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Tight-binding molecular-dynamics study of density-optimized amorphous GaAs

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We present the results of a tight-binding molecular-dynamics study of the structural and electronic properties of amorphous GaAs (*a*-GaAs), emphasizing the relationship between density and topological and chemical disorder. We find the amorphous state to have lower density than the crystal, in agreement with experiment. The coordination number (3.94) is very close to that of the crystal; nevertheless, a significant number of atoms possess defective coordination — either threefold or fivefold. We find, as a consequence, a proportion of wrong bonds of about 12%, consistent with experiment; yet, the system remains a semiconductor, with a band gap of 1.12 eV. We have also studied the effect of chemical disorder through random exchanges of atoms in the amorphous samples; both the density and the band gap decrease upon increasing chemical disorder, suggesting that the lower density of *a*-GaAs is partly a consequence of chemical disorder.

I. INTRODUCTION

Despite the fact that amorphous GaAs (*a*-GaAs) has been the object of a number of experimental and theoretical studies over the past approximately 20 years,[1–13] details of the structure of the material at short range remain, to a large extent, unresolved. In particular, it is of fundamental interest to understand how the short-range structure is affected by chemical disorder: since we are dealing with a compound semiconductor, which is tetrahedral in its crystalline state, the presence of odd-membered rings, almost certainly present in the amorphous phase, imply that there must be some ''wrong bonds,'' i.e., bonds between like atoms. [Crystalline GaAs (*c*-GaAs) has the zinc-blende structure in its ground state.] In fact, x-ray and electron diffraction,[2,3] extended x-ray-absorption fine structure (EXAFS),[4–6] and core-level and valence x-ray photoelectron spectroscopy[7,8] indicate that the fraction of wrong bonds in *a*-GaAs is somewhere in the range 0 (''negligible'') to 12%.

Another issue of fundamental importance (especially for the interpretation of diffraction data) is proper knowledge of the density, found experimentally to lie in the range 4.98–5.11 g/cm^3,[4,14,15] i.e., a few percent less than that of *c*-GaAs, 5.32 g/cm^3.[16] This quantity has not, to our knowledge, been calculated on the basis of realistic structural models. In the case of *a*-Si, the actual density has been the subject of numerous discussions and reported values found to depend strongly on the mode of preparation; only recently has the density of ''device-quality'' *a*-Si, prepared by ion implantation, been determined.[17]

In this paper, we present a detailed investigation of the structure of *a*-GaAs, including short-range chemical disorder effects, and its relation to density, which we obtain by minimization of the total energy of the system. Our study is based on a tight-binding (TB) description of the energetics of the system and optimal structures are obtained by a simulated-annealing minimization using molecular-dynamics (MD) simulations. We find, in accord with experiment, the density of the amorphous phase to be smaller than that of the crystal — 5.15 vs 5.34 g/cm^3. While the system in its ground state is clearly amorphous, the average coordination number is almost exactly 4, as it is in the crystalline state. Chemical disorder is undoubtedly present, however: we find a number of atoms to be under- or overcoordinated and 12% of the bonds to be of the wrong type. We also find that increasing the amount of chemical disorder causes the density, as well as the band gap, to decrease.

Our paper is organized as follows. First, in Sec. II, we present the model used in our calculations, together with computational details. In Sec. III we give a detailed analysis of the structural and electronic properties of *a*-GaAs at room temperature, as deduced from a structural model at the optimal density. In Sec. IV we discuss the role of chemical disorder in the amorphous phase. We summarize our findings and conclude in Sec. V.

II. COMPUTATIONAL DETAILS

As mentioned above, we use in this work a TB description of the energy of interaction between the atoms. More precisely, we employ the model developed by Molteni *et al.*,[18] where the TB interactions, which include only nearest neighbors, are parametrized in terms of an sp^3s^* basis set.[10,20] This model has been used successfully to simulate the structure of amorphous[13] and liquid[19] GaAs, as well as point defects in GaAs.[21]

