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Atomic structure and properties of polar Ge-GaAs(100) interfaces

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We present self-consistent calculations of the total energy, charge density, and electronic states of "compensated" (100) interfaces of Ge and GaAs. In this paper we test the methods using the simplest compensated interfaces—an abrupt single mixed layer, either (1/2)(Ge + Ga) or (1/2)(Ge + As), using the "average atom" approximation for the interface plane. The (1/2)(Ge + As) interface is found to be the more stable (however, this may be an artifact of the averaging). We find a large variation in the interface dipole with stoichiometry. This is not observed experimentally, suggesting that the stoichiometry is, in fact, varying only slightly in experimental Ga-rich and As-rich interfaces. No interface states are found in the fundamental gap although there are localized states at J and K in the two-dimensional Brillouin zone. Several points are discussed improving the efficiency of the self-consistent calculations. Finally, variation of the dipole with relaxation is used to determine interface effective charges.

I. INTRODUCTION

Interfaces between two different crystalline semiconductors are of much current interest because of the intrinsic questions which arise in the study of the properties of two-dimensional arrays of atoms in chemical environments, different from any that can be found in bulk crystals. The questions are (1) First and foremost, what is the stable structure of atoms in the interface region, (2) given the structure, what is the resulting electrostatic dipole at the interface and what unique electronic states are associated with the interfaces, and (3) what are other predicted properties that can be tested by experiments? The reason the semiconductor systems form interesting classes of materials for such studies is that the answers to these questions have well-defined consequences for electronic properties, which are both testable experimentally and important technologically.

The status of detailed calculations of interface properties has reached a point similar to that in bulk crystals—given the structure, the electronic properties can be predicted with considerable confidence. The interfaces, however, present situations in which the atomic structures are not known experimentally and, at this point in time, the challenge is to predict *a priori* the structures. Recent theoretical advances have shown that for bulk crystals, structural energies can be predicted from density-functional electronic calculations.[1-4] In this paper we report the first results of total energy calculations on a semiconductor interface to predict stable atomic structures and their resulting properties. Some of our results have been presented in a short communication.[5] We choose the Ge-GaAs system because comparison can be made with other calculations[6-13] and because considerable experimental work has been reported.[14-17] The polar (100) interface is chosen because it is a simple example of polar interface where different stoichiometries[13,14] of interface layers appear equally probable and no previous theoretical calculations or experimental results have determined which stoichiometry is most stable. Secondly, it is clear from theoretical considerations[13,14] that, whatever is the stable arrangement, it must involve mixed layers and the question arises of the effect of order or disorder of different atoms in these layers. Definitive theoretical calculations are needed to predict the stable structure(s).

The atomic structure of an interface is defined by the type and position of all the atoms in the interface region. The set of possible structures is greatly reduced if we consider only "lattice-matched" crystals in which the lattice is continuous across the interface. Then every atom can be associated with a site on an infinite lattice and the interface is defined as the region where the chemical identity of the atoms changes. In this case there are three types of degrees of freedom remaining[13]: (1) the stoichiometry of the interface, i.e., the number of atoms of each type in the interface region, (2) the order of the different types of atoms in the interface plane, and (3) displacements of the atoms from the ideal positions, which must be present because of the low symmetry of the interface. It has been pointed out by several authors[7,8,13,14] that the degree of band filling, i.e., number of free carriers is determined solely by counting charges, i.e., by the stoichiometry. The other degrees of freedom[13] can be cataloged, as described below, and shown to produce less important but well-defined effects.

This classification scheme[13] appears ideally suited for Ge-GaAs interfaces, where the lattice

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mismatch is <0.1%, and allows simple unique predictions of the interface structure. This is to be contrasted with surfaces where the picture is much more complex because the lowest-energy state may involve large atomic displacements, change in coordination, vacancies, etc.,[18-20] which completely change the electronic states.

There have been a number of calculations on Ge-GaAs interfaces, all assuming very ideal structures. The first self-consistent calculation was that of Baraff, Appelbaum, and Hamann[7] who considered a (100) Ge-GaAs interface defined by perfect Ga termination with no relaxation from ideal tetrahedral positions. A more recent tight-binding investigation has been reported by Pollmann and Pantelides.[8] These assumptions lead inextricably to a metallic interface which, as later arguments[8,13,14] have shown, cannot be a stable (100) interface. Because of the difficulties with the (100) interface, Pickett, Louie, and Cohen[9-11] and Herman and Kasowski[12] addressed the (110) Ge-GaAs interface, where they argued that the ideal nonpolar arrangements of atoms at this interface would be a favorable geometry. The properties of the interface were considered at the ideal tetrahedral positions[9,11,12] and as a function[10] of the spacing of the layers exactly at the interface, but no attempt was made to predict the precise stable geometry.

