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Pressure dependence of deep levels of the As antisite, the Ga-vacancy–As-interstitial pair, and of the stable and metastable states of $EL2$

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We report density-functional theory calculations of the tetrahedral, isolated arsenic antisite (As_{Ga}) in GaAs and of its metastable structure, the gallium-vacancy–arsenic-interstitial pair ($V_{Ga}As_i$). In order to determine the pressure dependence of the defect levels, the self-consistent Green-function method is applied. The calculated results are in agreement with experimental data on the stable and metastable states of $EL2$. This implies that the stable state of $EL2$ is indeed well described by the properties of the isolated As antisite. Furthermore, the results support the identification of the metastable state of $EL2$ with the $V_{Ga}As_i$ pair and identify the symmetry of the pressure-induced defect level.

The $EL2$ center in gallium arsenide is one of the mostly studied deep donors in III-V compounds. Of particular scientific appeal is its metastability, namely, that all its observable properties disappear under illumination with 1.2-eV light at low temperatures ($T < 130$ K) and normal pressure. Interestingly, all $EL2$ signals reappear when the temperature is increased.[1] The explanation of this metastability has been a significant challenge for experimentalists as well as for theoreticians.

In the following, we call the *calculated* systems according to their microscopic structure (e.g., the As antisite). On the other hand, the *experimentally* studied defect is called $EL2$, because the microscopic identification is still under debate. For the normal state of $EL2$ we write $EL2$-F (where F stands for "fundamental") and for the metastable state we write $EL2$-M (where M stands for "metastable").

From calculated total energies of the different centers, Dabrowski and Scheffler[2,3] and Chadi and Chang[4] had concluded that the electronic properties and the total-energy surface of the $As_{Ga} \rightleftharpoons V_{Ga}As_i$ metastability can explain most of the experimental results known for $EL2$. At that time, no experimental data were available about the $EL2$-M system. This situation has changed recently. The new experimental information is that the metastable state becomes observable under hydrostatic pressure.[5–7] At a first glance these experiments may be consistent with the electronic structure of the $V_{Ga}As_i$ pair, because there are two different acceptor levels at the bottom of the conduction band, and it is possible that at least one of them could enter the gap under pressure.[2,9] Obviously, a detailed comparison and an identification which state enters the gap are only possible if the pressure dependence of the $V_{Ga}As_i$ pair is calculated. Such calculations are, however, difficult since supercell calculations, the typical method for defect studies in recent years, give unreliable results due to artificial defect-defect interactions. For the study reported in this paper, we therefore applied the self-consistent Green-function method[8] to the isolated As antisite, the vacancy-interstitial pair, and the full reaction path between these two geometries. Thus, we deal with a single defect at several geometries in an otherwise perfect crystal. Some preliminary results of this have been published in Ref. 10.

Concerning the defect levels along the reaction path, the Green-function results specify (and to some extent correct) some earlier supercell findings.[2,3,9] In order to extract the pressure dependence of the defect levels for the stable and metastable geometries, the calculations were done for different lattice parameters of the host crystal. The comparison of the calculated pressure dependences of the defect levels of the As_{Ga} and of the $V_{Ga}As_i$ pair with the experimental $EL2$-F and $EL2$-M data gives additional support for the defect identification. Furthermore, our calculations identify the symmetry of the recently experimentally observed defect level of $EL2$-M as a_1 of the C_{3v} point group.

The paper is organized as follows. At first we summarize the technicalities of the method. We then present our results on the defects levels and their pressure dependences and we compare the calculated results with the experimental properties of $EL2$-F and $EL2$-M.

