Do Arsenic Interstitials Really Exist in As-Rich GaAs?

T. E. M. Staab and R. M. Nieminen
Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02015 HUT, Finland

J. Gebauer and R. Krause-Rehberg
Fachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, D-06099 Halle, Germany

M. Luysberg
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

M. Haugk and Th. Frauenheim
University GH Paderborn, Department of Physics, Theoretical Physics, D-33098 Paderborn, Germany
(Received 1 February 2001; published 9 July 2001)

To investigate the lattice distortion caused by point defects in As-rich GaAs, we make use of a self-consistent-charge density-functional based tight-binding method. Both relevant defects, the As antisite and the As interstitial, cause significant lattice distortion. In contrast to As interstitials, isolated As antisites lead to lattice strain as well as displacement of nearest neighbor As lattice atoms into the ⟨110⟩ channels, in excellent agreement with experiments. Therefore, our result gives powerful evidence for As antisites being the dominating defect in as-grown As-rich GaAs.

DOI: 10.1103/PhysRevLett.87.045504 PACS numbers: 61.72.Bb, 61.72.Ji, 71.15.Mb

Point defects determine many of the physical properties of semiconductors. Besides their well-known influence on the electronic structure, point defects may also induce significant lattice distortions thereby influencing the structural properties of a given material when existing in large densities. If a reliable model is available, nondestructive measurements of the lattice parameter by x-ray diffraction would allow for the determination of point defect concentrations.

A prominent example of lattice distortion caused by point defects is GaAs layers grown at low temperatures of ~200 °C under high As overpressure, the so-called LT-GaAs layers [1]. Such layers contain a large arsenic excess, incorporated in the form of point defects such as As_{Ga} antisites, Ga vacancies, or As interstitials [1]. LT-GaAs layers are tetragonally distorted (strained), which is attributed to the high densities of point defects (up to 10×10^{20} cm^{-3} As_{Ga} as shown by, e.g., infrared absorption [1,2] or scanning tunneling microscopy [3]). Liu *et al.* [2] found a linear correlation between the lattice expansion and the density of neutral As_{Ga}. Hence, it was concluded that As_{Ga} antisites are the dominating defects which account for all the lattice expansion. In contrast, other authors believed that As interstitials (As_i) are present in concentrations similar to or even larger than that of As_{Ga} [4]. Experimental evidence for As_i in LT-GaAs came from ion channeling experiments [5]. However, Liu *et al.* [2] later pointed out that the atomic displacements observed by ion channeling could also be due to displaced lattice atoms next to an As_{Ga} antisite, i.e., due to an increase of the As-As bond length.

There have been attempts in the past to calculate the lattice distortion caused by point defects in GaAs [6]. While in agreement for As_i interstitials, the results on As_{Ga} antisites obtained by simple elastic theory employing the chemical covalent radii of As and Ga [6] are in contradiction to *ab initio* results [7–9]. The former predict a lattice contraction, while the latter show that the As-As bond is slightly longer than the Ga-As bond — already noted earlier [10]. Therefore, As_{Ga} antisites should cause lattice expansion. However, in order to calculate the lattice distortion due to point defects in concentrations directly comparable to experiments, one needs rather large supercells of hundreds of atoms to avoid artificial defect-defect interactions. For such large-scale simulations *ab initio* methods are not very practical, and faster yet reliable simulation techniques are necessary.

In the present work, we calculate the lattice distortion due to As_{Ga} antisites and ⟨110⟩-split As_i interstitials by using a self-consistent-charge density-functional based tight-binding (SCC-DFTB) method. This method is capable of treating large supercells with 512 atoms efficiently, hence allowing, concerning defect concentrations, for a comparison with experiments on the same scale. Here, the periodic boundary conditions are not an artifact, but a needed precondition, since one As_{Ga} per 512 atoms corresponds to a concentration of $\sim 8 \times 10^{19}$ cm^{-3} — typical for undoped LT-GaAs grown at $T \sim 200$ °C [1,2]. It will be shown that both, As_{Ga} and ⟨110⟩-split As_i, cause significant lattice expansions. Comparing the theoretical results for both defects, we observe that they are in quantitative agreement with available experimental data provided that the measured lattice expansion is due to As_{Ga} antisites only, but not due to As_i.