A model of *a*-GaAs containing 64 atoms was constructed by cooling from the melt as follows: Since, as noted above, the density of *a*-GaAs is not known precisely, we assumed it, in a first step, to be the same as that of *c*-GaAs, namely, 5.32 g/cm^3.[16] Thus, following Molteni *et al.*,[13] we first prepared a well-equilibrated liquid at 1600 K and density appropriate to liquid GaAs at this temperature, viz., 5.71 g/cm^3, which we checked against the simulations of Ref. 19. After equilibration of the liquid, the density was changed (by rescaling the coordinates of the atoms) to that of the crystal, i.e., reduced from 5.71 to 5.32 g/cm^3; the system was then cooled down to 0 K progressively, ''slowly,'' at a rate of 1.5 K/ps. (We note that this cooling rate is somewhat slower than that used by Molteni *et al.*, 2.8 K/ps on average.) The resulting struc-

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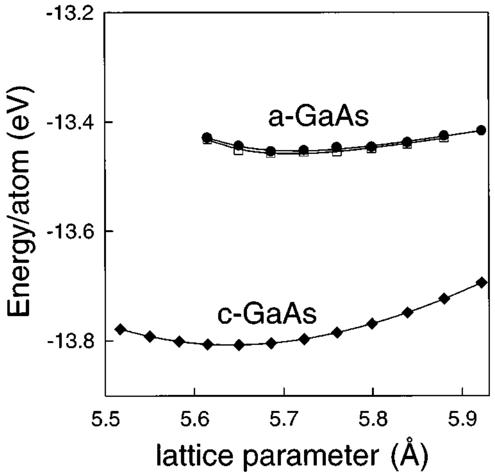

FIG. 1. Total energy vs lattice parameter at 0 K for crystalline GaAs and the two amorphous samples discussed in the text: 64 atoms (filled circles) and 512 atoms (open squares). The lines were obtained by fitting to Eq. (3.1).

ture at 0 K was further optimized using conjugate gradients. In order to determine, then, the optimal (ground-state) density of the system, we varied the density until a minimum-energy configuration could be identified, performing a full relaxation at every density. This configuration is our "ground-state model." A room-temperature model for the 64-atom system, which we will characterize in detail below, was generated by heating up the above model to 300 K at the optimal density, equilibrating for 92.5 ps, and accumulating statistics over an additional 52.9 ps. (The density of c-GaAs varies very little with temperature; we assume this also to be true for a-GaAs, especially in this temperature range.)

Other details of our calculations are as follows. Periodic boundary conditions were used in all three Cartesian directions so as to eliminate surface contributions. The TB energies were obtained by direct diagonalization of the TB matrices constructed by sampling only the Γ point in reciprocal space. In order to check for convergence with respect to size (or, equivalently, number of **k** points), we examined also a 512-atom system (at zero temperature only), obtained by simply enlarging the 64-atom system and equilibrating. The interactions were cut off at a distance of 3.185 Å; the time step for the integration of the equations of motion was 0.88 fs.

III. PROPERTIES OF a-GaAs AT ROOM TEMPERATURE

A. Structural properties

We present in Fig. 1 the variations of the total energy of our 64-atom amorphous sample at 0 K as a function of the "lattice parameter" (the side of a cube containing 8 atoms, i.e., half the side of the cubic supercell), as well as that for the 512-atom system mentioned above. It is evident from a comparison of the two curves that the energy depends very little on system size (or number of **k** points), ensuring us of the validity of our model. We also give, in Fig. 1, the corresponding data for c-GaAs, obtained using a 64-atom supercell. It is immediately clear from this plot that the total-energy curve is flatter for a-GaAs than for c-GaAs; this might explain, to some extent, the difficulty in determining experimentally the density of a-GaAs. Also, in spite of this, and consistent with experiments, the minimum in energy for a-GaAs occurs at larger lattice parameter, i.e., smaller density, than for c-GaAs.

The data of Fig. 1 can be used to calculate the bulk modulus B of the material. For a- and c-GaAs we obtain $B=$ 86.13 and 86.40 GPa, respectively. We know of no experimental measurement of this quantity for a-GaAs. For the crystalline phase, however, B is approximately equal to 75 GPa,[22] in fair agreement with our value. It appears that the bulk moduli of amorphous semiconductors does not differ much from their crystalline counterparts.

The equilibrium lattice parameter a_0 can be obtained precisely by fitting the total-energy curves with the "universal binding-energy function" (Ref. 23)

$$E(r)=\alpha\left(1+\frac{r-a_0}{\beta}\right)\exp\left(-\frac{r-a_0}{\beta}\right)+\text{ const}, \qquad (3.1)$$

where α and β are other fitting parameters. We obtain, using the data of Fig. 1, $a_0=5.64$ Å for c-GaAs, corresponding to a density of 5.34 g/cm^3; for a-GaAs, we find $a_0=5.71$ Å, i.e., 5.15 g/cm^3, a bit less (-3.2%) than the crystalline density.

