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Publication Date

1987-08-01

Center for Advanced Materials

CAM

Submitted to Physical Review B

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August 1987

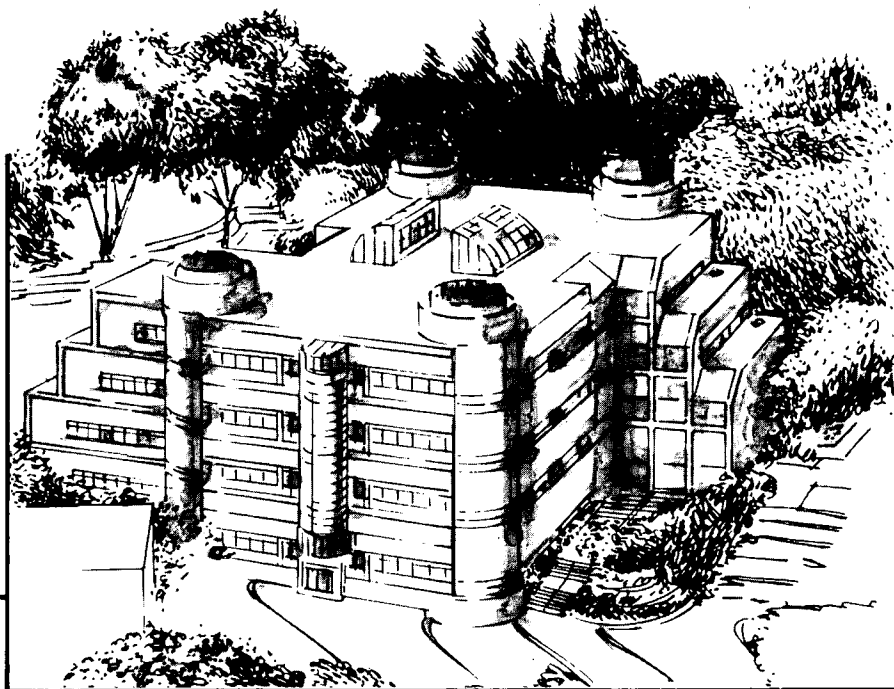
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Critical Criterion for Axial Models of Defects in as-Grown n-GaAs

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Abstract:

We present uniaxial stress deep level transient spectroscopy data on EL2 and EL6 in as-grown n-GaAs and obtain upper bounds for the axial deformation potentials. Using the recently determined band-edge hydrostatic deformation potentials of GaAs we further provide for the first time values for the change in the strength of the isotropic strain-coupling of a defect upon electron emission. The ratio of the change in the isotropic strain-coupling strength to the change in the axial strain-coupling for these defects is a critical criterion which must be satisfied by theoretical models that successfully describe axial defects.

There has been increased theoretical interest recently in axially symmetric native defect pairs as candidates for many of the defects¹ in as-grown GaAs single crystals. In particular, it has been suggested that some of the properties of the EL2 defect, one of the technologically most important deep levels, can be explained in terms of these axial complexes²⁻⁶. An axial model for EL6 has likewise been proposed⁷. In this Communication we present the first results for the changes in isotropic and axial strain-couplings upon electron emission from the EL2 and EL6 defects in as-grown GaAs. The validity of any model describing axial defects can, in part, be evaluated by whether the predicted strengths of these lattice couplings lie within the experimental boundaries.

Electron-lattice coupling lies at the heart of the Born-Oppenheimer approximation: electronic energies change adiabatically with changes in nuclear coordinates. In the case of a defect in a semiconductor, the total energy (electronic energy and elastic energy for a given charge state) depends on the lattice coordinates. Total energies therefore shift as the lattice coordinates are perturbed by phonons or by applied stress. The amount by which the defect energy shifts per unit strain is called the defect deformation potential of the specific charge state. Defect energy is sensitive, in general, to both the hydrostatic (trace) and shear (traceless) components of strain. The corresponding isotropic and axial deformation potentials can be separated by performing hydrostatic and uniaxial stress experiments individually. In practice (for instance using thermal ionization spectroscopy) only the difference in total energy between two charge states is measured. Rigorously, the defect activation energy is the difference

$$\Delta E = E(2, Q_2) - E(1, Q_1) + E(e_B) \quad (1)$$

where $E(2, Q_2)$ and $E(1, Q_1)$ are the total energies of the defects in the final and initial charge states at the respective equilibrium lattice positions Q_2 and Q_1 , and $E(e_B)$ is the energy of the carrier in the band. Typically, $E(e_B)$ is chosen as the origin, which causes no ambiguity in the case of an unperturbed crystal. As perturbations are applied, however, the effect of the perturbation on the band-edge enters on equal footing with the effect of the perturbation on the defect states. For the case of stress perturbation, the change in the activation energy is

$$d\Delta E/d\epsilon_{ij} = dE(2, Q_2)/d\epsilon_{ij} - dE(1, Q_1)/d\epsilon_{ij} + dE(e_B)/d\epsilon_{ij}. \quad (2)$$

The last term is the band-edge deformation potential.