The work reported in this paper is based upon an "average-ion" approximation for the mixed interface layers. This is essentially a virtual-crystal approximation[21] which we adopt to describe the average properties of the interface independent of the order or disorder in the interface layers. The size of the computations is vastly reduced by this approximation and therefore it is a very valuable case on which to test the computational accuracy and uniqueness of the total energy calculations. From our total energies we find two primary conclusions: (1) the average interface planes are displaced by very small amounts from the ideal position, and (2) within the virtual-crystal approximation, interfaces containing mixed Ge and As atoms are more stable than ones containing mixed Ge and Ga atoms. We predict the resulting dipoles and interface states in the two cases and compare them with the results of others.[9-11]

In a future paper (to be designated II) we plan to extend the calculations to various ordered arrangements of atoms in the interface layers. There we will properly retain the chemical identity of atoms in the interface—not making a virtual-crystal average-atom approximation. The interface energies will be more reliable in those calculations and definitive predictions of stable interface stoichiometries must await those results. Nevertheless, the present work is an essential step in our work on the Ge-GaAs interface. The tests for convergence as a function of the number of Fourier components, sampling points in the Brillouin zone, and iteration toward self-consistency and the methods for handling inevitable small errors in the ionic potentials developed here are important for all our calculations on the interfaces, and the results described here will be essential in the further developments to be described in II.

II. MODELS OF THE Ge-GaAs(100) INTERFACE

The (100) planes of atoms in zinc-blende-structure crystal are polar, meaning that alternate planes are composed completely of metal atoms (e.g., Ga) or completely of nonmetal atoms (e.g., As). For a diamond-structure crystal the planes change to become equivalent containing just one type of atom (e.g., Ge). At the interface between the crystals the planes retain their identity, but the atomic type, i.e., stoichiometry, changes. We consider "abrupt" interfaces in which the change takes place within a few layers. There is experimental evidence[14-17] that such abrupt interfaces have been made in the Ge-GaAs system; however, there is no direct evidence for the composition and structure of the transition layers. Harrison *et al.*[14] have given several examples of transition layers.

The simplest transitions are ones in which the GaAs side simply terminates on a Ga or an As plane. This is the geometry of Baraff, Appelbaum, and Hamann[7] and Pollman and Pantelides,[8] who showed that simple electron counting leads to extra electrons at an As interface or holes at a Ga interface. Since these free charges accumulated near the interface have not been observed experimentally, it was proposed by Baraff, Appelbaum, and Hamann that there are large reconstructions of the interface that remove the states from the gap. Other authors[8,13,14,22] have argued that it is not reconstruction but rather a different termination of atoms that is most favorable. Martin[13] has given a systematic analysis of the energies and has shown from empirical data that the energy will be lowered by substituting atoms in the layers to make mixed Ge-Ga and/or mixed Ge-As layers. He showed that the lowest energy should be for a completely "compensated" mixture of atoms in the interface. These fully compensated interfaces would have no free carriers and the arguments of Ref. 13 show that *all* such interfaces should be more stable than the Ge- or As-terminated interface.

The simplest examples of such compensated interfaces are ones in which only one layer is mixed. One case is shown in Fig. 1—a mixed $\frac{1}{2}$ Ge + $\frac{1}{2}$ Ga

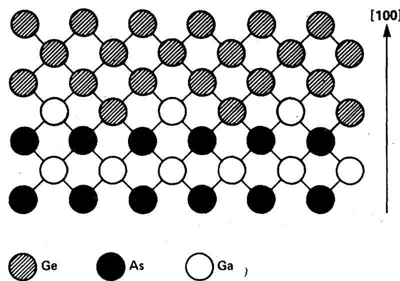

FIG. 1. The simplest example of a compensated Ge-GaAs(100) interface viewed along the [010] direction. Only *one* atomic layer is mixed and it consists of 50% Ge and 50% Ga atoms, regularly or randomly arranged. There is an equal number of Ga–Ge and As–Ge bonds in the interface region implying absence of free carriers. A symmetric case may be obtained by interchanging Ga and As atoms, a 50 at.% Ge + 50 at.% As interface.

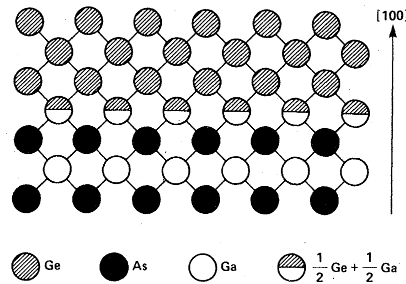

FIG. 2. Simplified model of the Ge-Ga interface of Fig. 1. The virtual-crystal approximation ignores the differences between the two types of atoms in the mixed layers and only takes into account their average properties: Symbol $\frac{1}{2}$Ge + $\frac{1}{2}$Ga stands for a (hypothetical) atom whose ionic pseudopotential is the average of the pseudopotentials of the respective atoms. This model can approximate both an ordered and a disordered interface. A symmetric situation is obtained by interchanging the róles played by Ga and As atoms.

layer. The other possible case with a single mixed $\frac{1}{2}$ Ge + $\frac{1}{2}$As layer is the same but with the interchange of Ga and As. These cases obey the simple rule given in Ref. 13 for compensated interfaces; there must be equal numbers of Ga–Ge and As–Ge bonds in the interface region. In fact, any linear combination of the two will also be compensated. Harrison, Kraut, Waldrop, and Grant[14] have given an example of an equal mixture of these two types of layers which give a single interface having two mixed layers.