The SCC-DFTB method has been used for total energy calculations and structure relaxation. The method employs a basis of numerically derived *s* and *p* confined atomic

orbitals which are obtained within the self-consistent field (SCF) local-density approximation (SCF-LDA). All two-center integrals of the density-functional theory Hamiltonian and overlap matrix are evaluated explicitly. Charge transfer is taken into account through the incorporation of self-consistency for the distribution of the Mulliken charges. This is based on a second order expansion of the Kohn-Sham energy. For a detailed description of the SCC-DFTB method and its application to GaAs see Refs. [11,12].

Recent results, including calculations for As_{Ga} antisites and extended defects, have demonstrated the validity of the SCC-DFTB method for modeling defects in GaAs [13]. These calculations are in good agreement with full *ab initio* SCF-LDA results [14], indicating that the accuracy of the SCC-DFTB method is comparable to that of the *ab initio* calculations. In contrast to these more sophisticated methods, the computing time and memory usage of SCC-DFTB is up to 2 orders of magnitude smaller. All calculations were done within the Γ-point approximation. The numerical error in total energy is less than 0.0005 eV, indicating well-converged results.

Although defects in GaAs can be charged we do not consider such cases and restrict the calculations to neutral As antisites (corresponding to charge-neutral supercells). This is justified by the fact that the concentration of the neutral As^0_{Ga} is more than 10 times larger than that of the positive As^+_{Ga} [2]. On the other hand, electrical measurements do not indicate high densities of other electrically active defects. Thus, As interstitials must also be neutral when existing. Hence, the lattice expansion must be dominated by *neutral* As_{Ga} or As_i. The overall lattice contraction due to Ga vacancies can be neglected, since their concentration is nearly 2 orders of magnitude smaller than that of neutral As_{Ga} [15].

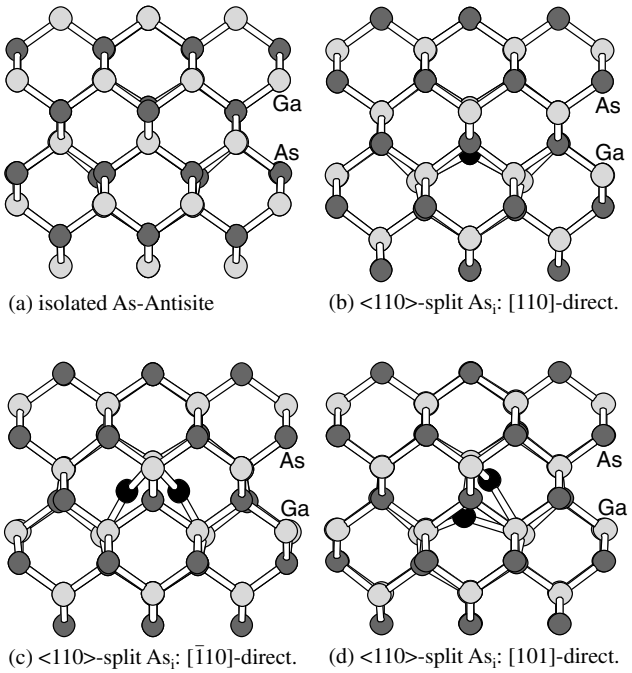
First, the lattice constant for an ideal GaAs crystal was calculated by carefully minimizing the total energy of a large 512 atom supercell without defects with respect to the lattice parameter. For the lattice constant in GaAs we found $a_0 = 565.454$ pm, in good agreement with the experimental result $a_0^{exp} = 565.36$ pm. The calculated value will be used as a reference for the further calculations of defect-induced lattice distortions. The long-range relaxations around a defect should be well described, since the bulk modulus deviates not more than 3% from the experimental value, while the deviations for the other elastic constants are within 14%, which is a good agreement for second order derivatives of the total energy (Table I).

