Identification of the 0.82-eV Electron Trap, *EL* 2 in GaAs, as an Isolated Antisite Arsenic Defect

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EL 2 is a technologically important deep level in GaAs whose identification has been the subject of intense study. In this paper we present uniaxial stress and magnetic field experiments which establish for the first time that *EL* 2 has tetrahedral symmetry and is, therefore, an isolated point defect. Combining this result with earlier data, we conclude that *EL* 2 is an isolated arsenic antisite defect.

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A deep donor with an activation energy of 0.82 eV, known as *EL* 2, is the dominant deep level in melt-grown and vapor-phase-epitaxy–grown GaAs crystals. It has been proved that this defect governs the electrical properties of high-purity GaAs making it possible to obtain semi-insulating undoped crystals which are crucial for integrated circuit technology. Besides its importance for the semiconductor industry, *EL* 2 has unique physical properties which make it a very interesting object for basic research. Altogether this defect has become a leading problem in deep-level physics, dominating all recent conferences in the field.

Various models of the origin of *EL* 2 have already been proposed, but none of them can explain coherently all of its properties. In the measurements reported in this Letter we have managed for the first time to get experimental insight into the microscopic structure of the defect. It was possible because, according to our report,[1] *EL* 2 exhibits intracenter absorption in the energy region between 1.0 and 1.3 eV with fine structure involving the 1.04-eV (8378 cm^{-1}) zero-phonon line (ZPL) and its replicas. As will be shown in this report, the behavior of the ZPL under external fields is providing qualitatively new information about the *EL* 2 center, allowing us to establish the *EL* 2 symmetry. Combining this result with the earlier data we explain *EL* 2 as an isolated antisite arsenic defect. We will show in the discussion that our *EL* 2 model is consistent with existing experimental results.

GaAs crystals used in this study were oriented and then cut into $3\times4\times7$-mm^3 samples with the longest dimension along various crystallographic directions. Aluminum mirrors were evaporated on portions of the front and back sides of each sample to make light traverse the sample several times. In this way the magnitude of the measured transmission changes was increased (at liquid-helium temperature the height of the zero-phonon line was about 0.02 cm^{-1}). A Zeiss model SPM2 grating monochromator and nitrogen-cooled PbS detector were used. The sample was placed in a beam of monochromatic light; thus it was possible to keep the intensity of penetrating light sufficiently low to prevent transition of the *EL* 2 to its metastable state.[2] During stress measurements, the temperature of the sample was 2 K. The effect of uniaxial stress on the ZPL was investigated up to 150 MPa for stress σ applied along [111], [100], and [110] directions with the light polarized parallel and perpendicular to the stress direction.

The results are shown in Fig. 1. The largest splitting into two components E_1 and E_2 was observed for the stress parallel to the [111] direction ($\sigma \parallel [111]$). E_1 signifies the component found when the electric field vector ϵ of the incident polarized light was perpendicular to σ ($\epsilon \perp \sigma$), and E_2 signifies that observed for $\epsilon \parallel \sigma$. A small splitting into two components denoted as E_3 and E_4 was observed for the stress σ parallel to the [100] direction for $\epsilon \perp \sigma$ and $\epsilon \parallel \sigma$, respectively. For the direction of stress parallel to the [110] direction a splitting into three components named E_5, E_6, and E_7 was observed. The components E_5 and E_7 were seen for the Poynting vector of the incident light **S** parallel to the [001] direction, whereas E_6 and E_7 were observed for $\mathbf{S} \parallel [1\bar{1}0]$. The E_5 and E_6 lines were observed for $\epsilon \perp \sigma$ and E_7 for $\epsilon \parallel \sigma$. For any given direction of stress, the intensities of the observed components were equal and they did not change with stress within the experimental error (the higher the stress, the bigger the error resulting mainly from the increase of the ZPL width with stress; for the highest stress applied the intensity was measured with an accuracy of about 15%).

The measurements of the magnetic field dependence of the ZPL were carried out for Faraday configuration with σ^+ and σ^- circular polarizations of monochromatic light beam. The samples were placed in a superconducting magnet which allowed a magnetic field up to 5 T. Since the half-width of the measured absorption line was 7 cm^{-1}, shifts as small as 1 cm^{-1} corresponding to a g-factor value of 0.2 could be detected. In both polarizations no shifts were observed in temperatures ranging from 2 to 10 K.