The experimental density of c-GaAs [5.32 g/cm^3 (Ref. 16)] is one piece of information used to determine the parameters of the TB model;[18] the difference between this and our calculated value can be taken as a measure of the quality of the fit. For a-GaAs, values in the range 4.98–5.11 g/cm^3 have been reported.[1,14] This is a bit smaller than the value we predict; however, small-angle x-ray scattering measurements suggest that sputtered material may contain sizable voids that could account for the observed difference between experiment and model (as well as, perhaps, variations in the values reported).

In their TB simulations, Molteni *et al.*[13] chose the density of a-GaAs at room temperature by interpolating between the density of the crystal at zero temperature and that of the liquid at 1600 K, thus obtaining 5.39 g/cm^3. This is larger than the crystalline density, and we therefore expect our results to exhibit quantitative differences from those of Molteni *et al.* This is discussed in detail below.

Having determined the optimal density of a-GaAs, we carried out a series of dynamical runs at 300 K, at this same density, long enough to accumulate reliable structural data for the calculation of the pair correlation functions (PCF's), structure factors, and other structural parameters. (In practice, these were obtained by averaging over 6000 configurations from a 60 000-time-step run, i.e., 52.9 ps) following thorough equilibration (92.5 ps).

The partial PCF's $g_{ij}(r)$ provide detailed information about the short-range arrangements of atoms in the amorphous state. They are shown in Fig. 2 for the three types of correlations, again at 300 K, as well as for the total, unweighted PCF $g(r)$. We also give, for reference, the corresponding functions for c-GaAs at 300 K. We observe that the partial Ga-As PCF is quite similar, at nearest-neighbor distances, to the total PCF, simply reflecting the fact that unlike-atom nearest-neighbor correlations largely dominate in the amorphous sample. In the ideal zinc-blende structure, of

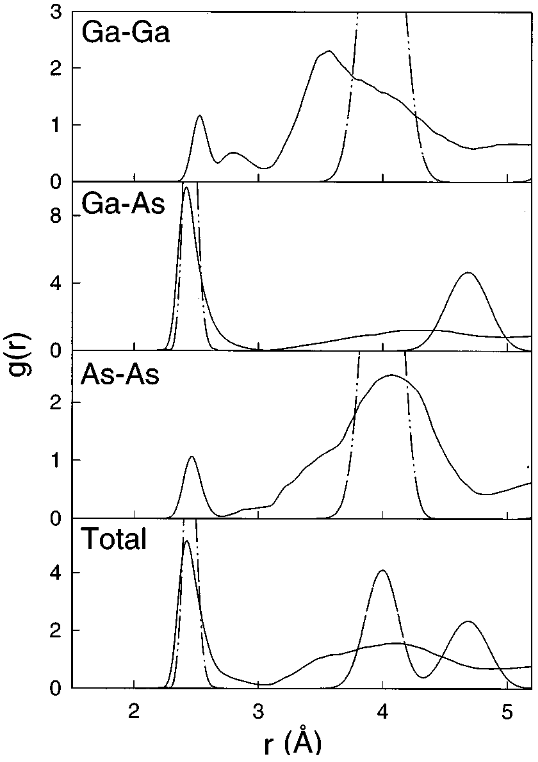

FIG. 2. Partial and total pair-correlation functions of a-GaAs (full line) and c-GaAs (broken line) at 300 K.

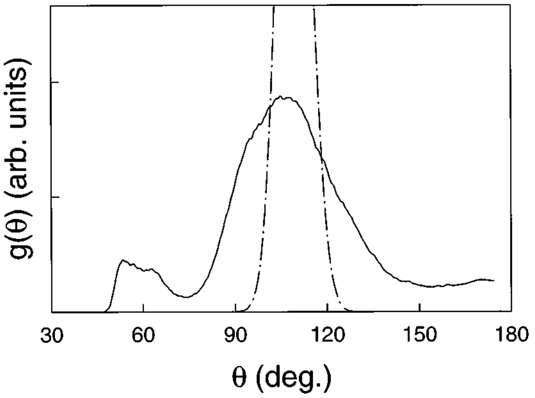

FIG. 3. Bond angle distribution function of a-GaAs (full line) and c-GaAs (broken line) at 300 K.