Given the compensation requirement, the interface is now specified by the amount of mixing on Ga and As planes, respectively, and by two further types of information, (1) the order of the atoms in the mixed layers and (2) displacements from the tetrahedral sites. It has been argued[13] that there will be "charge ordering," i.e., long-range crystalline order of the different charged atoms in the two-dimensional interface layers, but the distinct possibility remains that the layers are disordered. Also in Ref. 13, it was concluded that at growth temperature there should *not* be ordering of the atoms which have the same charge, i.e., no "dipole ordering". It is interesting to determine properties of the interfaces independent of the order. Therefore we carry out our explicit calculations by averaging the atoms in the interface layers. This virtual-crystal approximation ignores the differences of the atoms in the mixed layers but does take their average properties into account. Specifically, the two interfaces for which we have carried out calculations are the ($\frac{1}{2}$ Ge + $\frac{1}{2}$ Ga) and ($\frac{1}{2}$ Ge + $\frac{1}{2}$ As) single average-layer cases shown in Fig. 2. (Here parentheses are used to denote the average atoms which are $\frac{1}{2}$ Ge, $\frac{1}{2}$ Ga, or $\frac{1}{2}$ As.)

III. METHOD

Our actual calculations are carried out on the periodic supercell structures shown in Fig. 3. Each case involved unit cells with two equivalent interfaces back to back. The supercell assumption allows the solution to be carried out in a straightforward Fourier expansion, so that all calculations are the same as for any infinite crystal. The calculations are strictly for such a superlattice,[17] but to the extent that interfaces are well separated they give the results for an isolated interface. We shall show later that the charge density and the potentials are very bulklike in between the interfaces so that our dipoles and total energies are well converged for isolated interfaces. This agrees with the findings of Refs. 7, 9, 11, and 12. However, the results for electronic states bound to the interface are only qualitative and cannot be considered to be converged. In both cases the supercell contains the same atoms (4Ge, 2Ga, and 2As) so that the eventual differences can only result from difference in interface stoichiometries.

Evaluation of total energy is based on the local charge-density-functional approach of Hohenberg, Kohn, and Sham[23,24] which we apply in the momentum-space formalism as summarized by Ihm *et al.*[3] The only assumptions are the local form of the exchange operator $0.8(\frac{3}{2})[3n(\vec{r})/\pi]^{1/3}$ and the Berkeley form of the ionic potentials for Ge, Ga, and As.[25,26] Let us note that all parameters of the latter were fitted to the *bulk bands* of Ge and GaAs, and no adjustment was done to fit any properties of the interface. We have verified behavior of the ionic potentials by a self-consistent calculation on

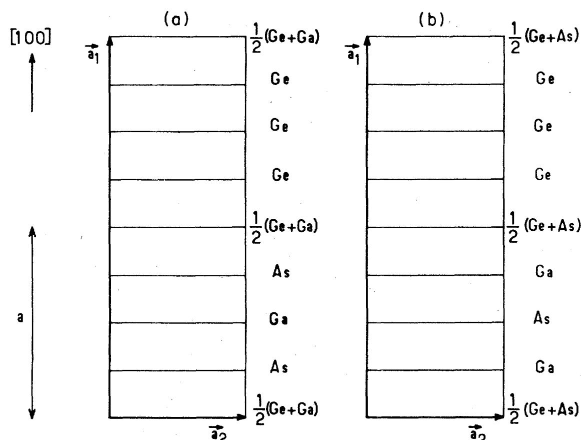

FIG. 3. (a) and (b). Periodic supercell used for studying the interface of Fig. 2 and its symmetric alternative. Each line represents a plane of atoms. Two interface planes are included in the unit cell. In both models the supercell contains the same eight atoms (4Ge, 2Ga, and 2As) so that the differences can only result from the difference in interface stoichiometries (i.e., whether the interface mixes Ge with Ga or with As) shown, respectively, by (a) and (b). Our calculations strictly apply to such a superlattice, but we show that at distance a the two interfaces in each cell are sufficiently separated so as to approximate an *isolated* interface (cf. Figs. 7 and 8).

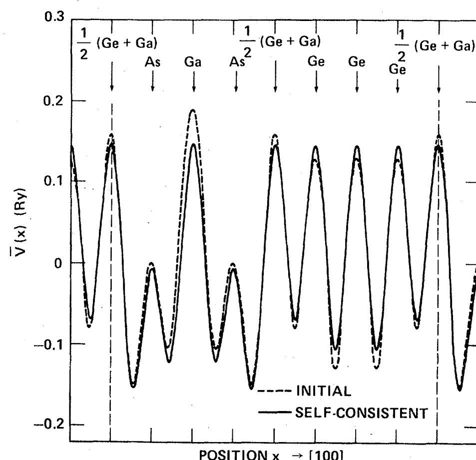

FIG. 4. The trial potential used for initiating the self-consistent iteration is obtained by screening the ionic pseudopotential by the dielectric function of free-electron gas. This choice (broken lines) is not too far from the final self-consistent potential (solid lines), a fact which reduces the number of cycles required for achieving good convergence. This plot corresponds to an (unrelaxed) $\frac{1}{2}$Ge + $\frac{1}{2}$Ga interface in the supercell geometry of Fig. 3. Variation of space coordinate $\vec{r}$ is limited to the component x, i.e., along the direction [100], across the interface, and values of the potential were averaged over the remaining two coordinates, i.e., in the plane parallel to interface [see Eq. (1)].

