Piezospectroscopic evidence for tetrahedral symmetry of the *EL*2 defect in GaAs

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Splittings of the *EL*2 zero-phonon line (ZPL) at 8378 cm^{-1} under uniaxial stress applied along the [100], [111], and [110] directions have been measured. The observed splittings together with polarization selection rules clearly indicate the tetrahedral T_d symmetry of the *EL*2 defect ruling out any other point groups, in particular, C_{2v} and C_{3v}. The ZPL is due to the $A_1 \rightarrow T_2$ (or $A_2 \rightarrow T_1$) electric dipole transition. A state of A_1 symmetry lying 65±10 cm^{-1} above the T_2 state is needed in quantitative analysis of observed splittings to account for the nonlinear stress dependence of certain split components. Contradiction between the symmetry of *EL*2 deduced from piezospectroscopic and optically detected electron-nuclear double resonance experiments is discussed.

I. INTRODUCTION

The *EL*2 defect in GaAs is one of the few observed intrinsic defects in III-V semiconducting compounds. Its technological importance and unique property of possessing an excited metastable state have made this defect the subject of intensive applied and basic research. The microscopic nature of this defect is still controversial. Two models currently dominate theoretical and experimental investigations of *EL*2: an arsenic antisite As_{Ga} of tetrahedral T_d symmetry[1–3] and an arsenic-antisite–arsenic-interstitial As_{Ga}-As_i pair of trigonal C_{3v} symmetry.[4–6] The identification of *EL*2 as a defect of T_d symmetry is based on the results of experiments on splitting of the *EL*2 zero-phonon line (ZPL) under uniaxial stress.[1] This assignment is in conflict with the results of optically detected electron-nuclear double resonance (ODENDOR) experiments,[5] which attribute *EL*2 to the As_{Ga}-As_i axial complex of C_{3v} symmetry. The conclusions of Ref. 1 have been questioned by Figielski and Wosinski.[7] An inconsistency of experimentally observed selection rules with those predicted theoretically[8] for transitions within a defect of T_d symmetry has been pointed out, and an alternative interpretation of observed splittings has been proposed leading to a conclusion that *EL*2 possibly has C_{2v} symmetry. Considering these facts we have performed a new uniaxial stress experiment.

In the next section we describe the samples and experimental technique. Section III gives a presentation of our results on the splitting of the ZPL of *EL*2 at 8378 cm^{-1} under uniaxial stress applied along [100], [111], and [110] directions. In Sec. IV, on the basis of known splitting patterns of zero phonon lines for various transitions at centers belonging to all possible symmetry systems, we show that the splittings of the ZPL of *EL*2 are incompatible with any type of transition other than $A \rightarrow T$ electric dipole transition in a center of T_d symmetry. Then the contradiction between T_d symmetry deduced from the results presented in Sec. III and the C_{3v} symmetry observed in ODENDOR experiments is discussed. Section V concludes the paper.

II. EXPERIMENTAL

Intentionally undoped as-grown semi-insulating (SI) GaAs crystals used in our experiments contained the *EL*2 defect in concentrations of approximately 10^{16} cm^{-3}. Typical sample dimensions were $12 \times 6 \times 2$ mm^3 with the long dimension oriented along the [100], [111], or [110] direction. The samples were different from those used in the experiments of Ref. 1. The optical experimental apparatus employed to measure the transmission consisted of the following: halogen lamp, lens, light chopper, monochromator, linear polarizer, lens, sample in cryostat for measurement under uniaxial stress, lens, and PbS detector. It was checked that the optical components between the polarizer and the detector did not change the polarization of the light. The signal from the PbS detector was detected by a two-phase lock-in amplifier at the frequency of the chopper. The spectra were collected by an IBM PC/XT "clone" computer. This experimental apparatus was entirely different from that of Ref. 1 including the cryostat and the uniaxial-stress apparatus. Uniaxial compressible stress was applied to the sample via two pistons placed in a slotted cylinder. One of the pistons was fixed; the other one was pushed by a rod. The force was applied to the rod by squeezing a calibrated spring. Transmission of uniaxially stressed samples was measured at 10 K using monochromatic polarized light with electric field parallel (π spectrum) or perpendicular (σ spectrum) to the direction of stress. The magnitude of the stress was increased typically in 12 steps from 0 to 200 MPa. For each value of stress π and σ spectra were collected. The values of the stress were well reproducible as inferred from measurements performed with increasing and decreasing values of the stress.