TABLE I. Bulk modulus B_0, second order elastic constants (c_{11}, c_{12}, c_{44}), and Poisson ratio ν for GaAs bulk (experimental data are taken from Landolt-Börnstein III/17a p. 235).

Method	B_0 (GPa)	c_{11} (GPa)	c_{12} (GPa)	c_{44} (GPa)	ν
Expt.	76.9	121.1	54.8	60.4	0.312
DFTB	74.7	130.9	46.6	66.7	0.263

Next, SCC-DFTB calculations were done for a single isolated As_{Ga} antisite or the $\langle 110\rangle$-split As_i in a GaAs matrix. The formation energies obtained are (*ab initio* results in brackets [14]): $E_F(As_{Ga}) = 3.5$ eV (2.5 eV), $E_F(As_i) = 6.4$ eV—$\langle 110\rangle$ split (6.1 eV—tetrahedral). Hence, the formation of As antisites should be favored to accommodate the excess As. The atoms in the supercell were allowed to relax without any symmetry restrictions with the average lattice constant fixed to the value $a_0 = 565.453\,88$ pm obtained above. The resulting minimum energy configuration for As_{Ga} is shown in Fig. 1(a). The As_{Ga}-As_{As} bond length increases to 275.9 pm, compared to the As-Ga bond length in the bulk (244.9 pm), and, thus, the four nearest neighbor As atoms relax outward by 12.7%. Even the next nearest neighbor Ga_{Ga} atoms are affected: their distance to the As antisite increases from 399.8 to 407.3 pm, i.e., by 1.9%.

As shown in Figs. 1(b)–1(d), much larger induced displacements are found for the $\langle 110\rangle$ split As_i, known to possess the lowest formation energy according to previous calculations [8,9]. For As_{Ga} our results are in agreement with earlier first principles calculations which also yielded a preserved T_d symmetry and an increased As_{Ga}-As_{As} bond length [7–9] compared to the As-Ga bond. However, the increase of the bond length was somewhat smaller (4% in [7], 8% in [8], and 9% in [9]) than our value of 12.7%. This discrepancy may be related to the typical LDA



(a) isolated As-Antisite (b) <110>-split As_i: [110]-direct.

(c) <110>-split As_i: [$\bar{1}$10]-direct. (d) <110>-split As_i: [101]-direct.

FIG. 1. GaAs lattice containing different defects. Ga atoms are light gray, As atoms are dark gray—both on lattice sites. As antisites or interstitial are black. (a) One As_{Ga} seen in the $\langle 110\rangle$ direction. The antisite is situated directly behind the Ga atom in the center. The As atoms next to the As_{Ga} are displaced into the $\langle 110\rangle$ channel as indicated in the figure. (b)–(d) $\langle 110\rangle$-split As_i (two atoms share an As lattice site) seen from different directions: (b) [110], (c) [$\bar{1}$10], and (d) [101]. The atomic displacements seen in the [101] direction are equivalent to those seen in [$\bar{1}$01], [011], or [0$\bar{1}$1].

overbinding in *ab initio* results (calculated lattice constants are about 1% too small). In general, however, the first principles calculations indicate that high densities of As_{Ga} antisites will result in a measurable net lattice expansion, in contrast to Ref. [6].