For the case of n-GaAs, there is no shear contribution to the deformation potential of the conduction band minimum. Therefore the contribution of shear strain to the change of the defect activation energy arises entirely from the shear dependence of the defect states. Uniaxial stress measurements can therefore unambiguously measure the change in the axial strain-coupling upon carrier emission. The situation for hydrostatic stress is more difficult. The last term in eq.(2) becomes the hydrostatic deformation potential of the conduction band, which is non-zero. The value of this deformation potential has recently been determined by us⁸ to be $a_C = -9.3 \text{ eV} \pm 1 \text{ eV}$. With this value for the conduction band, the pressure derivative of the defect activation energy can be directly related to the change in the isotropic strain-coupling upon carrier emission. This information is complementary to measurements of volume change upon carrier emission⁹.

Bastide et. al.¹⁰ studied the effect of uniaxial stress on the levels EL3($E_C - 0.60 \text{ eV}$) and EL2($E_C - 0.82 \text{ eV}$) and saw no evidence of orientational splitting for either level. However they did observe a shear anisotropy of 10 meV/GPa for

EL3 between stresses in the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions. We have extended their work, confirming their results for EL2 and including results for EL6 ($E_C - 0.37$ eV). We further utilize the hydrostatic component of uniaxial stress to obtain the pressure derivatives for these defects. Our diodes used in uniaxial stress experiments were fabricated from a Liquid Encapsulated Czochralski (LEC) grown $\langle 111 \rangle$ crystal with a concentration of $2 \times 10^{16} \text{ cm}^{-3}$ net donors. The Ohmic contacts were fabricated by evaporating Au-Ge alloy onto a freshly etched surface followed by annealing at 450° C for 3 minutes. The Schottky contacts were formed subsequently by evaporating 300 \AA of gold onto the opposite face of the sample. Oriented stress samples were cut into $1 \times 1 \times 6 \text{ mm}^3$ parallelepipeds to which stresses up to 0.5 GPa could be applied. Typical low-temperature stress data for a $\langle 111 \rangle$ oriented sample are shown in Fig. 1. The signature (capture cross-section and activation energy) of the defect with a peak near 115 K matches the values reported¹¹ for EL3, while the signature of the defect with the peak near 180 K matches with the reported signature of EL6. The peaks of both defects move to higher temperature under stress which indicates increased separation from the conduction band. The peak associated with EL6 has interfering peaks on both the low and high temperature side. For these reasons a detailed lineshape analysis cannot be carried out for EL6. In general, however, no significant broadening of the DLTS peaks can be observed under stress. The additional absence of significant shear anisotropy implies that axial contributions to the defect binding energies must be small. The mid-gap donor, EL2, suffers no interference from any neighboring defect peak. Therefore minute changes in the peak amplitude under stress, indicative of small splittings, should be observable. We applied stress up to 0.5 GPa on a $\langle 110 \rangle$ oriented sample containing $4 \times 10^{15} \text{ cm}^{-3}$ EL2 defects. All defect

degeneracies are broken by $\langle 110 \rangle$ stress. Within experimental error there was no change in amplitude of the DLTS peak. Assuming the DLTS peak is described well by a gaussian, and estimating an experimental error of 0.1% in the measurement of the peak amplitude, we find that the splitting of EL2 for $\langle 110 \rangle$ stress must be smaller than 5 meV/GPa.