course, only hetero bonds are allowed. In the amorphous material, homo bonds are possible to some extent, even though hetero bonds prevail. The homo bonds manifest themselves as small peaks at values close to the Ga-As bond length in the like-atom PCF's. For Ga-Ga, we observe a peak at 2.5 Å, close to the bond length in c-GaAs, as well as a peak at 2.8 Å, which is close to a Ga-Ga bond distance in bulk Ga.[24] For As-As, we find a single peak at 2.5 Å, corresponding to the GaAs bond length. Second-neighbor peaks differ significantly in shape from the corresponding peaks in crystalline material, owing to the wide spectrum of possible configurations that are allowed by disorder. We note in particular that the As-As PCF exhibits a shoulder near 3.3 Å, probably corresponding to the second nearest-neighbor distance in c-As (3.12 Å).[24]

We give in Fig. 3 the distribution of bond angles in the amorphous structure (as well as in the reference crystal). The definition of bond is a bit arbitrary; here we chose a value of 3.0 Å as the bond-cutoff distance, corresponding to the first minimum after the main peak in the total PCF and thus representing all types of correlations in an average sense. The main peak near 107° arises from the tetrahedral arrangements that still prevail, in spite of the disorder. There appears, in addition, a small peak near 60°, manifest of deviations from perfect tetrahedral order. A similar peak has been observed in models of amorphous Si (see, for instance, Ref. 25), though it is generally less important. This difference between the materials might well be due to the fact that III-V compounds are more ionic in character than group-IV semiconductors; of course, bond-bending forces are expected to vanish in the ionic-crystal limit.[26]

The average coordination number of the material can be obtained by integrating the total PCF up to the minimum following the nearest-neighbor peak; this and other relevant numbers are listed in Table I. We obtain in this way $Z=3.94$, which agrees extremely well with experiment,[1] $Z=3.93$, but disagrees a little bit with the first-principles results of Fois *et al.*,[12] 3.83, and the TB-MD value of Molteni *et al.*,[13] 4.09. In both cases, however, a much faster rate was used to quench the liquid. There are differences in density, also: Fois *et al.* assumed the density to be that of the crystal (5.32 g/cm^3), while Molteni *et al.* used a value interpolated linearly between that of the liquid at 1600 K and the cold solid, namely, about 5.39 g/cm^3. The first-principles simulations of Fois *et al.*, further, suffer from poorer statistics owing to the formidable computational expense of carrying out such calculations.

The remarkable agreement between our model and experiment can be taken as definite evidence that the density of

TABLE I. Structural properties of a-GaAs at 300 K, compared to other theoretical models [tight-binding molecular-dynamics (TB-MD) (Ref. 13) and first-principles (FP) (Ref. 12)] and to experiment (Refs. 1,2): coordination numbers Z (partial, species, total, and concentration-concentration), Warren chemical short-range order parameter α_W, and proportion of wrong bonds; all these parameters are discussed in the text.

Model	$Z_{\text{Ga-Ga}}$	$Z_{\text{Ga-As}}$	$Z_{\text{As-As}}$	Z_{Ga}	Z_{As}	Z	Z_{cc}	α_W	Wrong bonds
c-GaAs	0	4	0	4	4	4	−4	−1.0	0
a-GaAs	0.65	3.46	0.32	4.11	3.78	3.94	−2.98	−0.75	12.2
TB-MD	0.53	3.56	0.53	4.09	4.09	4.09	−3.03	−0.74	12.9
FP	0.38	3.45	0.38	3.83	3.83	3.83	−3.07	−0.80	10
Expt.				4.0−4.3	3.7−4.0	3.93			~0−12

TABLE II. Distribution (in %) of coordination for the *a*-GaAs sample at 300 K, as well as for the ideal *c*-GaAs structure. Also given are the corresponding results for the TB-MD model of Ref. 12 and the FP model of Ref. 13.