The pattern of splittings observed for the ZPL under stress applied along [111], [100], and [110] directions

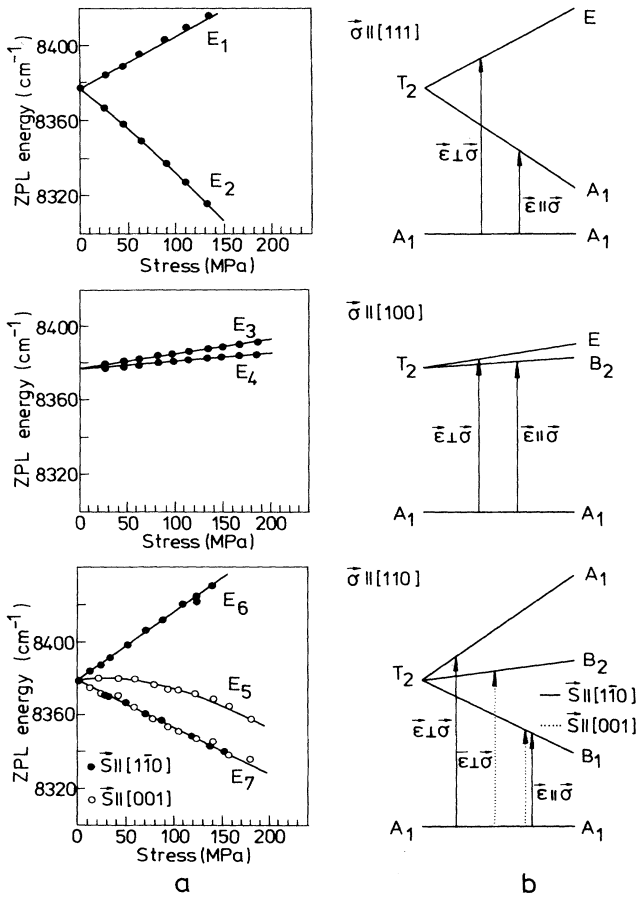

FIG. 1. (a) Experimental dependence (points) of $EL2$ zero-phonon line energy on uniaxial stress σ. E_1, E_3, E_5, and E_6 components were observed for $\epsilon \perp \sigma$; E_2, E_4, and E_7, for $\epsilon \parallel \sigma$. For $\sigma \parallel [110]$ the splitting for two inequivalent directions of **S** is shown. Theoretical fit (solid line) was obtained for $A_1 \rightarrow T_2$ transitions when the T_2 state is coupled with the τ Jahn-Teller mode. (b) Static-crystal-field–theory pattern of zero-phonon line splitting corresponding to an $A_1 \rightarrow T_2$ transition with polarization selection rules indicated. The values of splitting were calculated for the same values of V_0, V_1, and V_2 parameters as the fitting presented in (a).

(including [001] and [1$\bar{1}$0] inequivalent light propagation directions for [110] stress direction) was in agreement with the number of components expected for an $A_1 \rightarrow T_2$ optical transition in the static crystal-field (SCF) theory [see Fig. 1(b)]. According to Runciman[3] who made a classification of piezoabsorption spectra for different types of centers, there was no possibility for the explanation of the experimental data with the assumption of any other electronic, orientational, or electronic plus orientational degeneracy type of center. For an $A_1 \rightarrow T_2$ transition, the SCF theory predicts the unique ratios of component intensities for all stress directions and the light polarization selection

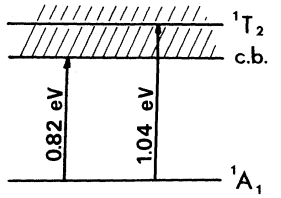

FIG. 2. The energy position of $EL2$ ground $^1A_1$ and excited $^1T_2$ terms in respect to GaAs band structure.

rules shown in Fig. 1(b). The lack of splitting under magnetic field suggests that the ground and excited states of the $EL2$ defect are spin singlets. The ground and excited states of the center can therefore be identified as $^1A_1$ and $^1T_2$, respectively. The position of the $EL2$ ground state within the GaAs band structure has been well established by deep-level transient spectroscopy measurements as 0.82 eV below the conduction band.[4] It follows then that the $^1T_2$ term is resonant with the GaAs conduction band (see Fig. 2).

In all those points (the pattern of splitting, the relative intensities of components, and polarization rules) the experimental data are in good agreement with the predictions of the SCF theory. The $^1T_2$ term is triply orbitally degenerate, which indicates T_d as the point-group symmetry of the close $EL2$ neighborhood.

This simple SCF model, however, cannot give good quantitative agreement with the experimental data, without taking into account the coupling of the $^1T_2$ term with lattice vibrations (see, for example, the work of Englman[5]).