A summary of the energy shifts with respect to the conduction band for EL2 and EL6 is presented in Table I along with the results from Bastide et al. for EL2 and EL3. The energy shifts under uniaxial stress are averaged and multiplied by a factor of three to produce the pressure derivatives for the defects with respect to the conduction band. From the hydrostatic deformation potentials of the conduction band edge, we are able to obtain the first absolute values for the pressure derivatives of these defects. In Fig. 2 the absolute hydrostatic-pressure derivatives of EL2, EL6 and EL3 are plotted as a function of the depth of the defect from the conduction band. Included in the figure are the pressure derivatives for the electron irradiation defects^{12,13} E1, E2, E3, E4, a native hole trap¹² HB, and the theoretical results¹⁴ for Ga-site and As-site defects. The pressure derivatives of the important extrema of the band structure are also indicated. The defect pressure derivatives presented in Fig. 2 are the change in the isotropic strain-coupling upon electron emission and are not merely related to the band edge, as has previously been the custom. This coupling to the lattice figures prominently in the phenomena of multi-phonon recombination and large-lattice relaxation. Most of the defect pressure derivatives lie within the range of the theoretical predictions. However the pressure derivative of the EL2 defect is extraordinarily large. This evidence suggests that EL2 has a complex structure, yet the insensitivity of EL2 to shear stress further indicates that the axial lattice-coupling of the defect is minimal.

By comparing the isotropic deformation potential with the axial deformation potential of the EL2 and EL6 defects we can provide a critical ratio of isotropic to axial lattice coupling that must be satisfied by any axial model of these defects. The quantities Ξ_{iso} and Ξ_{ax} are the isotropic and axial deformation potentials of the defect respectively. These defect deformation potentials are defined as the net change per unit strain of the total energies of the final states compared to the total energies of the initial states in the thermal ionization transition. The critical ratio is expressed by

$$\frac{\Xi_{\text{iso}}}{\Xi_{\text{ax}}} = \frac{s_{44} \left(\frac{dE}{dp}\right)_{\text{hyd}}}{\sqrt{3} 3(s_{11}+2s_{12}) \left(\frac{dE}{dp}\right)_{\text{ax}}} \quad (3)$$

where s_{11} , s_{12} , and s_{44} are compliance constants, while $(dE/dp)_{\text{iso}}$ and $(dE/dp)_{\text{ax}}$ are the respective isotropic and axial pressure derivatives. Using the limit of $(dE/dp)_{\text{ax}} < 5 \text{ meV/GPa}$ for both EL2 and EL6, with the corresponding hydrostatic pressure derivatives from Fig. 2, we find the following critical ratios:

$$\begin{aligned} \Xi_{\text{iso}} / \Xi_{\text{ax}} &> 14 && \text{EL2} \\ \Xi_{\text{iso}} / \Xi_{\text{ax}} &> 9 && \text{EL6} . \end{aligned}$$

The change in the isotropic strain-coupling upon electron emission is therefore at least an order of magnitude larger than the change in the axial strain-coupling for both EL2 and EL6 defects. These coupling strengths are defined for the relaxed equilibrium configurations of the different charge states. The coupling strength of EL2 is strongly non-linear and is a function of the degree of relaxation^{15,16}. In fact, the optical transition from the valence band to the

ground state of EL2 is relatively insensitive to applied stress, which has led to claims that EL2 has only a small coupling to the lattice. This is clearly wrong, considering the significant lattice relaxation which must occur to explain the differences between thermal and optical ionization energies of the defect.

To consider how the critical criteria mentioned above relate to defect structure, a detailed understanding of the microscopic origin of defect deformation potentials is required. A rigorous derivation of the dependence of deformation potentials on the localization of the defect wavefunction is beyond the scope of this article. An argument about qualitative trends can be made easily, however. For a defect state to have a large electron-lattice coupling strength, the product of the defect envelope wavefunction and the gradient of the wavefunction must both be large at the sites of the strongest contribution to the defect binding potential. If the defect wavefunction is either too localized or too extended, then the product $\Psi(r)(\nabla\Psi)$ will be small at the sites of the nearest or next-nearest neighbors (which are usually the sites of the strongest contribution to the defect potential), and the electron-lattice coupling will be correspondingly small. From the large ratios of Ξ_{iso} / Ξ_{ax} mentioned above for EL2 and EL6, we can conclude that the product $\Psi(r)(\nabla\Psi)$ must be large at the sites of the four nearest neighbors to explain the large hydrostatic pressure derivative, yet the strength of all potentials within the nearest neighbor distance must be equal within at least 10% to explain the lack of anisotropy. If the defect potential includes a strong potential off the central defect site, then the site of this potential must be next-nearest neighbor or farther from the central defect site. These considerations can be used to assess the validity of axial models of EL2. Our arguments are consistent with recent experiments which find that the stable EL2 level has no observable axial lattice coupling, while the metastable

state has a large axial lattice coupling¹⁷. This behavior has been tentatively explained in terms of an off-site constituent which can move from the next-nearest site to the nearest-neighbor site adjacent to an As_{Ga} . Such a model may explain the axial behavior of EL2, but the strong isotropic coupling of the defect to the lattice remains a challenge.

