Theoretical Evidence for an Optically Inducible Structural Transition of the Isolated As Antisite in GaAs: Identification and Explanation of *EL2*?

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We performed parameter-free, self-consistent calculations of the electronic structures, total energies, and forces of the As antisite, of an As-interstitial–Ga-vacancy defect pair, and of various configurations between these limits. The total-energy surface exhibits an interesting metastability. The theoretical results can explain all established properties of the so-called *EL2* defect.

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The so-called *EL2* defect in GaAs is the dominant deep trap in as-grown GaAs and probably the most intensively studied center in semiconductors (for a review see Martin and Makram-Ebeid[1]). The name *EL2* follows the usual classification in deep-defect physics for labeling a microscopically unidentified level. Basic research is attracted by the *EL2* defect because of a "mysterious" metastability. Despite an enormous worldwide interest in this center, a microscopic identification and explanation of its properties has not been succeeded so far.

Many different models have been suggested for *EL2*. In the beginning it was believed to be due to oxygen impurities or to dislocations, but now it seems to be established that *EL2* is an *intrinsic point* defect probably involving one (or more) As antisites.[2,3] The most recent suggestions for the *EL2* center are the $V_{Ga} \rightleftarrows V_{As}As_{Ga}$ defects,[4] complexes involving several As_{Ga} defects,[5,6] and the distant As_{Ga}-As_i defect pair.[7–9] Here V stands for vacancy and the indices indicate the site, as for example "Ga," the normally Ga site, and "i," an interstitial site. The search for defect *complexes* as an explanation for *EL2* was largely motivated by the fact that theory was unable to propose a mechanism by which optical absorption at the isolated antisite can produce the observed metastability (e.g., Refs. 4–6 and 9, and Bachelet and Scheffler[10]). In this Letter we show that this assessment is wrong. Our density-functional-theory calculations yield directly that the isolated As antisite undergoes a configurational transition upon optical excitation.

Let us first list in summary form the most important, experimentally established key properties of the *EL2* center[1]:

(1) The normal state of *EL2* (below labeled *EL2-F*, where *F* stands for fundamental) has a deep level at midgap.

(2) *EL2* is a native point defect.

(3) *EL2* is neutral.[11,12]

(4) No EPR signal has been observed for this neutral *EL2* center.

(5) *EL2-F* exhibits an internal optical transition at $1.0 < \hbar\omega < 1.3$ eV, the zero-phonon line being 0.14 eV below the main peak.[13]

(6) The symmetry of *EL2-F* is tetrahedral[3,13] (if at all, it may be weakly perturbed from T_d symmetry).

(7) *EL2* can be optically bleached (for T lower than 140 K). The bleached state of *EL2* (below labeled *EL2-M*, where *M* stands for metastable) is electrically and optically inactive.

(8) The bleaching of *EL2* happens without change of the charge state. Thus, *EL2-M* is neutral.

(9) With the *EL2* bleaching the GaAs sample changes its character from semi-insulating to *p* type.

(10) *EL2-F* can be thermally regenerated by heating above 140 K. The barrier between the fundamental and the metastable state is 0.34 eV.

(11) When electrons are induced into the conduction band, the thermal barrier is lowered to 0.1 eV. This effect is often called an Auger process or electron-induced deexcitation.

(12) Heating the sample to 850 °C and rapid cooling destroys the *EL2* defect. Subsequent annealing at 130 °C brings it back.[7]

We performed calculations for all native point defects in GaAs (see also Ref. 10, Baraff and Schlüter,[14] and Scheffler and Scherz[15]), as well as for defect pairs which contain the As antisite. Most calculations were performed with the self-consistent Green's-function method[15,16]; some were repeated and completed with the supercell approach, with a 54-atom fcc cell. We used first-principles pseudopotentials[17] and the Ceperley-Alder form of the exchange-correlation energy.[18] The supercell calculations were performed with the method of Car and Parrinello[19] with a plane-wave basis with $E_{cut}=8$ Ry for most calculations and with $E_{cut}=16$ Ry for some important points (minima and maxima) on the total-energy surface. Further details are described elsewhere.[20]