the (pseudo-) atoms Ge, Ga, and As; predicted energies of valence electrons are by $\lesssim 10-40$ mRy off those obtained in all-electron calculations and the pseudocharge densities approximate well the space variation of the real density outside the core region. We also checked the band structures obtained from the self-consistent potentials. The most relevant test for our purposes is, however, prediction of the bond length: this represents a stringent test of any given potential and the data are readily obtained by calculating the total energies of bulk Ge and bulk GaAs for several different lattice constants a. A calculation done in the same conditions as the subsequent interface calculations (number of waves, sampling, etc.) yielded the minimum of total energy at $a = 5.64$ Å for GaAs and $a = 5.21$ Å for Ge. [The error introduced by truncation of the number of plane waves is only of order 1%, as may be verified by comparison with more accurate calculations on GaAs with ≈ 3 times as many waves, which yield a lattice constant of 5.71 Å (Ref. 27).] As the experimental values are, respectively, $a = 5.65$ and 5.66 Å, the Ge–Ge bonds predicted by calculation are by 8% too short while the length of the Ga–As bonds is predicted correctly. The difference between the accuracy of the two predictions will have an important effect on the interface which will require a careful treatment; a similar problem has already been encountered, in different context, in Si.[2] The solution of the local-density-functional equations requires a self-consistent solution for the charge density and the total potential which is the sum of ionic, Hartree, and local exchange-correlation potentials. In each cycle of iteration a potential is used for generating the charge density, which in turn provides a new potential. This is used for constructing the input for the next cycle. The first cycle requires a trial potential and we have found that an excellent choice is the ionic potential screened by the dielectric function of a free-electron gas. An example of this starting potential is shown in Fig. 4. In this plot (as well as in all the subsequent ones, see Figs. 7 and 8) the variation of space coordinate $\vec{r}$ is limited to the component x, i.e., along the direction [100], across the interface, and values of the potential were averaged over the remaining two coordinates, i.e., in the plane parallel to interface

$$\bar{V}(x) = \frac{1}{Na^2} \int V(\vec{r})\, dy\, dz \, . \qquad (1)$$

In order to stabilize convergence of the self-consistent iteration, the initial and final potentials are weighted by factors $\alpha(G)$ and $1 - \alpha(G)$, res-

pectively, so as to produce the starting potential for the next cycle. The mixing coefficients are chosen to be $\alpha(G)=0.9$ for $G^2 \leq 0.9(2\pi/a)^2$ and $\alpha(G)=0.5$ for all other G's. With the exception of $V(\vec{G})$ with $G^2=0.25(2\pi/a)^2$ (the smallest ones) all components of the potential are well behaved in this crystal structure and converge fast to their self-consistent values; the smallest ones, however, require a special attention. A typical behavior of this component during the algorithm is shown in Fig. 5. About 16 cycles of iteration would be needed for achieving a self-consistency to within 0.1 mRy if only the linear mixing with $\alpha(G)$ described above were used for moderating the oscillatory behavior. To improve the convergence we have devised a scheme for predicting the converged potential. Near convergence the small errors in the final potential are linear in the errors in the initial potential. Therefore, with a constant mixing coefficient α, the initial and final potentials always converge exponentially. We can take advantage of this by using three points to determine the exponential and predict the limit. The value of this procedure is illustrated in Fig. 5 where the limit is very accurately predicted from steps 3, 4, and 5. The total energy is much less sensitive and converges rapidly and uniformly as shown in Fig. 5.

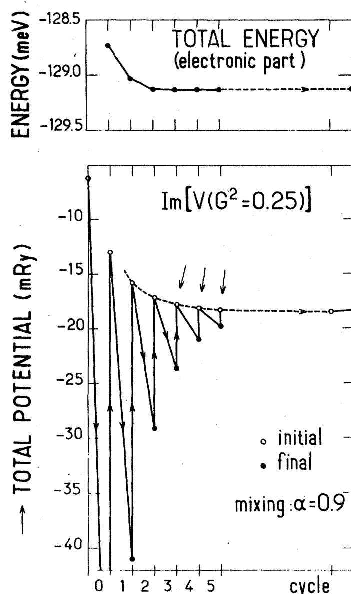

FIG. 5. A typical oscillatory behavior of $V(\vec{G})$ during the iteration process. Components of potential with the shortest $\vec{G}$ $[G^2=0.25(2\pi/a)^2]$ are the worst behaved and converge very slowly: If only linear mixing of 90% of "old" with 10% of "new" values is used, in order to stabilize the divergent process at least ten more cycles would be needed to achieve a self-consistency to within 0.1 mRy ($\approx$0.6%). Extrapolating exponentially from the three points marked by arrows, $V(\vec{G})$ can be predicted with about the same error. Only one more cycle is then needed to provide a checkout, ascertain error limits, and evaluate the total energy. The latter is very well behaved in all circumstances. The figure shown corresponds to the (unrelaxed) $\frac{1}{2}$(Ge + Ga) interface; only the electronic part of total energy is given.

