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As_{Ga}-X_I complexes as models for the $EL2$ center in GaAs

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Several As antisite-interstitial complexes are considered as models for the $EL2$ center in GaAs. Large-scale electronic-structure calculations show that the binding energy of the complex is insufficient to account for the annealing properties of $EL2$. The electronic structure of the complexes is also in disagreement with the majority of the experimental data. The isolated As_{Ga} remains thus the best candidate for the $EL2$ center. Some of the antisites may be associated with interstitials, but the salient properties of $EL2$ are due to the antisite rather than to the interstitial or the complex.

$EL2$ is probably the most important native defect in GaAs. It is the dominant defect in the undoped materials that is responsible for the pinning of the Fermi level near midgap. The $EL2$ defect level can be bleached by light and regenerated by annealing. This famous metastability has stimulated a large number of studies. Recently, a consensus began to develop that $EL2$ is an isolated As antisite (As_{Ga}).[1,2] It has been shown that As can occupy either a fully tetrahedral Ga site or a metastable threefold-coordinated site, in which the As antisite has moved away from one of its nearest neighbors. The level structure and the properties of As_{Ga} are consistent with most of the experimental data on $EL2$. In particular, the splitting of the optical-absorption spectra under stress[3] and its subsequent modeling[4] show that the $EL2$ ground state has tetrahedral symmetry. However, these findings were contradicted by electron-nuclear double resonance (ENDOR) data attributed to $EL2$. These data showed a weakly perturbed antisite spectrum, consistent with an axial defect of (111) symmetry, which was suggested to be an As_{Ga}-As_I pair. A very recent paper[5] presented additional experimental data and model calculations in support of this assignment. Since the properties of semi-insulating GaAs are to a large extent determined by $EL2$ defects, its identification is important for fundamental and technological reasons. In this paper, we examine theoretically the As_{Ga}-As_I and As_{Ga}-Ga_I pairs as candidates for $EL2$. *Ab initio* molecular-dynamics calculations in large supercells are used to predict the structural and electronic properties of these candidates. It is shown below that these properties are inconsistent with those attributed to $EL2$.

The *ab initio* molecular-dynamics methodology was developed by Car and Parrinello.[6] It uses local-density theory and the plane-wave and pseudopotential formalisms to compute the electronic structure and *ab initio* forces for atoms embedded in a periodically repeated supercell. Due to its computational efficiency, a large number of atoms can be included in the calculations. Most of the results presented here were obtained by placing a single defect in a supercell corresponding to 64 atoms in perfect GaAs. Some calculations involving the As_{Ga}-As_I pair were also carried out in a cell corresponding to 216 atoms, in order to minimize residual interactions between the periodically repeated pairs. The calculations in 64-atom cells used the standard Bachelet-Hamann-Schlüter (BHS) pseudopotentials,[7] as modified by Gonze and coworkers[8] to facilitate their use in the separable Kleinman-Bylander[9] form. In the 216-atom cell computational constraints made necessary the use of much softer pseudopotentials, which were developed by Heinemann and Scheffler.[10] Plane waves with kinetic-energy cutoffs smaller than 14 and 8 Ry were included in the 64- and 216-atom cells, respectively. We verified that the two different potentials with their respective cutoffs produced very similar results in the 64-atom cells.

In the calculations reported below all the internal atomic coordinates in the supercells were fully relaxed. Given the size of the cells, this is a formidable task. We used a procedure that we call "dynamical relaxation." In this procedure, the atoms follow Newtonian dynamics with a special friction term. At each step, the friction term reduces by a constant factor those components of the atomic velocities that are antiparallel to the forces acting on the atoms. In our tests on a variety of systems, we found that this procedure is much more efficient in relaxing the atomic coordinates than either the steepest-descent or the conjugate-gradient method.

In order to put the present results in context, it is necessary to first list a few of the well-established properties of $EL2$ and to summarize briefly previous experimental and theoretical developments. A full compilation can be found in Ref. 11, while the more recent developments are mentioned below. It is well established that $EL2$ is a native defect whose concentration increases in As-rich GaAs. It should thus be As-related. $EL2$ can exist in two atomic configurations: the ground state, labeled $EL2$-F (fundamental), and a metastable state $EL2$-M. The metastable state can be reached by an optically induced intracenter transition. Heating to 140 K regenerates $EL2$-F. Several measurements indicate that neither $EL2$-F nor $EL2$-M are electron paramagnetic resonance (EPR) active,[11] although a very recent model for $EL2$ (Ref. 12) suggests that $EL2$-F contains an unpaired electron. $EL2$-F has a level near midgap, while $EL2$-M does not have levels within the gap. Stress-induced splittings of the optical spectra require tetrahedral symmetry of $EL2$-F,[3] although it has recently been pointed out that the relevant transition is not necessarily intracenter, thus weakening the argument.[13] A major breakthrough oc-