Our calculations for the distant As_{Ga}-As_i pair show a very small binding energy which is not consistent with the experimentally known thermal stability of *EL2*.[7] Further, the electronic structure of this pair disagrees

with either property No. 3 or No. 4. On the other hand, for the isolated As antisite we find some remarkable properties, which had not been recognized before. Its electronic structure is shown in the top part of Fig. 1. The defect has a deep a_1 level in the gap and a t_2 resonance at the bottom of the conduction band. For the neutral center the a_1 level is filled with two electrons. The total (many-electron) wave function then has spin $S=0$. By photons with energy of about 1 eV an electron can be excited from the a_1 level into the t_2 resonance. Because of localization and wave-function character of the a_1 and t_2 states (see Fig. 1, top) this transition is expected to have high probability. Once the electron is in the t_2 state the system is unstable with respect to a Jahn-Teller distortion. From the calculations we find that the defect arsenic atom moves in the [111] direction (the Jahn-Teller forces for a distortion in the [100] and [110] directions are only about half of those for the trigonal distortion). This displacement of the arsenic atom splits the energy of the t_2 state into the $2a$ and $1e$ states and lowers the total energy (compare Fig. 2, upper part, and the curve labeled E in the lower part). At a distance of about $Q=0.25$ Å we find a minimum of this total-energy curve. How will the system go back from this electronic excited state (E) to an electronic ground state? Of course, one possibility would be a Franck-Condon transition down to the curve labeled F (Fig. 2, bottom). The single-particle energies (Fig. 2, top) also suggest another possiblity: With the displacement of the As atom away from the tetrahedral position ($Q=0$) the $1a$ and the $2a$ states mix, and an alternative occupation becomes possible. This alternative electronic configuration gives rise to the total-energy curve labeled M in Fig. 2. This is also (like the F curve) an electronic ground state. On this M total-energy curve the displaced As atom ends at about 1.4 Å away from its original Ga-site position. Now the defect is a $V_{Ga}As_i$ defect pair. The electronic structure of this M configuration is such that there is a localized deep level ($2a$) close to the valence-band edge, filled with two electrons. The electronic properties of this center can be understood (in a simplified picture) as that of a threefold negative Ga vacan-

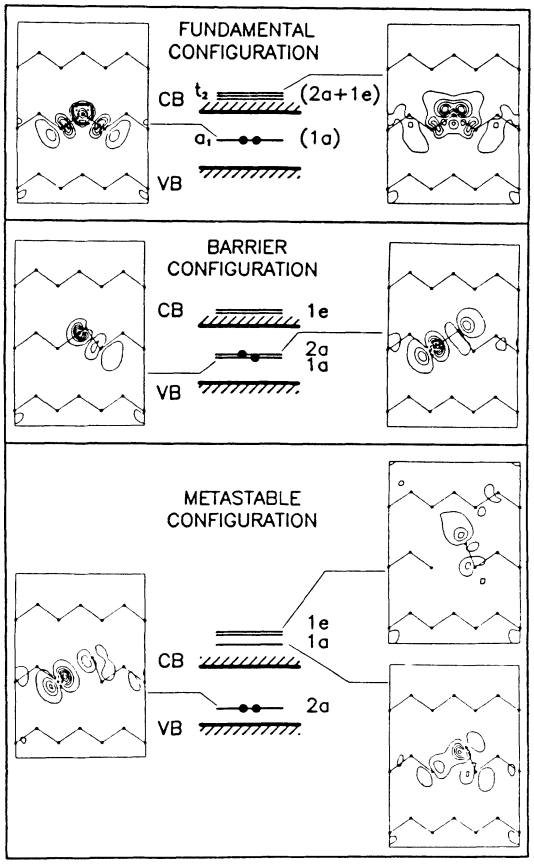

FIG. 1. Wave functions in the (110) plane of the tetrahedral As_{Ga} defect ($Q=0$) (top), of the displaced As atom ($Q=0.7$ Å) (middle), and of the metastable $V_{Ga}As_i$ complex ($Q=1.4$ Å) (bottom). The configurational coordinate Q describes the position of the As defect atom along the [111] direction.