Two experimentally observed effects, namely, the larger splitting under trigonal than tetragonal stress and the quenching of the Zeeman splitting of the orbitally degenerate $^1T_2$ term, indicates the domination of τ-mode Jahn-Teller effect in the $^1T_2$ term.[6] Apart from those two, also the other quantitative features of the observed splittings, not intelligible in the SCF theory, can be precisely described in this way. The piezoabsorption measurements show a larger total splitting for $\sigma \parallel [111]$ than for $\sigma \parallel [110]$ in contrast to equal values predicted by the SCF theory. Besides, the E_6 component exhibits nonlinear behavior with increasing value of stress whereas in the SCF model this line stays at the center of gravity of the E_5 and E_7 components. The above-mentioned features can be explained by taking into account possible interaction between the lowest T_2^v vibronic level and the closest A_1^v vibronic level coming from the T_2 electronic state coupled to the τ mode. The nonlinearity of E_6 combined with the linear behavior of the E_5 and E_7 components is consistent with the fact that the A_1^v vibronic level interacts only with the central component of the T_2^v vibronic level for stress $\sigma \parallel [110]$. However, for stress $\sigma \parallel [111]$ the A_1^v interacts with the lowest line of the T_2^v vibronic level yielding the largest value of split-

ting for this direction of stress.

The solid lines in Fig. 1 show the fitting of experimental points which is obtained in the model of $A_1 \rightarrow T_2$ transition, including T_2 coupling with the τ mode when the vibronic functions of T_2^{ν} and A_1^{ν} were taken in the static τ-mode Jahn-Teller limit.[6] In this model the following formulas for the dependence of the energy position of the observed components on stress σ are obtained:

$$E_1 = E_n - \tfrac{1}{3} V_2 \sigma,$$

$$E_2 = E_n + \tfrac{1}{3} V_2 \sigma + \tfrac{1}{2}\Delta - [(\tfrac{2}{3} V_2 \sigma)^2 - \tfrac{1}{3}\Delta \sigma V_2 + \tfrac{1}{4}\Delta^2]^{1/2},$$

$$E_3 = E_n - V_1 \sigma,$$

$$E_4 = E_n + 2V_1 \sigma,$$

$$E_5 = E_n + \tfrac{1}{2} V_1 \sigma - \tfrac{1}{2} V_2 \sigma,$$

$$E_6 = E_n - \tfrac{1}{2} V_1 \sigma + \tfrac{1}{2}\Delta - \tfrac{1}{2}[(\Delta + V_1 \sigma)^2 + (V_2 \sigma)^2]^{1/2},$$

$$E_7 = E_n + \tfrac{1}{2} V_1 \sigma + \tfrac{1}{2} V_2 \sigma,$$

where

$$E_n = E_0 + V_0 \sigma; \quad \sigma = |\sigma|.$$

The value of the ZPL energy position without any stress, $E_0 = 8378$ cm^{-1}, and the stress coefficients (hydrostatic $V_0 = 0.065$ cm^{-1}/MPa, tetragonal $V_1 = -0.01$ cm^{-1}/MPa, and trigonal $V_2 = -0.61$ cm^{-1}/MPa) were obtained directly from the results of piezoabsorption measurements. There was only one adjustable parameter: the so-called tunnel splitting Δ which is the energy position of A_1^{ν} with respect to T_2^{ν}. A good fit to the experimental points was obtained with the value of $\Delta = 60$ cm^{-1}.

Because of the T_2^{ν} interaction with the A_1^{ν} vibronic level, the intensities of the E_2 and E_6 components should decrease with stress. The present model predicts about a 10% change in those line intensities when the value of stress grows to 100 MPa which is within the experimental error.

Starting from 1977, when the first classification of deep defects in GaAs was made,[4] up to until recently it was commonly believed that $EL2$ is the only mid-gap level in melt-grown GaAs. Recent years have brought experimental evidence that this is the case in Bridgman crystals grown under typical conditions,[7] whereas in Czochralski material[8] as well as in heavy oxygen-doped Bridgman-grown GaAs[7] more than one mid-gap level is present. The variety of defects caused some doubts whenever the absorption band 1.0 to 1.3 eV with its ZPL belongs to $EL2$.[9] Recent measurements made on Bridgman GaAs have shown the direct proportionality between ZPL intensity, as well as the maximum of the intracenter absorption band, and $EL2$ concentration taken from deep-level transient spectroscopy.[10] The name $EL2$ should therefore be reserved for this defect which is present alone in typical Bridgman GaAs. It is also a member of the mid-gap level family in all melt-grown GaAs crystals since the absorption band 1.0 to 1.3 eV with its ZPL is common for all melt-grown materials.