The calculations are performed using density-functional theory (DFT) together with the local-density approximation (LDA) for the exchange-correlation potential.[11] We applied norm-conserving pseudopotentials[12] and the self-consistent Green-function method of Scheffler *et al.*[8] The perfect-crystal Green function is evaluated in a plane-wave basis (with 307 plane waves for all lattice parameters, corresponding to an average energy cutoff of 15.5 Ry). For solving the self-consistent Dyson equation, the localized, defect-induced *changes* of the effective potential and of the electron density are represented in a basis set defined by Gaussians with s, p, and d angular character centered at various lattice sites. The calculations reported below are obtained

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using Gaussians with two decays (0.3 and 0.6 bohr^{-2}). Test calculations with three decays (0.2, 0.5, 0.8 bohr^{-2}) gave the same results for the calculated pressure dependences. For all trigonal geometries, 162 Gaussians are used which are centered at the gallium-vacancy site, its four nearest neighbors, at the arsenic interstitial, and its three gallium neighbors. Accordingly, 144 Gaussians were used for the tetrahedal As antisite. The expanse of the numerical problem forces us to "freeze" the atoms of the host crystal at the perfect crystal geometries. We assume that this approximation is not very important, i.e., that the pressure dependence of the defect-induced lattice-relaxation energy is small.

Typically, *ab initio* defect calculations suffer from several difficulties. Assuming that the numerical accuracy is tested carefully (i.e., the completeness of the basis set and related aspects), the use of supercells gives rise to a significant defect-defect interaction. Usually, 18-,[4] 32-,[13] or 54-atom[2] cells are used but it is well known that the (in principle, discrete) defect level is then a $\sim$ 1-eV broad band. This is the first reason why we use the Green-function approach for our study. An additional problem is related to the DFT-LDA. Although it is well known that such calculations give accurate results for geometries, elastic properties, and pressure dependences of the perfect crystal (see, e.g., Ref. 14), the Kohn-Sham single-particle band gap is much smaller than the experimental semiconductor band gap. As a consequence, defect levels which lie in or close to the conduction band are difficult to investigate theoretically. A proper way to deal with this problem is the self-energy approach which for defect calculations is only feasible using a Green-function method and approximating the self-energy by the "scissor operator."[15] For the calculation of the pressure dependence, we therefore evaluated our host-crystal Green function from the DFT-LDA wave functions and the scissor-operator self-energy such that the zero-pressure single-particle band gap agrees with the experimental gap. Then, for the lattice constant $a = 5.57$ Å (which is the mean value of the experimental and theoretical lattice constant), the topology of the conduction band is approximately correct [the calculated band gaps at Γ, L, and X are 1.63, 1.78, and 1.92 eV, and the corresponding experimental values are 1.63, 1.85, and 2.18 eV (Ref. 16)].

The defect levels for the stable and metastable geometries are calculated self-consistently for several host-crystal lattice constants. From these calculations we obtain directly the pressure dependence of the deep levels, multiplied with the bulk modulus B_0,

$$[d\epsilon(i/j)/dp]B_0 = -d\epsilon(i/j)/d\ln V \quad . \tag{1}$$

Here $\epsilon(i/j)$ stands for a calculated donor ($i = 2, j = 1$) or acceptor ($i = 0, j = 1$) level and V and p are the crystal volume and applied pressure. The numbers i, j denote the occupation of the single-particle eigenvalue which is changed from i to j. We will be careful to distinguish the *single-particle eigenvalues* ϵ, which follow from a ground-state calculation, from the *transition state levels* $\epsilon(i/j)$, which are good estimates of measurable ionization energies. The difference between these two quantities for deep

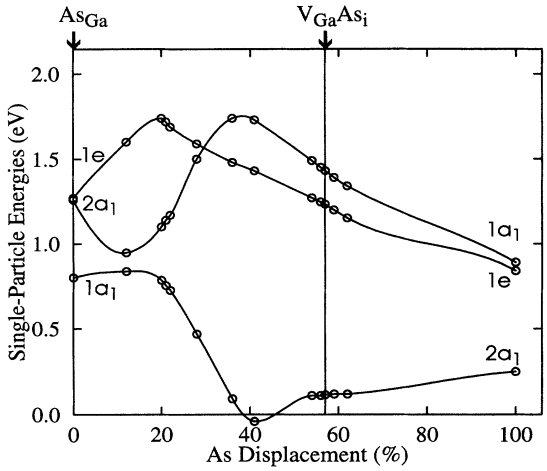

FIG. 1. Single-particle DFT-LDA energies of the neutral defect with the As atom displaced along the [111] direction.

levels is typically about 0.15 eV. We found, however, that the *pressure dependence* of the difference is negligible for the systems considered here.