We are indebted to C. Brandt of the Electronics Materials group at MIT for providing the GaAs material. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under contract DE-AC03-76SF00098.

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Table I

Uniaxial Stress Shifts with respect to the conduction band (meV/GPa)
 (All errors are ± 5 meV/GPa)

Defect --->	EL2	EL3	EL6
<111>	9 8*	---- 28*	18
<110>	10	----	23
<100>	5 12*	---- 18*	18
<hr/>			
Anisotropy	<5	≈ 10	<5

* Bastide et. al. Ref.10

Figures:

- Fig. 1** Stressed DLTS data for EL3 and EL6 for $\langle 111 \rangle$ stress. The emission time constant is held at a fixed value as the stress is increased from 0 GPa up to 0.3 GPa.
- Fig. 2** Absolute pressure derivatives of the bulk defects EL2 and EL6 from the present work (filled squares). Also included (filled circled) are results for EL3 and HB from Ref.10 and the electron irradiation defects E1, E2, E3, and E4 from Refs.12-13. The theoretical results of Ref.14 for Ga-site and As-site point defects are represented by the dashed lines. The absolute pressure derivatives of the important band extrema are also indicated. All errors are ± 20 meV/GPa.

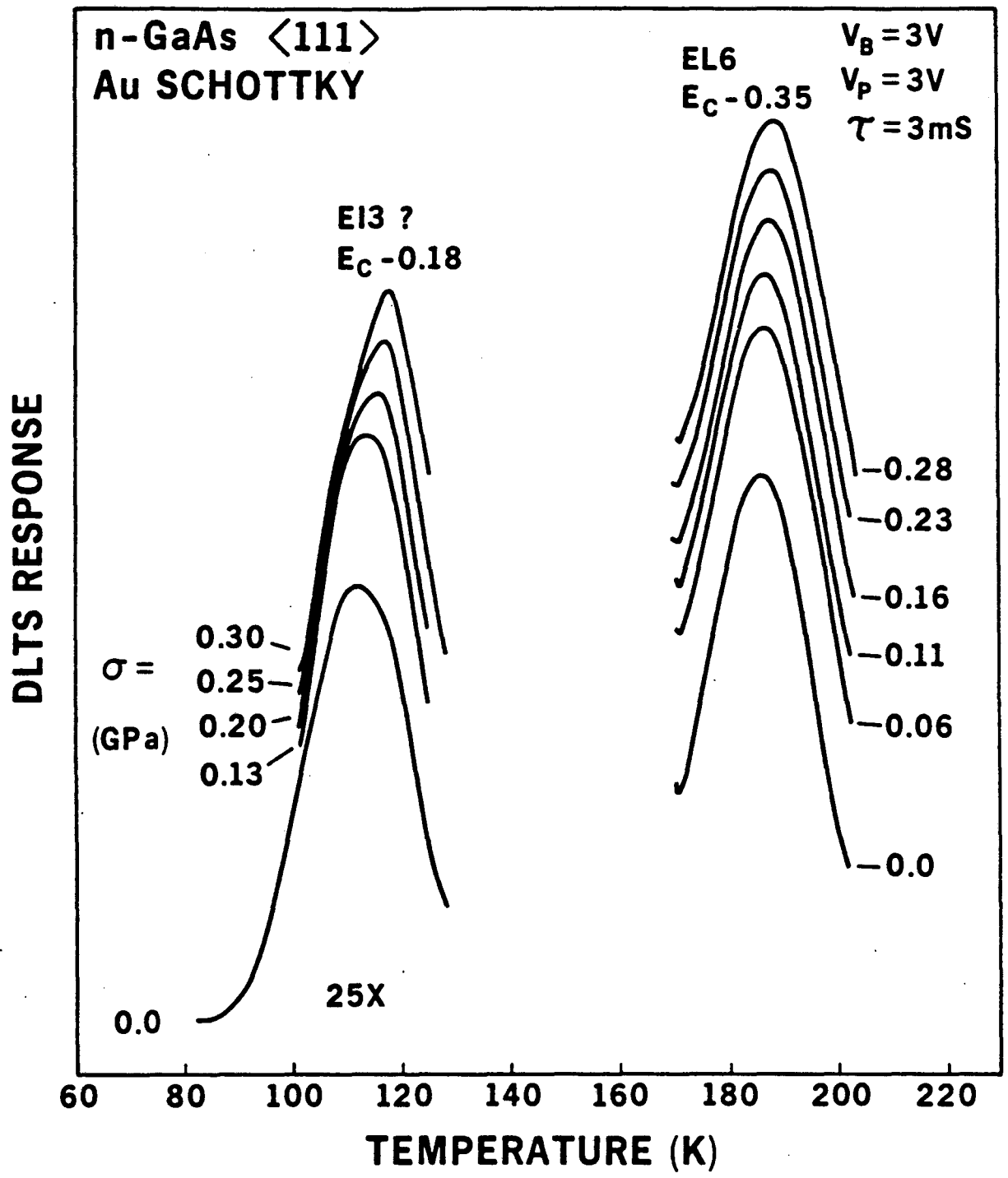
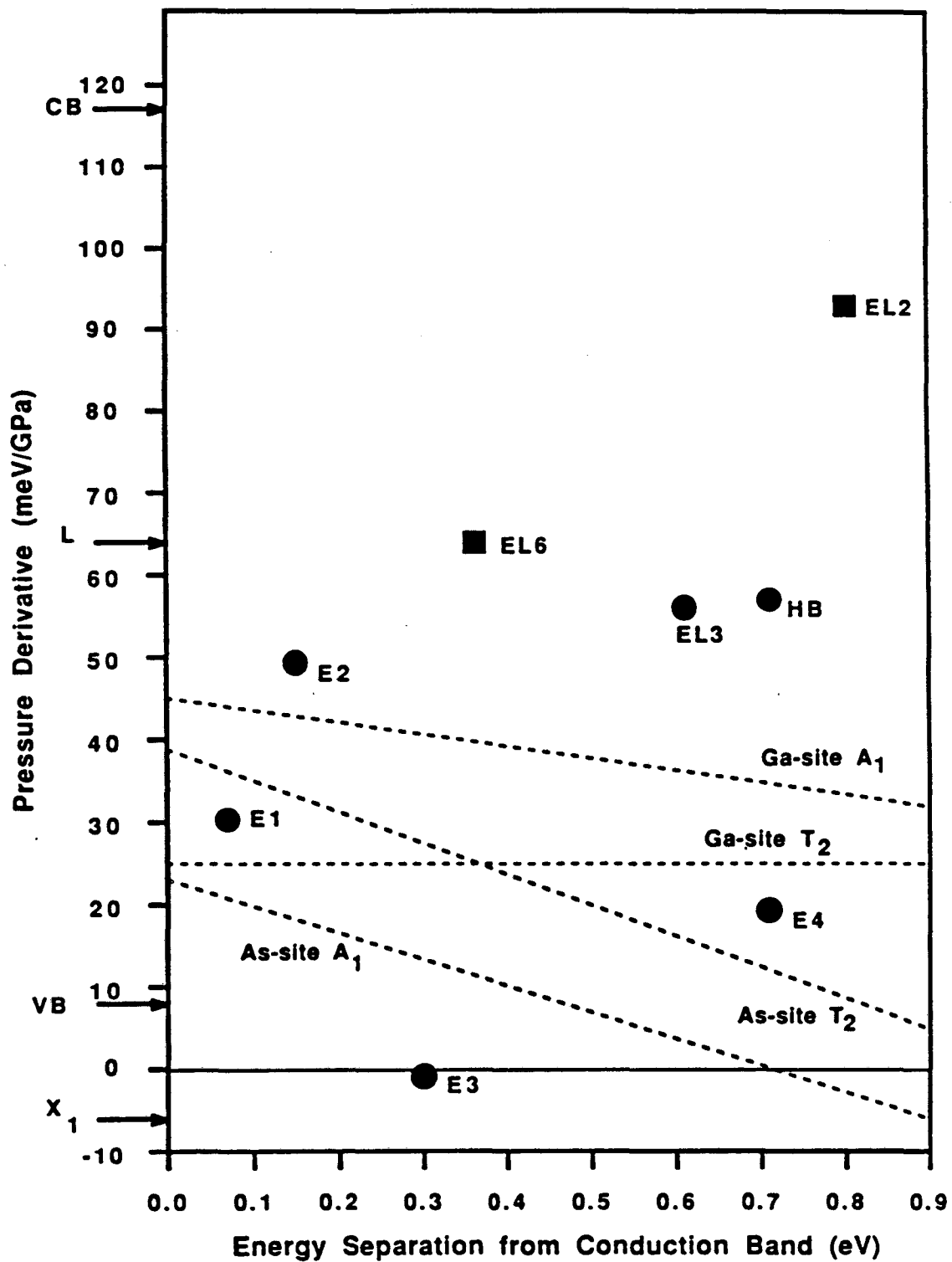


Figure 1.

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Figure 2.

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