Model	$Z=3$	$Z=4$	$Z=5$	$Z=6$	$Z=7$
c-GaAs	0	100	0	0	0
a-GaAs	24.2	59.8	12.9	2.4	0.7
TB-MD	14	66	18		
FP	21	79			

a-GaAs is lower than that of the crystalline phase. The reduced density of the amorphous material might be explained by the existence in the amorphous phase of a large number of *undercoordination* defects and in particular threefold by virtue of the "$8-N$" rule (where N is the number of valence electrons), as pointed out by O'Reilly and Robertson.[10] We give in Table II the distribution of the various coordination numbers in our sample, as well as, for comparison, in the other theoretical models. Indeed, we observe a large number of threefold-coordinated atoms, which are almost twice as numerous as overcoordinated atoms (so that the overall coordination number is close to 4). The existence of threefold-coordinated atoms in the amorphous phase would thus reflect the relaxed atoms' "natural" valence requirements in III-V compounds.

A more detailed picture of the short-range structure is provided by the partial coordination numbers Z_{ij}, also listed in Table I. We find the partial coordination numbers of Ga and As to be 4.11 and 3.78, respectively, which agree well with the experimental values[5] of 4.0–4.3 for Ga and 3.7–4.0 for As. Our values are again in slight disagreement with other models, for the same reasons as discussed above. It was suggested by Udron *et al.*[5,6] that the low (less than 4) coordination of As might be due to a deficit of Ga in an otherwise tetrahedral (or almost), chemically ordered, structure. Our calculations indicate that such coordination defects arise because of the presence of chemical disorder. We will return below to another important consequence of chemical disorder, the presence of wrong bonds.

A quantitative measure of disorder, or "chemical correlations," is provided by the "concentration-correlation" coordination number $Z_{cc}=c_2(Z_{11}-Z_{21})+c_1(Z_{22}-Z_{12})$,[27] where c_i is the concentration of i-type atoms in the system; here $c_{\rm Ga}=c_{\rm As}=0.5$. $Z_{cc}=-4$ exactly in *c*-GaAs; for our amorphous sample, we find $Z_{cc}=-3.0$ (Table I), indicating, as was already evident from the PCF's, a certain amount of chemical disorder. Chemical disorder can also be quantified in terms of the generalized Warren chemical short-range order parameter[27] $\alpha_W=Z_{cc}/(c_2Z_1+c_1Z_2)$, where $Z_i=\Sigma_jZ_{ij}$. $\alpha_W=0$ indicates complete randomness whereas positive and negative values indicate preference of homo and hetero nearest-neighbor coordination, respectively. Evidently, in *c*-GaAs, $\alpha_W=-1$, while it is 0 in a perfectly random system. For *a*-GaAs, we obtain $\alpha_W=-0.75$ (cf. Table I), revealing, again, a strong preference for chemical ordering.

The overall similarity between the PCF's of group-IV materials and the III-V semiconductors suggests that the materials have comparable short-range structure.[1] However, in spite of the fact that the average coordination number of *a*-GaAs is almost exactly 4, a significant number of atoms ($\sim$40%) are under- or overcoordinated, as we have seen above. Likewise, the structure exhibits a significant number of "anomalous" rings — as can be seen from Table III — and in particular odd membered, just as they can be found in *a*-Si or *a*-Ge. An immediate consequence of this is that there must exist "wrong" bonds in the structure. We find in our model that 12.2% of the bonds are wrong (cf. Table I), in agreement with other models. Experimentally, this number has been reported to lie in the range $\sim$0–12 %.[1,2]

TABLE III. Number per atom of n-membered rings for the *a*-GaAs sample at 300 K as well as for the ideal *c*-GaAs structure.

n	3	4	5	6	7
c-GaAs	0	0	0	4	0
a-GaAs	0	0.40	0.97	2.28	3.35

It is usually considered, for both energetic and topological reasons, that wrong bonds are the most probable defects in *c*-GaAs: One expects that replacing a heteropolar bond by a homopolar bond will occur more readily than losing the bond altogether; this is confirmed by total-energy calculations for antisites and vacancies in *c*-GaAs,[21,28] which show antisites to occur more favorably than vacancies. The energy difference between a hetero and a homo bond may be estimated from the formula proposed by Pauling,[29] $\Delta H=0.995(X_A-X_B)^2$ (eV), where X_A and X_B are the electronegativities of the two species. For the III-V compounds, $X_A-X_B\approx 0.4$, so that the typical energy of the homo bond is about 0.16 eV per bond. More specifically for the case of GaAs, $X_{\rm Ga}=1.81$ and $X_{\rm As}=2.18$ and the energy of a homo bond is 0.136 eV. Since we find 12.2% of wrong (or homo) bonds, the contribution of these to the heat of crystallization of *a*-GaAs is 0.017 eV per bond, i.e., a very small portion of the heat of crystallization of GaAs.