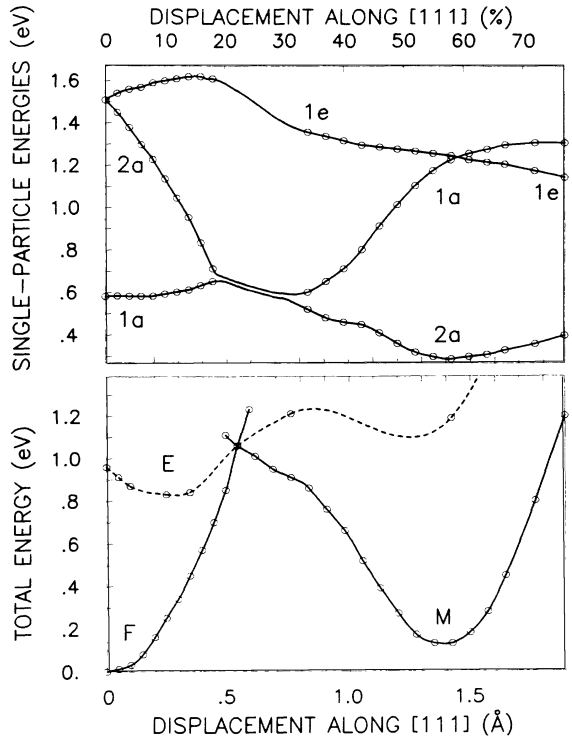

FIG. 2. Single-particle energies (with respect to the top of the valence band) and total energies of the $S=0$ electronic ground states (curves F and M) as functions of the position of the As defect atom. Zero displacement refers to the As antisite. These calculations were performed with a basis set of $E_{cut}=8$ Ry, with neglect of lattice distortions. The curve labeled E is an electronic excited state with electronic configuration $1a^1 2a^1$.

cy close to a threefold positive As interstitial (see Fig. 1, bottom). Unlike the isolated As_{Ga} defect, the electronic structure of the $V_{Ga}As_i$ complex does not indicate a high-probability internal optical transition (see Fig. 1, lower part).

We now compare our results for the $As_{Ga} \rightleftarrows V_{Ga}As_i$ system to the above-mentioned key properties of $EL2$. We already explained the electronic properties of the $EL2$-F center, including the internal optical transition ($EL2$-$F \rightarrow EL2$-E), the experimentally observed Jahn-Teller relaxation energy of 0.14 eV (Ref. 13) (our calculated number is 0.13 eV), and the transition into the metastable state ($EL2$-$E \rightarrow EL2$-M). With this transition (bleaching of $EL2$) the highest occupied level shifts down in energy. Therefore a compensation of shallow acceptors is no longer efficient and the crystal becomes p type. The theory also suggests two mechanisms for the regeneration of the normal $EL2$ state. Of course, the $EL2$-M system can thermally overcome the barrier and go directly from the $EL2$-M into the $EL2$-F state. A transition with a smaller barrier is possible, if we allow the capture of a conduction-band electron in the $1a$ state of the M configuration. For this negatively charged center the barrier between the M and F configurations is found to be nearly zero. This capture of a conduction-band electron in the $1a$ state can thus explain key property No. 11 (see above). We may also mention that the theory predicts that the isolated *paramagnetic* arsenic antisite should not be quenchable *directly* (for As_{Ga}^{+} the energy barrier between the F and M configurations is found to be zero), in agreement with recent experimental work of Meyer, Hofmann, and Spaeth[21] and Kaufmann, Wilkening, and Baeumler.[22]