curred when calculations showed that an isolated tetrahedral As_{Ga} can assume a metastable position, corresponding schematically to the reaction $As_{Ga} \rightarrow V_{Ga} + As_I$.[1,2] The resulting isolated As_{Ga} model accounted for most of the experimental data, the notable exception being optically detected ENDOR (ODENDOR) spectra of the paramagnetic state of $EL2$.[14,15] These data show weak structure beyond the major peaks associated with As_{Ga}. This structure has been interpreted as indicative of a presence of an As interstitial in near proximity to As_{Ga}. The early analysis[14–16] suggested that the As_I was located along the antibonding $(-1,-1,-1)$ direction behind the As_{Ga}. However, calculations by two groups[17,18] found no or negligible binding between As_{Ga} and As_I, we well as a level structure that did not agree with that expected for $EL2$. A more recent analysis of the ODENDOR data pointed out that the As_I could reside in the other antibonding direction, also around the second nearest neighbor (see Fig. 1).[19,5] Reference 5 also provided a wealth of new data about $EL2$ and related defects in irradiated GaAs. In particular, a new spectrum associated with As_{Ga} *without* the additional lines was found in "as-irradiated" GaAs. It was assigned to an isolated As_{Ga}. This spectrum could only be bleached very weakly under conditions that completely bleach $EL2$. Upon partial annealing, the As_{Ga} spectrum acquires additional lines, which were identified as due to a distant Ga interstitial. The As_{Ga}-Ga_I defect has bleaching and recovery properties very similar to $EL2$. Upon further annealing, the $EL2$ ODENDOR spectrum is recovered. Magnetic circular dichroism of the absorption (MCDA) of As_{Ga} and $EL2$ in Ref. 19 are also different. A simplified tight-binding calculation of MCDA for As_{Ga}-As_I has features that agree qualitatively with that of $EL2$.[5] On the other hand, recent high-resolution studies[20] of the splitting of the photoluminescence band associated with $EL2$ (the 0.61-eV band) under uniaxial stress provide strong evidence that the $EL2$ defect has tetrahedral symmetry. Even more recent theoretical work[12] has identified bound As_{Ga}-As_I complexes with alignment sufficiently close to the (111) axis to be within the experimental error bounds of the ODENDOR analysis.[21] These complexes thus serve as new candidates for $EL2$. In the present work, we examine theoretically the properties of the various As_{Ga}-X_I models and compare them to the experimental data for $EL2$. Our efficient calculational procedures allow for the use of very large supercells, thereby separating the periodically repeated defects sufficiently for the detailed examination of their wave functions.

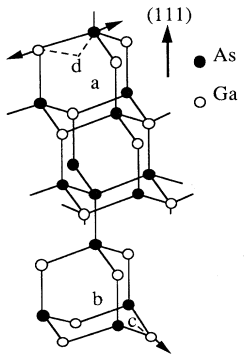

FIG. 1. The positions of the As interstitial in the second-nearest-neighbor shell of the As_{Ga} antisite: (a) along the $(-1,-1,-1)$ direction; (b) along (111); (c) after relaxation, starting from position (b); (d) as suggested by Chadi (Ref. 12).

The various interstitial sites are shown in Fig. 1. An As interstitial residing on site (a) was studied in Refs. 17 and 18. Both studies restricted the motion of As_I to the (111) axis. Although a shallow minimum near the hexagonal interstitial site was found, the binding energy between the As_{Ga} and As_I was close to zero. We have considered site (b) for As_I, which was suggested in Ref. 19. Starting from this initial configuration, we have relaxed the As_{Ga}-As_I system without imposing any symmetry constraints. The As_I spontaneously moved towards a Ga site, forming a split $\langle 010 \rangle$ As-Ga interstitial pair, marked (c) in Fig. 1. The relaxation energy is 2.8 eV, which incorporates the gains due to the motion of all atoms in the 64-atom supercell, including those around the As antisite. To investigate whether this distortion is associated with the antisite, we also studied the isolated As interstitial, starting from site (b). It also moved spontaneously to site (c), gaining 1.9 eV of relaxation energy. The computed binding energy between the neutral As_{Ga} and the relaxed As_I at site (c) in the 64-atom cell is 0.23 eV. In order to compare with EPR data, we also investigated the wave functions associated with the As_{Ga}-As_I pair. However, it turned out that even in the 64-atom cell, the wave functions associated with the antisite- and interstitial-induced levels overlapped too strongly with those of the adjacent cells, leading to level mixing. We thus repeated some of the calculations using a 216-atom cell. In this cell, the overlap between the wave functions is much smaller, allowing for the separation of As_{Ga}- and As_I-induced levels. Their respective wave functions are shown in Fig. 2. The As_{Ga} level is in the upper part of the gap and is occupied by one electron for the neutral pair. The As_I-derived level is around midgap and is doubly occupied. The neutral pair would thus be EPR active. The other EPR-active configuration would be $(As_{Ga}\text{-}As_I)^{++}$. In this configuration the interstitial level would be in the lower part of the gap and be half-filled, while the antisite level would be empty. The binding energy of the neutral pair in the 216-atom cell is 0.08 eV, as compared to 0.23 eV in the 64-atom cell. Part of this difference (about 0.1 eV) is due to different cutoffs used in the two calculations. A fairly accurate value of the binding energy of defect pairs can thus be obtained using 64-atom cells, despite level mixing. We note that the convergence of the total-energy differences with supercell size is much faster than that of the individual energy levels. This is expected on general grounds[22] and is due to the screening of the defect potential by the host crystal.