Before proceeding with the calculation of lattice strain, it is very interesting to compare our calculations with the ion channeling data of Yu *et al.* [5]. In this work, the data were interpreted by As atoms in LT-GaAs displaced by about 30 pm into the ⟨110⟩ channels. This was explained by excess As interstitials close to As lattice sites [5]. Our calculations yield displacements of 29.3 and 18.3 pm for the As lattice atoms neighboring the As_{Ga} antisite (50% each, depending on the position around the antisite, or, respectively, the projection), while the displacements in the case of ⟨110⟩-split As_i are much larger and affect also Ga atoms [see Figs. 1(b)–1(d)]. When taking the average over the different ⟨110⟩ projections, the As atoms belonging to the As split interstitial are displaced by about 86 pm into the ⟨110⟩ channel (between 39 and 118 pm), while another six As_{As} atoms on second next neighbor positions are displaced between 10 and 17 pm (average: 11 pm). Also the nearest neighbor Ga atoms are displaced between 12 and 42 pm (average: 23 pm).

Considering the experimental uncertainties in Ref. [5], the results for As_{Ga} are in excellent agreement with the displacement estimated from ion channeling, whereas the lattice displacement calculated for the split ⟨110⟩ As_i is significant larger. Because neutral As_{Ga} antisites exist in very large concentrations in LT-GaAs [1,2], we have to conclude that the displaced As lattice atoms account for all ion channeling results. The calculation thus directly confirms the suggestion of Liu *et al.* [2] that the ion channeling results should be explained by the displaced lattice atoms around As antisites rather than by excess As interstitials.

According to the above results, the incorporation of As_{Ga} antisites during growth will result in lattice strain, leading to an increase in the total energy of the lattice. The crystal will thus seek to reduce its energy by lattice expansion. However, during the growth of LT-GaAs, the lattice parameters perpendicular to the growth direction are fixed to that of the substrate (pseudomorphic growth). Hence, the only way for the crystal to lower its energy is by relaxing the internal strain caused by point defects in the ⟨001⟩ growth direction. This has to be considered for a comparison of the calculated lattice expansion with experimental results in LT-GaAs. In the following calculations, the lattice constant will thus be varied only in the [001] direction while it stays fixed perpendicular to that.

Additionally, the value $a_0 = 565.453\,88$ pm for the bulk lattice constant was confirmed as the minimum energy value by varying the lattice parameter only in the [001] direction. The lattice distortion (expansion or compression) is defined as the relative change $(\Delta d/d_0)$ of the lattice parameter in the [001] direction. The total energy of the 512 atom supercell was plotted as a function of the lattice expansion to obtain the value d_0.

In the next step, we calculate the lattice distortion caused by As_{Ga} antisites. For that purpose, up to five As_{Ga} were put into the supercell so that they are evenly distributed when imposing periodic boundary conditions. The atoms in the supercell were then allowed to relax without any symmetry restrictions and the total energy was calculated. This calculation was performed for several different values of the lattice constant in the [001] direction, i.e., for different values of the tetragonal lattice expansion. The minimum of the total energy was obtained as described above. For one As_{Ga} in the 512 atom supercell the minimum energy corresponds to a positive lattice distortion (expansion) of 0.122%.

In Fig. 2, we show the calculated lattice expansion (solid circles) as a function of the amount of excess As. Here, we assumed that all excess As is incorporated to the lattice as As antisites. The top axis shows the corresponding number of As_{Ga} in the supercell. The lattice expansion exhibits a linear dependence on the excess As concentration. The energy gain per As_{Ga} compared to the unstrained supercell (open squares) is plotted in Fig. 2. Again, a linear dependence is found. The strain caused by the As_{Ga} thus adds linearly. Since this linear relationship contains also the zero value, the theory describes a universal relationship between concentration of As_{Ga} and lattice expansion in the concentration range considered. Hence, the linearity can be extrapolated to lower concentrations experimentally accessible.