The ZPL of the $EL2$ intracenter absorption band is the unique feature which made possible the identification of the point-group symmetry of the $EL2$ defect as T_d. T_d symmetry implies that $EL2$ is an isolated center. As the technological data show that antisite arsenic is involved in the formation of $EL2$,[11] it can be concluded that $EL2$ is an isolated antisite arsenic.

Experimental evidence of the existence of antisite arsenic defects in melt-grown GaAs was given a few years ago by electron paramagnetic resonance (EPR) experiments.[12] The strong argument for correlation of these centers with $EL2$ defects has been given recently by photo-EPR measurements.[13] It has been shown that the $EL2$ defect and antisite arsenic demonstrate practically identical optical and photoelectronic properties. However, the EPR signal is not sensitive to the antisite-arsenic neighborhood and EPR experiments cannot distinguish between an isolated antisite and its complexes. Very recent electron-nuclear double-resonance measurements revealed the presence of antisite arsenic defects with four arsenic atoms in the neighborhood in melt-grown GaAs.[14] The existence of such centers supports our model of $EL2$.

In addition, the model of isolated antisite arsenic is consistent with the theoretical calculations made for the neutral state of antisite arsenic (twofold occupied with valence electrons when three other electrons are taken by the bonds[15]) which gives the ground $^1A_1$ level below the bottom of the conduction band and the excited $^1T_2$ level resonant with the conduction band. It is in agreement with the experimentally observed situation presented in Fig. 2. Further support for $EL2$ identification comes from recent theoretical calculations of antisite arsenic total energy.[16] These calculations show that a metastable state of isolated neutral antisite arsenic is possible and it is the metastability which is being regarded as the $EL2$ fingerprint. The model of isolated antisite arsenic can therefore describe properly the $EL2$ level's energy position and the intracenter transition with ZPL behavior under external fields as well as the best known $EL2$ feature—its metastability.

The central result of the present work is the identification of the point-group symmetry of the $EL2$ defect as T_d which, combined with other experimental results, leads to the $EL2$ model as isolated antisite arsenic. That model explains all known $EL2$ features.

[1]M. Kamińska, M. Skowroński, J. Lagowski, J. M. Parsey, and H. C. Gatos, Appl. Phys. Lett. **43**, 302 (1983).

[2]G. Vincent, D. Bois, and A. Chantre, J. Appl. Phys. **53**, 3643 (1982).

[3]W. A. Runciman, Proc. Phys. Soc., London **86**, 629 (1965).

[4]G. M. Martin, A. Mitonneau, and A. Mircea, Electron. Lett. **13**, 191 (1977).

[5]R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972), p. 70.

[6]F. S. Ham, Phys. Rev. **138**, A1727 (1965).

[7]J. Lagowski, D. G. Lin, T. Aoyama, and H. C. Gatos, Appl. Phys. Lett. **44**, 336 (1984).

[8]M. Taniguchi and T. Ikoma, J. Appl. Phys. **54**, 6448 (1983).

[9]J. Lagowski and H. C. Gatos, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors, Coronado, California, August 1984,* edited by L. C. Kimerling and J. M. Parsey (The Metallurgical Society of the AIME, Warrendale, Pennsylvania, 1985), p. 73.

[10]M. Skowroński, D. G. Lin, J. Lagowski, L. M. Pawlowicz, K. Y. Ko, and H. C. Gatos, in Proceedings of the Material Research Society Symposium on Microscopic Identification of Electronic Defects in Semiconductors, San Francisco, 1985 (to be published).

[11]J. Lagowski, H. C. Gatos, J. M. Parsey, K. Wada, M. Kamińska, and W. Walukiewicz, Appl. Phys. Lett. **40**, 342 (1982).

[12]R. J. Wagner, J. J. Krebs, G. H. Stauss, and A. M. White, Solid State Commun. **36**, 15 (1980).

[13]M. Baeumler, U. Kaufmann, and J. Windssheif, Appl. Phys. Lett. (to be published).

[14]D. M. Hofmann, B. K. Meyer, F. Lohse, and J.-M. Spaeth, Phys. Rev. Lett. **53**, 1187 (1984).

[15]G. B. Bachelet, M. Schlüter, and G. A. Baraff, Phys. Rev. B **27**, 2545 (1983); P. J. Lin-Chung and T. L. Reinecke, Phys. Rev. B **27**, 1101 (1983).

[16]J. M. Baranowski, J. A. Majewski, M. Hamera, and M. Kamińska, in Ref. 9, p. 199.