For completeness, we present in Fig. 4 the partial $[S_{ij}(k)]$ and total $[S(k)]$ structure factors (SF's) for our model sample. The structure factors are related to the PCF's by a Fourier transform and are available directly via scattering experiments (neutrons, x rays, etc.). It is, however, difficult in general to extract individual contributions to the total SF, while models can easily provide this information. The SF's were evaluated directly in reciprocal space in order to avoid the spurious oscillations that arise in the Fourier transform of a PCF that does not terminate smoothly (as is the case for finite-size models). The total SF presented in Fig. 4 was obtained by combining the partial $S_{ij}(k)$ with equal weights. In principle, $S(k)$ is a weighted sum of the partials, where the weights are related to the scattering lengths of the atoms for the probe used. However, the scattering lengths for either x rays or neutrons are almost identical in the case of Ga and As; we therefore neglect them here.

The SF of *a*-GaAs has been measured by Udron *et al.* using a combination of EXAFS and x-ray anomalous scattering experiments.[5] This is also presented in Fig. 4. Our model SF is in excellent agreement with the measured one with regard to peak positions, shapes, and intensities. In particular, the "onset" of $S(k)$ at small wave vectors, as well as the weak and broad structure for k values in the range 6–8

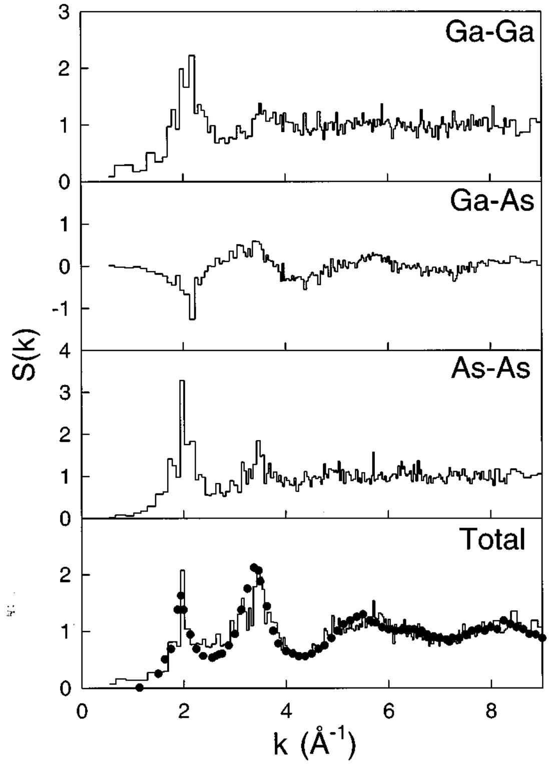

FIG. 4. Partial and total structure factors of a-GaAs at 300 K. The dots in the lower panel are the experimental data of Udron *et al.* (Ref. 5).

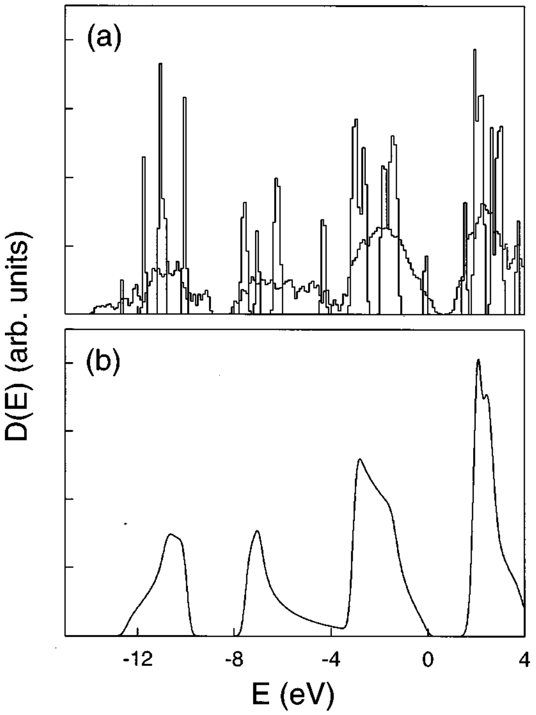

FIG. 5. Electronic density of states of (a) a-GaAs and c-GaAs at 300 K and (b) c-GaAs at 0 K; in (b), full Brillouin-zone integration was carried out and the density of states was smoothed with a Gaussian function of width $\sigma = 0.2$ eV.