Finally, we compare the calculated lattice expansion directly with available experimental results for the lattice strain in LT-GaAs [2,15,16], where the density of As_{Ga} is in the range covered by the calculations (see above). In

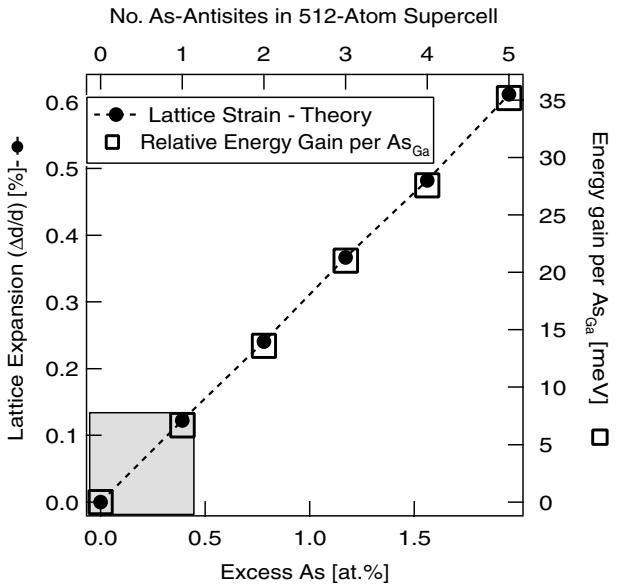


FIG. 2. Calculated lattice expansion in the [001] direction as a function of excess As (closed circles). The excess As is defined as density of As_{Ga} only. The open squares give the energy gained per As_{Ga} compared to a supercell with the lattice constrained in all directions to the ideal value. The hatched area indicates the experimentally accessible region.

Fig. 3 the excess As is set equivalent to the As_{Ga} concentration, usually determined by infrared absorption. The experimental data [2,15,16] are in excellent quantitative agreement with the calculations shown by the dashed line. Thus, the lattice expansion in LT-GaAs can be entirely explained by As_{Ga} antisites.

On the other hand, our calculations for the isolated As_i yield a significant lattice expansion as well. Therefore, concentrations of As_i comparable to that of the As_{Ga} would also lead to a measurable lattice expansion in agreement with common assumptions [2,6,9]. Our calculations give a lattice expansion of 0.217% for one $\langle 110 \rangle$-split As_i in the 512 atom supercell, twice as much as for the single As_{Ga}. Thus, if the concentration of the As_i would be comparable to that of the As_{Ga}, a deviation between theory and experiment in the order of a factor of 3 is expected. However, in Fig. 3 the deviation between experiment and theory is not larger than 10%–20%, reflecting the absolute errors of experiments and calculations. This observation is supported by experimental evidence that the number of As_{Ga} present in as-grown LT-GaAs equals the concentration of excess As present in As precipitates after thermal treatment [15]. Thus, arsenic interstitials are indeed not present in significant concentrations in LT-GaAs. Both experiment and our calculations allow for the conclusion that the lattice expansion is determined exclusively by the As_{Ga} antisites.

Hence, our results question some earlier interpretation of x-ray diffraction data in LT-GaAs which seemed to favor large concentrations of As interstitials [4,17]. Often, these interpretations are based on simple empirical models [6]. Our calculations indicate that such models might lead to significant errors by estimating the influence of a particular point defect on the lattice expansion. X-ray diffraction

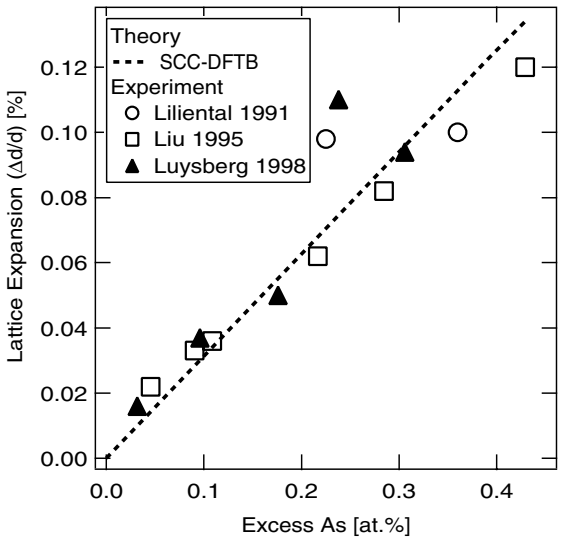


FIG. 3. Lattice expansion in the [001] direction vs the excess As concentration (density of As_{Ga} only) in LT-GaAs taken from different experimental works (see text). The dashed line is the lattice expansion calculated with the SCC-DFTB method and not a fit to the data.