III. RESULTS

Under [100] and [111] stress the crystal becomes uniaxial, so that the direction of propagation of light is immaterial as long as it is in the plane perpendicular to the stress. Therefore we did not have to take care about the crystallographic orientation of the faces of [100] and

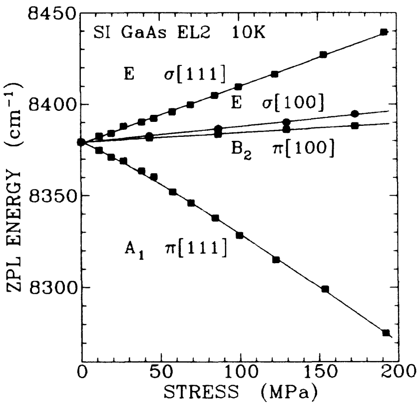

FIG. 1. The splitting of the *EL*2 ZPL under [100] and [111] stress. The points were experimentally determined. The solid lines represent fit to the theory. Symbols π and σ indicate components present in π and σ spectra, respectively. Indices [100] and [111] denote components observed under [100] and [111] stress.

[111] samples which were parallel to the direction of stress. For the [100] direction of stress the ZPL was observed to split into two components of equal intensity (Fig. 1). The higher-energy one appeared in the σ spectrum, the lower-energy one in the π spectrum. The magnitude of the splitting and the shift of the energy center of gravity were equal to 0.036 and 0.076 cm^{-1}/MPa, respectively. In the case of [111] stress the splitting was analogous with that for [100] stress except that the splitting was larger (0.72 cm^{-1}/MPa) and the π component revealed a slight nonlinearity of its energy as a function of the stress (Fig. 1). Under [110] stress the crystal becomes biaxial and spectra were recorded with the direction of propagation of the light along the [1$\bar{1}$0] ([1$\bar{1}$0] view) and [001] directions ([001] view). In this case the ZPL split into three equal-intensity components, as is shown in Fig. 2. Exactly one was observed for each propagation direction and polarization. Polarization selection rules for this direction of stress indicate an electric dipole character of the transition giving rise to the ZPL. The

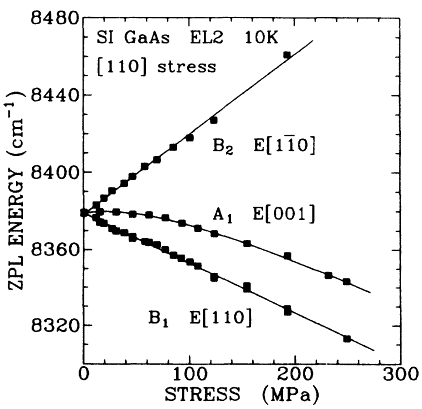

FIG. 2. The splitting of the *EL*2 ZPL under [110] stress. The symbol $E[hkl]$ denotes that incident light was polarized in the $[hkl]$ direction. The points were experimentally determined. The solid lines represent fit to the theory.

energy of a component observed for electric field of the incident light parallel to the [001] direction varied nonlinearly with the stress. Intensity of this component decreased by about 35% at 200 MPa; on the other hand, the intensities of the other components were observed to be constant within the experimental error.

IV. DISCUSSION

Runciman has classified[9] all possible centers in cubic crystals with respect to the numbers of components of allowed electric dipole transitions under stress applied along the [100], [111], and [110] directions. According to this classification, there are two possibilities: *EL*2 is a center of tetrahedral T_d or orthorhombic $I\ C_{2v}$ symmetry. To decide between these two symmetries we have to refer to the polarization selection rules (see Fig. 3). In the case of an orthorhombic I center, there are two distinct splitting patterns corresponding to different orientations of the electric dipole moment of the transition. Let the C_2 symmetry axis of the center lie along the [110] direction. The first pattern corresponds to a π dipole oriented along the [110] or [1$\bar{1}$0] direction; this type of transition is denoted in Fig. 3 by $A_1 \rightarrow B_2$. The second corresponds to a π dipole oriented along the [001] direction; this type of transition is denoted by $A_1 \rightarrow B_1$. In the case of $A_1 \rightarrow B_2$ transition within an orthorhombic I center the ZPL should split for the [001] view under [110] stress into two equal-intensity components in the π spectrum and two in the σ spectrum. No splitting should be observed under the above conditions in the case of $A_1 \rightarrow B_1$ transition. This is in conflict with what is experimentally observed: one component in each spectrum (see Fig. 2). To be more convincing, in Fig. 4 we present the actual absorption spectra of SI GaAs for the [001] view under [110] stress. One split component is observed