Concerning a quantitative comparison between our theoretical results for $As_{Ga} \rightleftarrows V_{Ga}As_i$ and experiment, we note that converged density-functional-theory calculations give a "single-particle energy gap" which is only about half of the experimental band gap. The position of defect levels with respect to band edges is therefore somewhat uncertain. The difference between two defect-induced levels may be less affected by this uncertainty. The internal excitation energy is calculated as 0.97 eV (the experimental number is 1.18 eV), the Jahn-Teller energy is 0.13 eV (the experimental number is 0.14 eV), and the barrier height in Fig. 2 is 0.92 eV (the experimental number is 0.34 eV). Concerning the calculated barrier we note that in Fig. 2 we have not taken lattice distortions into account. Further, the electronic structure of the barrier is such that the system would prefer a total spin $S=1$, but the calculations of Fig. 2 were performed for $S=0$. From the localization of the wave functions and from calculated forces and force constants we obtain that the effects of lattice distortions and spin polarization will lower the barrier by about 0.4–0.5 eV, which brings the theoretical barrier height of our $As_{Ga} \rightleftarrows V_{Ga}As_i$ defects close to the experimental value for $EL2$.

Finally we comment on the recent model of the distant As_{Ga}-As_i complex which was indicated by experimental results.[7,8] The distance between the two constituents was concluded from the experimental analysis to be about 4.88 Å. We do not exclude that these defects exist. In fact, we believe that many defects of this type (and similar ones) as well as As_{Ga} defects close to dislocations are possible. However, we note that the thermal experiments of von Bardeleben *et al.*[7] may be also explained by our results for the isolated As antisite: According to our calculations, the As_{Ga} (or $V_{Ga}As_i$) defect will dissociate at high temperature into a Ga vacancy and an As interstitial (the positive charge state of the antisite being more stable than the neutral one). Unfortunately, a quantitative analysis of this dissociation process is not possible at present, because it appears to be controlled by the crystal environment (the gas phase). Thus, it is not clear where the Ga vacancy and the As interstitial will end. Association of the Ga vacancy and the As interstitial will occur only when the thermal energy is sufficiently high to allow migration of the As interstitial. This regeneration of $EL2$ was observed by von Bardeleben *et al.* to occur at 130 °C.

In conclusion, we reported electronic-structure and total-energy calculations of the electronic ground states and of the excited state of the $As_{Ga} \rightleftarrows V_{Ga}As_i$ defects. The driving mechanism which starts the system to move into the metastable configuration is the Jahn-Teller effect, as was already speculated by Bachelet and Scheffler.[10] The hitherto unexpected result of our calculations is that the central As atom of an As antisite can (if optically excited) move really far, to build up a new bonding situation. There is a barrier of about 0.4 eV between these two configurations. This result may be understood by the fact that the covalent radius of an As atom is 1.2 Å. Therefore the As_i is too "thick" to pass easily through the (111) plane of three As atoms. Once it is on the other side of this plane, it can build up a threefold bonding, similar to the bonding in crystalline grey arsenic. This stabilizes the metastable configuration.

We further noted that the $As_{Ga} \rightleftarrows V_{Ga}As_i$ defects exhibit essentially the same properties as are known for the famous $EL2$ center and explicitly considered twelve most characteristic and currently accepted properties of $EL2$. Our identification of $EL2$ relies on the comparison with these properties. If any of them should turn out to be incorrect, this may also affect our $EL2$ identification. It must be said that there are experiments (e.g., those of Refs. 7 and 8 and Levinson and Kafalas[23]) whose *interpretations* favor an axial defect in the fundamental state of $EL2$. These experimental studies are, however, at variance with other experiments (e.g., Refs. 3 and 13). It remains to be seen whether these interpretations will prevail and if the axial character (if it really exists) is

essential for the $EL2$ metastability. We hope that the theoretical results presented above will help to design further experiments in order to test our proposed assignment.

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