Since annealing of irradiated GaAs first leads to As_{Ga}-Ga_I pairs,[5] we also studied this pair with the Ga intersti-

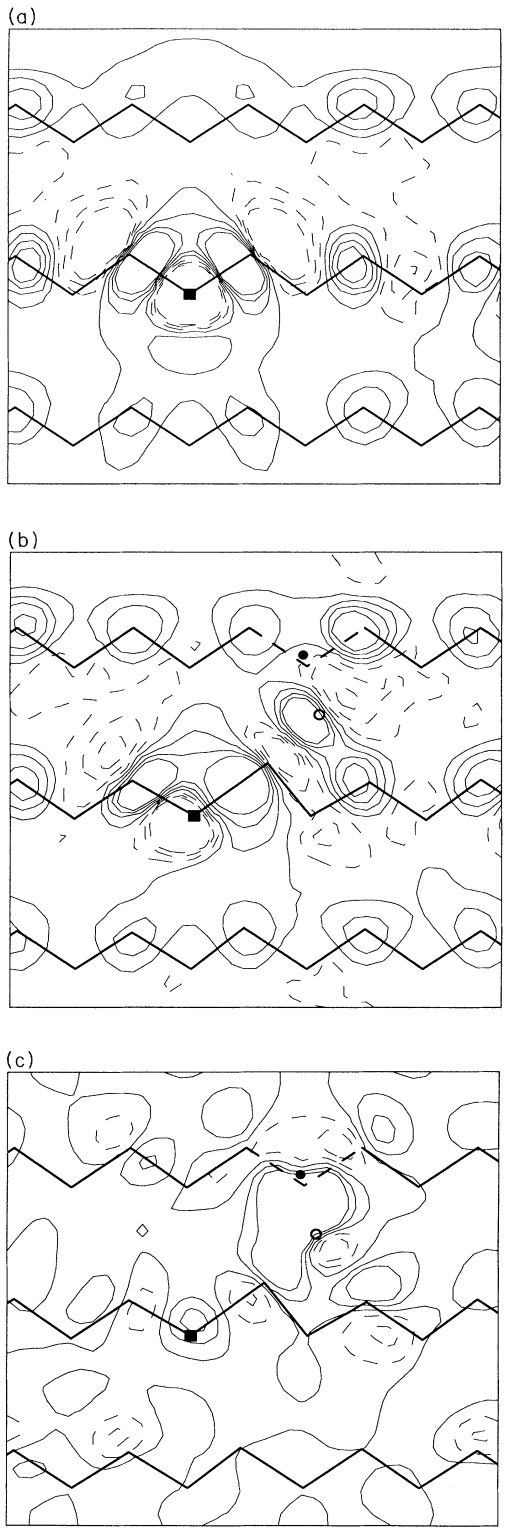

FIG. 2. The wave functions associated with the isolated As_{Ga} and with the As_{Ga}-As_I pair, when As_I occupies site (c) in Fig. 1. The filled square shows the position of As_{Ga}, while the open and filled circles show the projection of the As-Ga split interstitial pair onto the (110) plane. (a) The isolated As_{Ga} level; (b) the As_{Ga} level of the As_{Ga}-As_I pair; (c) the As_I level of the As_{Ga}-As_I pair.

tial occupying either site (a) or (b). Since Ga_I introduces a very shallow donor level in GaAs, we chose to study the $(As_{Ga}\text{-}Ga_I)^+$ system. In both cases the Ga_I stayed at the tetrahedral site after relaxations. Only the As_{Ga} level remained in the gap of our 64-atom supercell. It was occupied by two electrons. The binding energies for the pair with Ga^+ at sites (a) and (b) were 0.01 and -0.15 eV, respectively. It is thus clear that a distant As_{Ga}-Ga_{TI} pair (where T denotes a tetrahedral interstitial site) would not be stable even at room temperature. Although the position(s) of the Ga atom(s) in the experimentally observed As_{Ga}-Ga complex have not yet been determined, the present results are consistent with its low stability.