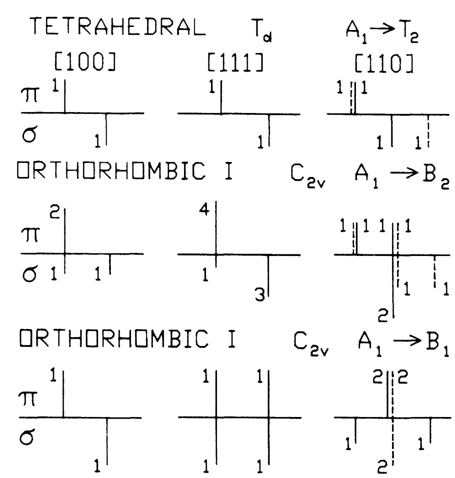

FIG. 3. Theoretical (Refs. 8, 10, and 11) stress splitting patterns for transitions in the centers where 2, 2, and 3 components are expected under [100], [111], and [110] stress. The numbers are the predicted relative intensities of the components. In the patterns for the [110] stress, dashed lines indicate components present for the [001] viewing direction, and solid lines correspond to the [1$\bar{1}$0] viewing direction.

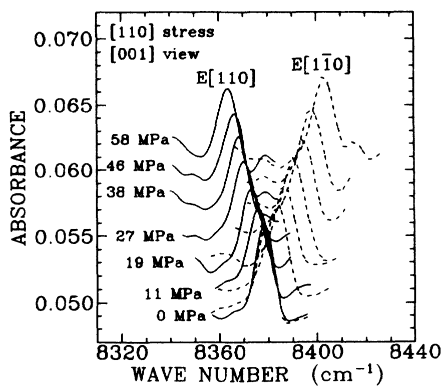

FIG. 4. The absorption spectra for SI GaAs in the region of the *EL*2 ZPL collected at 10 K under [110] uniaxial stress for light incident along the [001] direction.

in the π spectrum E[110] and one in the σ spectrum $E[1\bar{1}0]$ as predicted for the $A_1 \rightarrow T_2$ transition. Observed numbers of components, polarizations, and intensities for all stress directions are in agreement with predictions[8] for the $A_1 \rightarrow T_2$ electric dipole transition within a center of T_d symmetry. Therefore the *EL*2 ZPL is unambiguously due to the $A_1 \rightarrow T_2$ (or $A_2 \rightarrow T_1$) transition within a center of T_d symmetry. Uniaxial stress experiments cannot distinguish between $A_1 \rightarrow T_2$ and $A_2 \rightarrow T_1$ transitions. We will refer to the $A_1 \rightarrow T_2$ transition as it is commonly assumed in the literature on *EL*2. Uniaxial-stress experiments distinguish between $A \rightarrow T$ and $T \rightarrow A$ transitions. The fact that the intensities of stress-split components in the absorption spectra do not significantly depend upon applied stress at a fixed temperature of 10 K is an indication that splitting is observed in the excited state. The split components are due to transitions from the A_1 ground state to sublevels of the split T_2 state. These sublevels transform as $A_1, E, B_2, \ldots$ irreducible representations of the point symmetry groups of stressed crystal. With the help of polarization selection rules we can attribute these representations to corresponding split components as shown in Figs. 1 and 2. The components which were observed to move nonlinearly with the stress are due to transitions from the A_1 ground state to A_1 symmetry sublevels of the split T_2 state. This indicates the presence of an A_1 state lying above the T_2 state. Stress-induced interaction with this state produces bending of the A_1 components. The perturbation of the Hamiltonian of *EL*2 due to the uniaxial stress is assumed to be linear in the stress. We have started with a general empirical 4×4 Hamiltonian with the number of independent matrix elements limited only by the T_d symmetry of the defect. Exact eigenvalues of this Hamiltonian in the basis of the T_x, T_y, T_z, and A_1 states were fitted to the experimental points (Figs. 1 and 2). This fitting procedure was unable to determine the value of the splitting between A_1 and T_2 excited states. Equally good fits were obtained for the splitting ranging from 30 to 200 cm^{-1}. Assuming that the hydrostatic shift coefficient in the excited A_1 state is the same as in the T_2 state, fitting to the A_1 line under [110] stress placed the A_1 state 65±10 cm^{-1} above the T_2 state at zero stress. The same value of the splitting was obtained from two independent sets of data collected on two different samples. This value of the splitting between A_1 and T_2 states gives the correct magnitude of the intensity decrease of the A_1 split component under [110] stress. Dynamical Jahn-Teller coupling of the T_2 state with lattice modes of T_2 symmetry accounts for the presence of this A_1 state,[12] as well as for the huge difference between the stress splitting coefficients under [111] and [100] stresses.