In the actual calculations we have used exponential extrapolation of $V(G^2=0.25)$ inspired by Fig. 5, but based on the starting points of cycles 1, 2, and 3, so that running only the cycles 0, 1, and 2 is necessary; we then perform one more iteration, starting from the extrapolated value of $V(\vec{G})$, so as to provide a checkout to ascertain error limits and to evaluate the total energy. For the accuracy of ≈ 0.5 mRy the amount of the necessary computations is thus reduced by factor ≈ 3. Plane waves with kinetic energy up to $E_2=26.5(2\pi/a)^2=9.15$ Ry are included into the expansion of wave functions (≈ 570 waves). Only those with $E_1 \leq 7.4(2\pi/a)^2=2.55$ Ry are dealt with exactly (≈ 85 waves) and the remaining ones are treated by Loewdin perturbation theory up to second order. The ionic potential is cut off at $G^2=38.1(2\pi/a)^2=13.15$ Ry, a set of 1 and 3 special $\vec{k}$ points [respectively, $(q_1, q_2, q_3)=(2,2,2)$ and $(4,4,2)$ in the notation of Ref. 28] is used for sampling, and a fast Fourier transform on a grid of $8\times8\times32$ points in real space is used to evaluate the Fourier expansion of $\rho^{1/3}$. Further experimentation has shown that the 3 special $\vec{k}$-point scheme does not need to be used through all four cycles and we are safe to replace it by the one-point scheme in the first three cycles. The three point scheme needs to be used only once. This shortens the algorithm further by another factor of 2. Together with the factor of 3 from the exponential extrapolation these simple measures reduce the computational time by a factor of 6.

With the aid of the above short cuts we obtain the potential which is consistent with its own charge density. All our computations are convergent to within <0.6 mRy ($\leq 6\%$ which is the difference between the initial and final value in the last cycle) for the "worst behaved" $V(\vec{G})$ and to within 0.25 meV/atom ($=0.0016\%$) in total energy. The potential and the total energy may be as much as 0.9 mRy and 150 meV/atom (equal to 1%) off the "exact" value (many waves). However, these last deviations are systematic and cancel when comparing cases with slightly different displacements.

IV. RESULTS ON Ge-GaAs

By looking for the minimum of total energy we attempt to establish how far from the ideal crystal configuration the interface will relax. All atomic planes are assumed fixed, except those of aver-

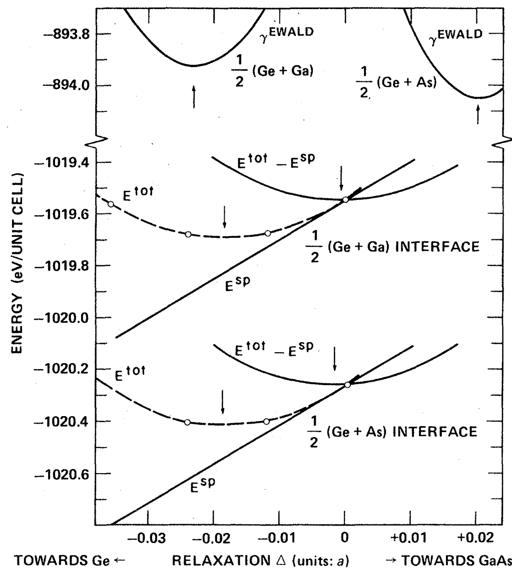

FIG. 6. Variation of total energy of the eight-atom supercell with relaxation of the (averaged) interface. Arrows indicate minima of the parabolas. Upper curves include only electrostatic terms (γ^{Ewald}). Broken lines indicate the complete calculations of total energy. These contain spurious contributions (E^{sp}) which originate in the over-attractiveness of the Ge- ionic potential. When the calculated E^{sp} (linear with relaxation) is subtracted the corrected total energy (solid lines) predicts minima essentially at the unrelaxed position, within the limits of accuracy of the calculations. [The numerical uncertainty of the energy values displayed is only ±2 meV (the size of the circles) although the absolute value of energy may be in error by as much as ≈1.3 eV per cell.] In the framework of our model, the total energy predicted for the averaged $\frac{1}{2}$ (Ge + As) interface is lower by 360 meV per interface atom than that of $\frac{1}{2}$ (Ge + Ga) interface.

aged atoms (interfaces), which are allowed to move by a small amount of Δ, all towards the Ge or the GaAs side; all these shifts conserve the volume of the unit cell. We expect that the interface of averaged atoms will relax into average positions between the real atoms.

The total energy is a sum of ion-ion, electron-ion, and electron-electron terms, the first one giving (in absolute value) the largest contribution. It is, therefore, natural to solve the problem first in electrostatic approximation, neglecting the presence of all valence electrons. This reduces to evaluation of simple Ewald sums and the electrostatic energy γ^{Ewald} is plotted in Fig. 6 for various relaxations Δ, of one or another interface. This approximation predicts an energy minimum at $\Delta = -0.023a$ for the $\frac{1}{2}$ (Ge + Ga) interface (i.e., 0.13 Å or 9% of interlayer distance towards Ge) and $\Delta = +0.020a$ for the $\frac{1}{2}$ (Ge + As) interface (= 0.11 Å towards GaAs). For $\Delta = 0$ (the unrelaxed case) the electrostatic energy is the same for both interfaces.