Å^{-1}, are well reproduced; this suggests that the local structure we find in our model reproduces quite accurately that in real a-GaAs.

B. Density of electron states

We present, in Fig. 5(a), the "raw" (unsmoothed) density of electron states (DOS) for our model a-GaAs at 300 K (sampling only the Γ point), as well as that for a corresponding crystalline sample. Clearly, the features are considerably broader in the amorphous material, a direct consequence of disorder (both topological and chemical). Further, in spite of the fact that it contains a large proportion of wrong bonds (about 12%), a-GaAs still exhibits a gap between valence and conduction bands, i.e., remains a semiconductor. The band gap here is about 1.12 eV, smaller but comparable to that of c-GaAs (1.50 eV at 300 K); in contrast to the crystal, however, a-GaAs exhibits band tails, again a consequence of disorder. For reference, we show, in Fig. 5(b), the DOS of c-GaAs at 0 K using detailed Brillouin-zone integration and smoothed with a Gaussian filter of width $\sigma = 0.2$ eV.

The experimental value of the band gap of a-GaAs is not known with precision; values in the range 0.61 – 1.45 eV have been reported, depending on the method of preparation and in particular thermal history. (For a complete set of references, see Ref. 30.) It seems clear, however, that the gap of a-GaAs (i) is smaller than that of c-GaAs and (ii) increases upon annealing, by as much as 0.3 eV. We conclude that the gap of optimized a-GaAs must be close to 1 eV, in line with the value we obtain. In fact, we can make this conclusion even stronger by noting that Molteni *et al.*,[13] using the same TB model but a *faster* cooling rate, have obtained $E_g \sim 0.5$ eV, comparable in fact to the gap of "as-made" material.[30]

Small peaks within the valence-band DOS of a-GaSb and a-GaAs, at about -9 eV (measured with respect to the valence-band minimum), have been reported by Shevchik *et al.*,[7] and attributed to wrong bonds. A peak at -9 eV, and another one at -14.5 eV, was also observed by Karcher *et al.*[31] during the recrystallization of a-GaAs and also assigned to wrong bonds. Consistent with this, we clearly see contributions to the DOS of a-GaAs near -9 eV that are not present in the DOS of c-GaAs [Fig. 5(b)]; we also see some contributions at energies in the range -14 to -13 eV, which are likely related to the peaks seen by Karcher *et al.*[31] at -14.5 eV.

IV. EFFECT OF CHEMICAL DISORDER

It is of interest to examine how chemical disorder affects the structural and electronic properties of the material. In order to do this, we "fabricated" a-GaAs samples with varying amount of disorder by manipulating the chemical identity of the atoms in the amorphous matrix obtained above. This is done by simply interchanging the atoms from randomly chosen Ga-As pairs in the zero-temperature 64-atom a-GaAs model and statically relaxing. The following five systems were examined, in order of increasing disorder: (a) the annealed a-GaAs sample at 0 K and (b)–(e) one to four exchanges, respectively. We note that, by definition, the annealed sample (a) contains the smallest possible number of wrong bonds, i.e., is the least disordered, chemically (apart,

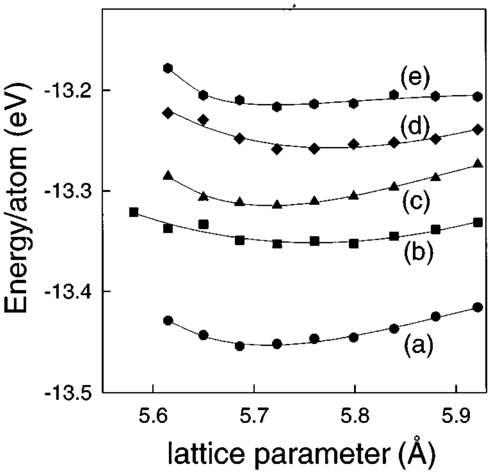

FIG. 6. Total energy vs lattice parameter at 0 K for (a) the annealed amorphous GaAs sample and (b)–(e) samples with varying amount of chemical disorder (cf. the text and Table IV). The lines were obtained by fitting to Eq. (3.1).