It has been proposed that *EL*2 is the complex As_{Ga}-As_i of C_{3v} symmetry;[4] this complex has been observed in GaAs in ODENDOR experiments.[5] Presence of As_i lying along the [111] antibonding direction at 1–3 bond lengths from As_{Ga} is expected to produce larger perturbation of the T_2 state than a 10-MPa [111] uniaxial stress which displaces ligands by less than $\frac{1}{1000}$ of the bond length. This stress produces a splitting of the ZPL equal to its width. Baraff has estimated[13] the splitting of the T_2 state due to the presence of As_i to be ≅573 cm^{-1}. In the case of the presence of As_i close to As_{Ga} there should be observed splitting of the ground A_1 state under [111] and [110] stresses due to the orientational degeneracy of the defect making the spectra richer than it is observed. Recently Baraff has reported[14] calculation of the effect of As_i on the uniaxial stress splitting of the ZPL; he has concluded that it is definitely not possible to explain the observed splittings assuming that *EL*2 is the As_{Ga}-As_i complex. Therefore the possibility that *EL*2 is the As_{Ga}-As_i complex is ruled out by the present experiment. Our results are essentially in agreement with those of Kaminska, Skowronski, and Kuszko,[1] the major difference being that the viewing directions for [110] stress in Fig. 1 of Ref. 1 are interchanged as pointed out in Refs. 7 and 15. The presented results strongly support the identification of *EL*2 as an isolated defect of tetrahedral symmetry.

The 8378-cm^{-1} ZPL is undoubtedly due to the *EL*2 defect. This line is present in the spectrum of excitation of *EL*2 to the metastable state in *n*-type[16] and SI GaAs.[17] On the other hand, the attribution of the ODENDOR signal to *EL*2 is circumstantial[18] and therefore disputable. Recent extensive study[19] supports the attribution of the magnetic-circular-dichroism (MCD) signal on which the ODENDOR experiments were performed to the paramagnetic state of *EL*2. It is not clear if the observed correlations indicate the identity of the defect(s) giving rise to the 8378-cm^{-1} ZPL, EPR quadruplet, and MCD signal or are a result of charge transfer between different defects in semi-insulating GaAs. The interpretation of the MCD-detected ODENDOR experiments performed on the arsenic antisite seems to be complicated and indirect. When discovered, the MCD signal was attributed[20] to As_{Ga}, and it was argued[20] that this signal was not related to *EL*2. Then, presence of a regular isolated As_{Ga} and a perturbed As_{Ga} in as-grown semi-insulating GaAs was deduced[21] from the analysis of the ODENDOR data. Currently the MCD-detected ODENDOR signal is attributed to the paramagnetic state of the *EL*2 and angular dependence of this signal indicates that it is due to an As_{Ga}-As_i axial defect.[5,18]

Manasreh and Covington have reported[22] on the fine structure of the ZPL and concluded that *EL*2 has a complex structure which is in disagreement with the assignment of *EL*2 to the isolated As_{Ga}. We did not find any trace of this fine structure in our spectra. Nonexistence of this fine structure has been recently demonstrated[23] by Kuszko *et al.*

The main reason for doubt in the identification of *EL*2 with the isolated arsenic antisite As_{Ga} was that this substitutional defect was regarded to be too simple to possess a metastable state. This opinion was supported by early theoretical studies[24] which concluded that As_{Ga} was a well-behaved simple point defect and was not subject to large lattice relaxation. Recently two independent pseudopotential calculations[2,3] have shown that As_{Ga} has an excited distorted state which is a reasonable candidate for the metastable state of *EL*2. The theoretically calculated[3] energy barrier of 0.34 ± 0.1 eV between the metastable and the ground state of As_{Ga} is in very good agreement with the experimental value[25] of 0.34 eV.

V. CONCLUSIONS

Piezospectroscopic experiments performed on the 8378-cm^{-1} ZPL of *EL*2 clearly indicate tetrahedral symmetry of the local crystal field around the *EL*2 defect. In view of the presented experimental results, their interpretation, and recent theoretical investigations, the isolated arsenic antisite As_{Ga} most successfully accounts for the properties of the *EL*2 defect. Further work is needed to resolve the conflict between the piezospectroscopic and the ODENDOR data.

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