Figure 1 shows the calculated single-particle energies of the neutral defect with the As defect atom displaced along the [111] direction. There the results of the LDA-DFT calculations with the lattice parameter 5.57 Å are given. We note that the shape of Fig. 1 does not depend on the lattice parameter. Zero displacement refers to the As_{Ga} defect and the displacement of 57% of the As-Ga bond length corresponds to the metastable configuration, $V_{Ga}As_i$.[2]

For the stable geometry, we obtain an a_1 level at mid gap and a t_2 resonance in the conduction band. As in previous supercell studies,[2] their wave-function character and energies describe the properties of *EL2-F* very well. When the As atom is displaced along [111], the symmetry of the center is reduced from T_d to C_{3v}. Therefore, the t_2 level splits in two components labeled $2a_1$ and $1e$ in Fig. 1. If the scissor operator is applied, the deep levels are shifted to higher energies: for the metastable geometry, the $2a_1$ level is shifted by 5%, the $1a_1$ level by 85%, and the $1e$ level by 70% of the scissor-operator self-energy.

There is a general agreement between these results and the supercell calculations (compare with Fig. 4 of Ref. 2) but there are also two noticeable differences. The crossing of the $2a_1$ and $1e$ state now takes place already at 30% displacement, not at 57% which was the result indicated by the supercell calculations.[2] This difference reflects the artificial defect-defect interaction of supercell calculations which is still significant even if a cell size of 54 atoms is used.[2] As a further aspect which is obscured in supercell calculations, we note that the $1a_1 \rightarrow 2a_1$ energy level passes through the valence band. Thus the $V_{Ga}As_i$ eigenvalue labeled $2a_1$ is a split-off valence-band state. Note that this state can be ionized and that the corresponding donor level should lie about 0.15 eV below the single-particle eigenvalue of Fig. 1, i.e., at the top of the valence band. The wave functions at the stable and metastable geometries are practically identical with those of the supercell results (see Figs. 3 and 8 of Ref. 2).

We now turn to the pressure dependence of the electronic transitions related to the eigenvalues shown in Fig. 1. For the tetrahedral As antisite, i.e., for zero displacement of the As defect atom, we analyzed the first donor level, $\epsilon_{1a_1}(2/1)$. For the metastable center, $V_{Ga}As_i$, i.e., for the 57% displacement in Fig. 1, there is one donor level, $\epsilon_{2a_1}(2/1)$, and there are two different possibilities for an acceptor: $\epsilon_{1e}(0/1)$ and $\epsilon_{1a_1}(0/1)$. Strictly taken, Fig. 1 suggests for the $V_{Ga}As_i$ pair that the acceptor wave function is of e symmetry. We remember, however, that DFT-LDA calculations suffer from the band-gap problem and therefore the ordering of two states which are close in energy and which are both in the conduction band is not reliable. Therefore, we consider both levels as possible candidates for the first acceptor level.

The calculated pressure derivatives are given in Table I and compared with the experimental results of the measured donor level of *EL2-F* and the measured acceptor level of *EL2-M*. It can be seen that the results for the As_{Ga} and those for *EL2-F* are in excellent agreement. This strongly supports the identification of *EL2-F* with the isolated As antisite. Concerning the calculated acceptor levels of the $V_{Ga}As_i$ pair and the measured result for *EL2-M*, there is good agreement only for the $1a_1$ level not for the $1e$ level (see Table I). Experimentally, the symmetry of the *EL2-M* acceptor level has not been identified so far. Thus, if the wave-function symmetry would be confirmed as a_1 of the C_{3v} point group, the agreement between the calculated and measured pressure dependences would be a most important support of the identification of the $V_{Ga}As_i$ pair model with the metastable geometry of *EL2*.