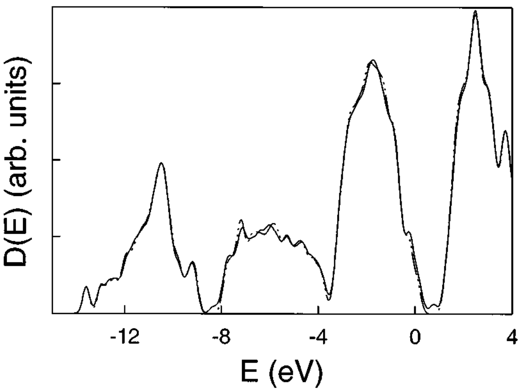

FIG. 7. Electronic density of states of the 512-atom *a*-GaAs model at 0 K (broken line) and a corresponding model with three exchanges (full line), i.e., a 1.2% perturbation. Both curves were smoothed with a Gaussian function of width $\sigma=0.2$.

of course, from the crystal). This is in fact confirmed by the curves of energy versus lattice parameter, presented in Fig. 6. We find indeed that the annealed sample has the lowest energy, indicating that the system is well equilibrated as far as chemical order is concerned; the energy of the other samples increases with the number of exchanges.

The physical properties of the five samples are summarized in Table IV. Evidently, Z_{cc} and α_W increase with the number of wrong bonds. It is interesting to note that the density of the more-disordered samples is lower than that of the annealed sample, suggesting that the decrease in density observed in *a*-GaAs relative to *c*-GaAs arises, to some extent, from chemical disorder. From Table IV, we also see that the band gap decreases quite sharply upon the introduction of even a modest amount of additional chemical disorder. In the presence of excessive chemical disorder, which is the case of liquid GaAs, of course, the band gap closes and the system becomes metallic. The effect of chemical disorder on the electronic properties of *a*-GaAs is in fact illustrated in Fig. 7, where we plot the DOS for the annealed 512-atom system described earlier, as well as for a corresponding system where three exchanges were introduced, equivalent to a chemical disorder perturbation of about 1.2%. In both cases, the raw data was smoothed with a Gaussian function of width 0.2 eV so as to approximate an infinite system. (The band gap is defined as the energy difference between the lowest unoccupied state and the highest occupied state; the smoothing procedure causes band tails to appear in the gap of the amorphous samples.) Evidently, both the valence-conduction band gap and the gap at about -8 eV shrink with chemical disorder.

V. CONCLUDING REMARKS

We have presented a detailed investigation of the structure of *a*-GaAs, including short-range chemical disorder effects and its relation to density, based on a TB description of the energetics of the system. We have generated a true ground-state amorphous GaAs sample, using molecular dynamics, by allowing the density to vary. We find, in accord with experiment, the density of the amorphous phase to be smaller than that of the crystal — 5.15 vs 5.34 g/cm^3. While the system in its ground state is clearly amorphous, the average coordination number is almost exactly 4, as it is in the crystalline state. Chemical disorder is present, however: we find a sizable number of atoms to be under- or overcoordinated and 12% of the bonds to be of the wrong type; yet, the system remains a semiconductor. We also find that increasing the amount of chemical disorder causes the density of the material, as well as the band gap, to decrease. Our structural

TABLE IV. Structural and electronic properties of *a*-GaAs and of the chemically disordered 64-atom samples (b) – (e) at 0 K; also given for reference are the corresponding numbers for the crystalline material. E_p is the potential energy per atom, $a_{\min}$ is the optimal lattice parameter, ρ is the corresponding density, Z_{cc} is the concentration-concentration coordination number, α_W is the Warren short-range order parameter, and E_g is the band gap.

Sample	E_p (eV)	$a_{\min}$ (Å)	ρ (g/cm^3)	Z_{cc}	α_W	E_g (eV)
c-GaAs	-13.81	5.64	5.34	-4	-1	1.54
a-GaAs	-13.45	5.71	5.15	-2.91	-0.72	1.12
(b)	-13.35	5.76	5.02	-2.44	-0.61	0.48
(c)	-13.31	5.72	5.13	-2.16	-0.53	0.54
(d)	-13.26	5.78	4.97	-1.88	-0.46	0.40
(e)	-13.21	5.72	5.13	-1.72	-0.42	0.49

study should help in the analysis of diffraction studies and in particular in the extraction of partial atomic correlations from the measured spectra.

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