ,$$

$$\delta E_4 = a_2\sigma .$$

For $\sigma \| [110]$:

$$\delta E_5 = (a_2 - a_3)\sigma ,$$

$$\delta E_6 = \tfrac{1}{2}(a_1 + a_2)\sigma + \tfrac{1}{2}\Delta - \tfrac{1}{2}(\Delta^2 + 4b^2\sigma^2)^{1/2} ,$$

$$\delta E_7 = (a_2 + a_3)\sigma .$$

These formulas have been fitted to the experimental data obtained by Kaminska *et al.*[3] with the following values of adjustable parameters:

$$a_1 = 0.08 \text{ cm}^{-1}/\text{MPa}, \quad a_2 = 0.06 \text{ cm}^{-1}/\text{MPa},$$

$$a_3 = -0.31 \text{ cm}^{-1}/\text{MPa}, \quad b = 0.3 \text{ cm}^{-1}/\text{MPa},$$

$$\Delta = 50 \text{ cm}^{-1} .$$

From the adjusted value of b we were able to estimate the JT coupling coefficient to be 2.73 eV/Å. The fitted curves are shown in Fig. 1 as solid lines. Thus the splitting pattern can be quantitatively explained in the framework of the orthorhombic complex model, under the assumption that the defect is subjected to the dynamic JT instability. So, both possible models correctly describe also the ob-

served shift of the split components as a function of stress.

To complete this discussion, we examine the third characteristic of splitting: the light-polarization selection rules, exploiting also the classical results of Kaplyanskii. The expected light polarizations and relative line intensities for the $A_1 \rightarrow B_2$ transition within an $\langle 110 \rangle$ orthorhombic center are shown in Fig. 2. In contrast to this picture, the intensities corresponding to different lines predicted for the $A_1 \rightarrow T_2$ transition within a tetrahedral center are all equal, and each line appears at a polarization either parallel or perpendicular to the stress direction. Obviously, the light-polarization selection rules are softened for a defect of lower symmetry, i.e., for an orthorhombic complex some lines appear at both light polarizations, but always the direction of the dominant polarization coincides with that predicted for the tetrahedral-center model. Therefore, in order to distinguish between the two models, very careful measurements are required, since for a small ZPL the differences easily may be overlooked.

If we compare the light-polarization selection rules predicted for the orthorhombic complex with those reported in Ref. 3 we meet a disagreement; the upper and central split lines for the [110] stress direction should be observed with the light propagating along the [001] and $[1\bar{1}0]$ directions, respectively, while the directions ascribed to these lines in Fig. 1 are opposite. At closer inspection we find that a similar disagreement appears also between the experimental results presented by Kaminska *et al.*[3] and their original interpretation in terms of the tetrahedral-center model. The central split line for the [110] stress direction unambiguously corresponds to the A_1 irreducible representation of the C_{2v} point group of the distorted crystal, since only this line may suffer from a coupling of the T_2 term to the τ lattice vibration mode. According to Kaplyanskii[9] this line should be observed with light propagating along the $[1\bar{1}0]$ direction, while the experimental points in Fig. 1 indicate the [001] direction (this discrepancy cannot be removed by a conversion of the labels E_5 and E_6 at the lines in Fig. 1 of Ref. 3, which are evidently opposed to those used in the text).

If we assume that the revealed inconsistency is simply due to an erroneous description of the picture then both possible models can in principle account for the piezospectroscopic results, and precise measurements should be performed to select one of them. Alternatively, if the picture were completely correct neither of the models would be confirmed.

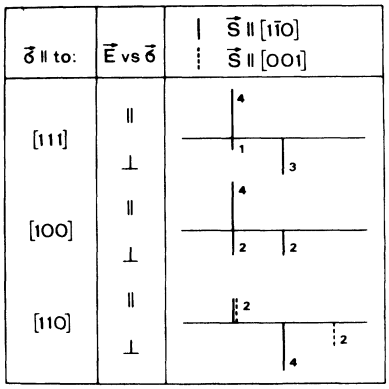

FIG. 2. Intensities and polarizations of split components predicted for the $A_1 \rightarrow B_2$ electric dipole transition within the othorhombic complex of C_{2v} symmetry, in the low-stress limit. Numbers denote relative line intensities. For the $A_1 \rightarrow T_2$ electric dipole transition within the tetrahedral center the corresponding picture is changed, compared to the present one, in two features: (i) each line appears at only one polarization corresponding to the dominant one in this figure, (ii) all the lines are of the same amplitude.

In conclusion, two different schemes may be responsible for the $EL2$ zero-phonon line in GaAs: the $A_1 \rightarrow T_2$ transition within a center of T_d symmetry, and $A_1 \rightarrow B_2$ transition within an orthorhombic complex of C_{2v} symmetry. They both lead to very similar characteristics of the line splitting under external stress, and careful measurements are required to distinguish between these two cases. The presently available piezospectroscopic data are insufficient to decide which of the two cases (if any) actually corresponds to $EL2$. So, as far as the model of an orthorhombic complex is not in conflict with the piezospectroscopic data, the modified $(As_{Ga})_2$ dimer[7] is likely the best candidate for $EL2$, because it allows the inclusion of the As_i interstitial into the system (in accordance with the recent magnetic resonance results) without breaking its symmetry.

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*Permanent address: Institute of Physics, Polish Academy of Sciences, Warsaw, Poland.

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