Taking into account the valence electrons amounts to screening the bare core charges by kinetic, electrostatic, and exchange-interaction terms. As the electronic contributions to total energy weaken the electrostatic repulsion of cores, we may expect that the minimum of E^{tot} in the full calculation will be closer to $\Delta = 0$ than in the electrostatic approximation. Indeed, a *complete* calculation of total energy performed as described above provides E^{tot} varying slowly with relaxation and having minimum at $\Delta = -0.018a$, *the same for both interfaces* (i.e., relaxation by 0.10 Å = 7.4% of interlayer distance towards the Ge side), see the broken lines on Fig. 6. The four calculated points at the $\frac{1}{2}$ (Ge + Ga) curve lie on the same parabola to within less than 1 meV.

The main reason the interface layer is displaced towards Ge in our calculation is the ionic potential of Ge which is too attractive, as the predictions of bond lengths in the bulk have shown. It is obvious that the (calculated) Ge–Ge bonds pull the interface too stronly from their side and make it relax towards the Ge side much further in calculation than in reality. In other words, the small inadequacy of the Ge potential gives a spurious contribution to E^{tot} which decreases E^{tot} when the interface is relaxed towards the Ge side. There is no obvious way to check the predicted length of the Ge–Ga and Ge–As bonds, which also are present around our interfaces. However, as each of the two bond types occurs from one or another side of interface in equal number, it is the most natural assumption to expect that their respective imprecisions will cancel each other. Under this assumption the spurious contribution will originate from only the Ge–Ge bonds and will be the same for both interface types. We will now correct for these spurious contributions.

Relaxation of the interface from the position $\Delta = 0$ to $\Delta = -0.018a$, displayed on Fig. 6, changes the bond length by 2.5%; for such a small change the corresponding increase in bond energy can be written as $[dE^{\text{bond}}(r)/dr]\delta r$, where δr is the change in bond length corresponding to Δ, and it is understood that the derivative of the (calculated) bond energy is evaluated in the situation corresponding to the interface position $\Delta = 0$, i.e., for the "normal" experimental bond length. This is zero for Ga–As bonds because the experimental bond length falls into minimum of the bond energy, but is nonvanishing for Ge–Ge bonds because the "$\Delta = 0$ situation" does not coincide with the minimum calculated in the bulk. Information about $E^{\text{bond}}(r)$ is easily obtained from the knowledge of

$E^{Ge}(a)$, the total energy of Ge calculated in the bulk (equal to four Ge–Ge bonds per unit cell) as a function of lattice constant with $r = a\sqrt{3}/4$. It follows from the geometry of our interface that its relaxation by Δ increases the Ge–Ge bond length by $\delta r = \Delta/\sqrt{3}$. With two Ge–Ge bonds per unit supercell we finally obtain for the spurious contribution to the total energy,

$$E^{\text{spurious}}(\Delta) = \tfrac{2}{3}\,[dE^{\text{Ge}}(a)/da]\Delta + \text{const} \qquad (2)$$

and it is understood that the derivative is to be evaluated at $a = 5.66$ Å, or whatever else might correspond to the $\Delta = 0$ situation. With $dE^{\text{Ge}}(a)/da = 4.82$ eV/Å found in a self-consistent calculation on bulk Ge, Eq. (2) is the straight line plotted in Fig. 6.

Subtracting $E^{\text{spurious}}(\Delta)$ from the calculated $E^{\text{tot}}(\Delta)$, we get new parabolas (solid lines in Fig. 6, the corrected total energies) which show minima at less than 0.01 Å from the unrelaxed situation—*the same* for both types of interface. Our model of averaged interfaces thus predicts as stable configuration the *unrelaxed* interface.

We note that the calculated total energy of the $\frac{1}{2}$ (Ge + As) interface is 720 meV per unit cell ≡ 360 meV per interface atom lower than that of the $\frac{1}{2}$ (Ge + Ga) interface, suggesting that the former interface would be more favorable. This difference between the two interfaces is contrary to the prediction based on the tight-binding scheme[13,14] where the two interfaces have equal energy. We do not know whether our result is a consequence of averaging the atoms (i.e., an artifact of the model) or whether it is real. Further calculations which are *not* based on the virtual-crystal approximation will be needed to provide a definite answer.

Returning to Fig. 4 we may conclude that, by allowing the electrons to adapt to the interface environment, we have caused a redistribution of electrons which changed the electric dipole in the interface region. Indeed, the iteration has lowered the potential in the GaAs part and raised it in the Ge part of the system. These relative shifts determine the magnitude of the above-mentioned dipoles. In Fig. 7 we have plotted variation of the *final* self-consistent potential across the periodic supercell, i.e., along the [100] direction, for the case of unrelaxed interfaces. As it is expected that in the regions far from interfaces the crystal should recover properties of the bulk, we have also shown (broken lines) the self-consistent potential determined separately on the bulk Ge and bulk GaAs, by exactly the same procedure and in exactly analogous conditions. One can see that at a distance of less than one layer from the interface the potential recovers the form of the bulk potential exactly; only when approaching the interface quite closely, does the $\overline{V}(x)$ start to differ from the bulk. Basically the same situation is found when comparing the charge densities $\overline{\rho}(x)$ [see Figs. 8(a) and 8(b)]. This answers *a posteriori* the question of whether the two interfaces in our relatively small supercell are sufficiently apart to be decoupled; apparently they are, at least