experiments have been used to estimate As_i concentrations also in As-rich as-grown *bulk* GaAs on the order of some 10^{19} cm^{-3} [17], thus indicating a deviation from exact stoichiometry in the same range [18]. It is not clear whether the lattice expansion observed in bulk GaAs can be entirely explained by the As_{Ga} defects known to be present. However, it appears highly probable that the As_i concentration and thus the phase range in bulk GaAs is smaller than previously believed [18].

In summary, we applied a density-functional based tight-binding method to calculate the lattice strain due to point defects in As-rich LT-GaAs. It was shown that the incorporation of As_{Ga} *antisites* leads to an expansive lattice distortion (strain). The increased As-As bond lengths result in a displacement of the As *lattice atoms* neighboring the antisite into the $\langle 110 \rangle$ channel. This explains the results of earlier ion channeling experiments in As-rich LT-GaAs [5]. In comparison, calculations for the $\langle 110 \rangle$-split As *interstitials* yielded a significantly larger displacement of As as well as Ga atoms into the $\langle 110 \rangle$ channel and roughly twice the lattice strain. Excellent agreement of the calculated lattice expansion with experimental data is achieved, considering only the effect of isolated As antisites in LT-GaAs layers. Therefore, other defects causing lattice expansion, especially As interstitials, cannot exist in comparable concentrations. Hence, it appears also questionable whether high concentrations of As interstitials are present in as-grown bulk GaAs.

T. E. M. S. acknowledges support from a Marie-Curie Grant.

[1] M. Kaminska *et al.,* Appl. Phys. Lett. **54**, 1881 (1989).
[2] X. Liu *et al.,* Appl. Phys. Lett. **67**, 279 (1995).
[3] R. Feenstra, J. M. Woodall, and G. Pettit, Phys. Rev. Lett. **71**, 1176 (1993).
[4] R. E. Pritchard *et al.,* J. Appl. Phys. **78**, 2411 (1995).
[5] K. Yu, M. Kaminska, and Z. Liliental-Weber, J. Appl. Phys. **72**, 2850 (1992).
[6] N. Chen, Y. Wang, H. He, and L. Lin, Phys. Rev. B **54**, 8516 (1996).
[7] J. Dabrowski and M. Scheffler, Phys. Rev. B **40**, 10 391 (1989).
[8] D. Chadi and K. Chang, Phys. Rev. Lett. **60**, 2187 (1988).
[9] J. Landman *et al.,* Phys. Rev. B **55**, 15 581 (1997).
[10] J. A. D. Cueto and N. J. Shevchik, J. Phys. C **11**, 829 (1978).
[11] M. Haugk, J. Elsner, and T. Frauenheim, J. Phys. Condens. Matter **9**, 7305 (1997).
[12] M. Haugk *et al.,* Comput. Mater. Sci. **13**, 239 (1999).
[13] T. Staab, M. Haugk, T. Frauenheim, and H. Leipner, Phys. Rev. Lett. **83**, 5519 (1999).
[14] J. Northrup and S. Zhang, Phys. Rev. B **47**, 6791 (1993).
[15] M. Luysberg *et al.,* J. Appl. Phys. **83**, 561 (1998).
[16] Z. Liliental-Weber *et al.,* Appl. Phys. Lett. **58**, 2153 (1991).
[17] N. Chen, Y. Wang, H. He, and L. Lin, Jpn. J. Appl. Phys. **35**, L1238 (1996).
[18] D. Hurle, J. Appl. Phys. **85**, 6957 (1999).