Concerning the $2a_1$ donor level of the $V_{Ga}As_i$ pair, it has been suggested earlier[6] that it plays an important role in the pressure induced photorecovery of *EL2*. Dreszer, Baj, and Korzeniewski[6] concluded from a strong and narrow peak in the optical cross section for *EL2* photorecovery, that under pressure, the *EL2-M* acceptor level captures an electron and binds a photocreated hole. Nonradiative recombination of this bound exciton then provides the energy to overcome the barrier between the metastable and stable configuration of *EL2*: The hole is assumed to ionize the *EL2-M* donor level (corresponding to the $2a_1$ level of $V_{Ga}As_i$) at the valence-band top. Then for this excited but neutral *EL2-M* center, the barrier is assumed to vanish leading to the recovery of *EL2-F*. Thus the scenario is

$$(V_{Ga}As_i)^-[1a_1^1 2a_1^2] + \hbar\omega \longrightarrow (V_{Ga}As_i)^-[1a_1^1 2a_1^2] + (h^+ + e^-) \longrightarrow (V_{Ga}As_i)^*[1a_1^1 2a_1^1] + e^- \longrightarrow (As_{Ga})^0[1a_1^2 2a_1^0] + e^-.$$

This idea[6] is indeed consistent with our calculated electronic structure. The only unclear point is whether the acceptor level is of a_1 or e symmetry. The calculated pressure dependences support the suggestion by Dreszer, Baj, and Korzeniewski that their results are due to the $1a_1$ level.

Recently, Steiner *et al.*[7] reported additional support of the above-noted process. They detected a luminescence line which was connected with the presence of negatively charged *EL2-M* and concluded that it corresponds to the optical recombination of the bound exciton. The pressure dependence of the luminescence energy was roughly the same as that of the band gap. It is not yet clear if the luminescence is due to a recombination of the electron with a shallow hole or with the localized hole in the $2a_1$ level. For both possibilities, the calculated pressure dependences are very similar, namely, that of the band gap.

In summary, the above-discussed results on the pressure dependences of the levels of the isolated As_{Ga} and the agreement with the results for the stable state of *EL2* make the existence of a nearby chemically bound interstitial (as proposed by von Bardeleben *et al.*,[21] Meyer *et al.*,[22] and Spaeth, Krambrock, and Hoffman[23]) most doubtful. The theoretical results for the pressure dependences of the acceptor and donor levels of the $V_{Ga}As_i$ pair and the comparison with experimental results for the metastable state of *EL2* give additional support, that the key properties of *EL2* are determined by the metastability of $As_{Ga} \rightleftharpoons V_{Ga}As_i$.

One important question, however, remains to be answered. The work reported here suggests that the symmetry of the $V_{Ga}As_i$ acceptor wave function is a_1 of the C_{3v} point group. We hope that future experiments will be able to determine the wave-function character of the acceptor level of *EL2-M*. The experimental result will then either prove or disprove the suggested identification of *EL2-M*. Furthermore, we hope that our study stimulates further experimental search for the metastable donor state $2a_1$ at the valence-band top.

TABLE I. Calculated pressure derivatives ($B_0 d\epsilon/dp = -d\epsilon/d\ln V$) of different levels of As_{Ga} and $V_{Ga}As_i$ (see text and Fig. 1) and of the experimental donor level of *EL2-F* and the acceptor level of *EL2-M*. All energies are taken with respect to the top of the valence band.

defect	As_{Ga}	$V_{Ga}As_i$		
wave function	$1a_1$	$2a_1$	$1e$	$1a_1$
$B_0 d\epsilon/dp$ (eV)	1.52	−0.1	0.6	2.3
defect	*EL2-F*	*EL2-M*		
$B_0 d\epsilon/dp$ (eV)	1.20,[a] 1.65,[b] 1.88[c]		3.0[d]	

[a]See Refs. 17 and 20.
[b]See Refs. 18 and 20.
[c]See Refs. 19 and 20.
[d]See Ref. 5.

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