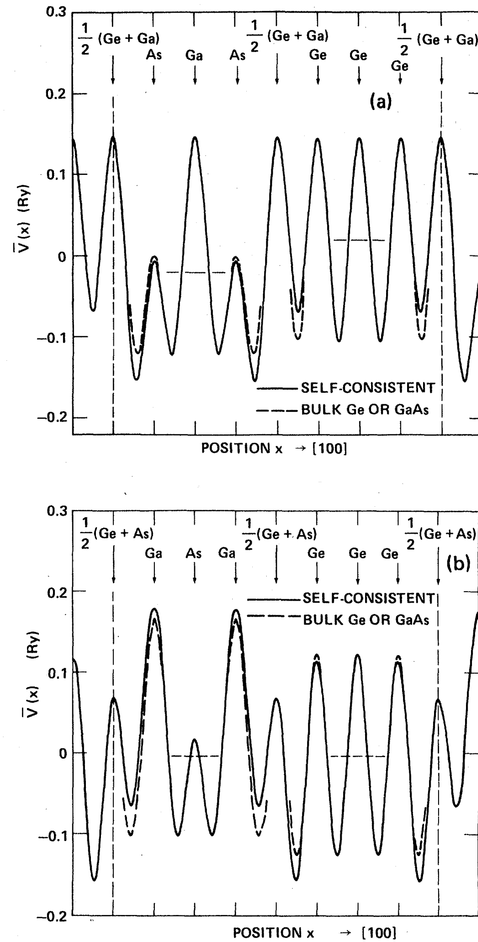

FIG. 7. (a) and (b). Variation of the self-consistent potential across the periodic supercell for the two models of (unrelaxed) interfaces shown in Fig. 3. The averaging of $\overline{V}$ is defined in the caption of Fig. 4 and in Eq. (1). Comparison with self-consistent calculations done on bulk Ge and bulk GaAs (broken lines) shows that in the regions far from interfaces the crystal recovers properties of the bulk. However, the average levels of the two bulk potentials (i.e., the zero of energy, broken horizontal lines) are shifted with respect to each other. These shifts are the consequence of "static" dipoles in the interface region which result from charge redistribution caused by formation of interface; they are responsible for band-structure discontinuities shown in Fig. 9.

as the charge densities and, namely, potentials are concerned. This agrees with the conclusions of Baraff *et al.*[7] However, we do not expect it to apply to the *individual* eigenenergies, i.e., accurate calculation of the energies of the bulk states or of any interface states which may require a larger cell.

We have given in Fig. 7, by broken horizontal lines, the average levels of potentials V_0 which correspond to the two separate bulk calculations [i.e., the zero of $V^{Ge}(\vec{r})$ and $V^{GaAs}(\vec{r})$]. The amount of the shift can be read out from Fig. 7: $\Delta V_0 \equiv V_0^{Ge} - V_0^{GaAs} = +570$ meV for the (unrelaxed) $\frac{1}{2}$ (Ge +Ga) interface and $\Delta V_0 = -33$ meV for the $\frac{1}{2}$ (Ge +As) interface; estimated uncertainty of these data is ± 20 meV. These values are mainly determined by the stoichiometry of the interface and change very little with relaxation. In the situation corresponding, e.g., to $\Delta = -0.018a$ (the "spurious minimum" of Fig. 6) they would become +0.42 eV instead of 0.57, and +0.06 eV instead of − 0.03.

These results may be compared with two types of experiments on Ge-GaAs interfaces. The most direct comparison is with x-ray photoelectron spectroscopy,[15] and the measurements[14] on various carefully controlled Ge-GaAs interfaces made it possible to ascertain the variation of the interface dipole with orientation of interface. As our calculations were limited to only one orientation, a direct comparison is impossible; nevertheless, if $\Delta V_0 = 0.25$ eV *calculated* in Refs. 9 and 11 is taken as reference value, then the experiments[14] would suggest $\Delta V_0 = 0.265$ eV for the (100) Ga interface and $\Delta V_0 = 0.215$ eV for the (100) As interface. These values are rather different from our predictions $\Delta V_0 = 0.57$ and −0.03 eV, respectively. We notice, however, that the same experiments suggest the ΔV_0 for (110) interface to be the average of the ΔV_0 corresponding to the two types of the (100) interface; indeed, the average of our calculations $\Delta V_0 = 0.27$ eV for the unrelaxed interface (as well as $\Delta V_0 = 0.24$ eV, corresponding to the spurious minimum of Fig. 6) matches the value of 0.25 eV found[9,11] for (110). Apparently, our predictions for ΔV_0 follow the experimental trend but exaggerate the magnitude. One possible explanation is the one given in Ref. 14, and, namely, that all (100) interfaces extend over more than one layer so that the experimental Ga- or As-rich interfaces may be only slightly different combinations of our two cases in which we have pure Ge-Ga and Ge-As interfaces.