Very recently, a new position for the As interstitial in the As_{Ga}-As_I complex was suggested.[12] In this model, the As interstitial occupies a bridging twofold-coordinated As site, e.g., position (d) in Fig. 1. The alignment of the pair deviates somewhat from the (111) axis, but according to the very recent analysis of the ODENDOR data,[21] this deviation is within the experimental error. Since the bridging As_I is relatively far away from the antisite, several bridging configurations with similar binding energies are possible.[12] We studied the configuration (d) in the 64-atom supercell. The binding energy of the pair, compared to neutral relaxed As_{Ga} and As_I at the same sites, turned out to be only 0.13 eV. The positions of the energy levels of As_{Ga} and As_I at site (d) are within 0.1 eV in 64-atom cells, indicating that charge-transfer effects will not result in sizable gains in the binding energy of this pair.

The accuracy of the above results is limited by the use of the local-density approximation (LDA). The LDA is well known to give accurate geometries and elastic properties, but it overestimates cohesive energies and seriously underestimates band gaps. The overestimates of the cohesive energies are mostly due to underestimates of the atomic total energies. When two solid-state geometries are compared, the results are very accurate. For example, the computed value[23] of heat of formation of GaAs from bulk Ga and bulk As differs by only 0.04 eV from the experimental value. Therefore, the computed values of the binding energies of defect pairs should be accurate. However, the uncertainties associated with the positions of the energy levels are substantially greater. Even when energy-level positions are referred to the nearest band edge, errors of several tenths of an eV are possible. A quasiparticle calculation[24] would eliminate this problem, but it is too costly at present.

From the As_{Ga}-X_I candidates for $EL2$ examined here, none appears to agree with the majority of the experimental data. In particular, the binding energies of all the complexes are too small to be consistent with the experimental annealing data, which require that the ground state of $EL2$ be stable well above room temperature. In addition, the As_{Ga}-As_I complex, which has been advocated by several authors,[16,15,5,12] would be EPR active in its ground state. This would require a plausible explanation why the EPR signal is not more easily detected. One could also consider more intimate forms of As_{Ga}-As_I pairs, e.g., the nearest-neighbor pair investigated in Ref. 12. However, high-resolution measurements[20] of the

splittings of the photoluminescence band of $EL2$ are completely consistent with tetrahedral symmetry, thereby ruling out any closely coupled As_{Ga}-As_I pairs. The isolated As antisite thus remains the most likely candidate for $EL2$, and the majority of the experimental data can be explained using this model. However, one still needs to explain the results of ODENDOR and MCDA experiments[5] and in particular explain the differences between the "isolated As_{Ga}" and $EL2$ signals. One clue is provided by the fact that although bleaching of the As_{Ga} signal is three orders of magnitude slower than that of $EL2$, the recovery occurs at the same temperature as for $EL2$ or for the As_{Ga}-Ga_I complex (140 K).[21] This is strong evidence that the key properties of $EL2$ are determined by As_{Ga}. Due to the low binding energy of As_I to As_{Ga} and the relatively high formation energy of the As interstitials when compared to the antisites,[25,26,23] it is unlikely that the As_{Ga} and As_I would be present in GaAs in comparable concentrations.

A major puzzle is, of course, the very different bleaching properties of $EL2$ and the isolated antisite.[5] However, the isolated antisite has so far only been observed in irradiated GaAs *before* any annealing. It is thus likely that the observed decrease in bleaching efficiency is due to the presence of other defects and recombination centers in irradiated material, which strongly limit the number of photons (and electrons) available to stimulate the $EL2\text{-}F \rightarrow EL2\text{-}M$ transition. Indeed, a decrease in bleaching efficiency of the $EL2$ signal in highly defective material was previously noted by Weber and coworkers.[27] The most likely conclusion is that the majority of $EL2$ centers are isolated antisites and that the isolated antisites are responsible for the salient properties of $EL2$. A fraction of antisites will complex with interstitials and the presence of these complexes can be detected by highly sensitive techniques, such as ODENDOR or MCDA. The "spectator" role for the As interstitials was also advocated previously,[28] but the presence of new theoretical and experimental information has made their role much clearer.

In summary, we examined several antisite-interstitial complexes as models for the $EL2$ center by large-scale electronic-structure calculations. It was shown that the binding energy between the antisite and the interstitials is insufficient to account for the stability of the $EL2$ center. The level structure of the complex is also in disagreement with the majority of the experimental data. At present, the isolated As antisite is the best candidate for the majority of the $EL2$ centers. Spectator interstitials may be present in the vicinity of some of the antisites, but it appears that the salient properties of $EL2$ are due to the antisite, rather than to the antisite-interstitial complex.

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