Another source of experimental data are measurements of current- and capacitance-voltage characteristics of the interface. It is clear that knowledge of the relative raising and/or lowering ΔV_0 of the two bulk potentials (as displayed, e.g., in Fig. 7 for the unrelaxed situation) can be used for situating the relative position of the Ge band structure with respect to the GaAs band structure and, in particular, for deciding how the difference in the two band gaps is distributed between the valence and conduction bands—information which is of crucial importance for all technological applications. If the average potentials $\overline{V}^{Ge}$ and $\overline{V}^{GaAs}$ were assumed to be equal, our calculations would situate the top(s) of valence bands in both materials at the same level (within ≈ 6 meV). However, as we found that the $\frac{1}{2}$ (Ge +Ga) interface raises the Ge potential by 570 meV, we obtain $\Delta E_v \equiv E_v^{Ge} - E_v^{GaAs} = \Delta V_0 = 570$ meV which implies discontinuity of conduction bands $\Delta E_c \equiv E_c^{GaAs} - E_c^{Ge} = 190$ meV. (We take the position of the valence-band edges from our calculations; for the conduction bands we add the experimental gaps.) Similarly, for the $\frac{1}{2}$ (Ge +As)

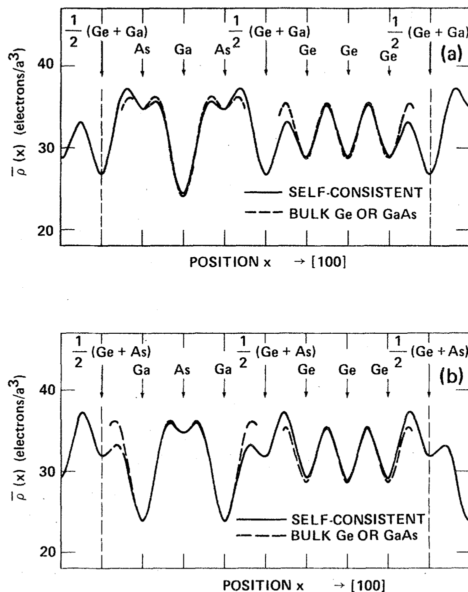

FIG. 8. (a) and (b). Variation of the self-consistent electronic charge density across the periodic supercell for the two models of (unrelaxed) interfaces shown in Fig. 3. The averaging of $\bar{\rho}$ is analogous to that defined in the caption of Fig. 4 and Eq. (1). Comparison with self-consistent calculations done on bulk Ge and bulk GaAs (broken lines) shows that in the regions far from interfaces the crystal recovers properties of the bulk. At and around the "central" layers (i.e., on the midway between two interfaces), the solid curve cannot be distinguished from the broken lines, showing that the two interfaces are not interacting and that charge density, potentials, and total energies of our superstructures [Figs. 3(a) and 3(b)] are a good approximation to isolated interfaces.

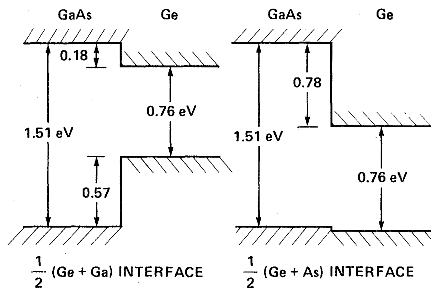

FIG. 9. Relative positions of the Ge and GaAs band structures for the two types of (unrelaxed) interfaces. Positions of the Ge and GaAs valence-band maxima are predicted by our model for the two averaged interfaces [viz., $\Delta E_v = \Delta V_0 \equiv V_0^{Ge} - V_0^{GaAs}$ of Figs. 7(a) and 7(b)]. The gaps are taken from experiment (Ref. 29).

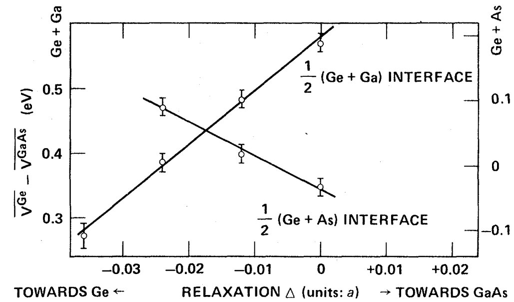

FIG. 10. Difference in average levels $\Delta V_0 \equiv V_0^{Ga} - V_0^{GaAs}$ of the bulk potentials $\bar{V}^{Ga}(x)$ and $\bar{V}^{GaAs}(x)$ as a function of relaxation. The values corresponding to $\Delta = 0$ (unrelaxed case) are those displayed in Figs. 7(a) and 7(b) and they reflect the static dipole of the interface. The slopes of the above lines determine the dynamic dipole of interface which may be expressed in terms of the interface's effective charges e_L^* given in the text.

interface we find $\Delta E_v = 30$ meV, $\Delta E_c = 780$ meV. This gives band schemes which are shown schematically in Fig. 9. They differ considerably from the simplified picture in which ΔE_c is estimated to be the difference of electron affinities of both materials: $\chi(\text{Ge}) - \chi(\text{GaAs}) = 4.13 - 4.07 = 0.06$ eV. [Data taken from Ref. 30 refer to the (110) surface of GaAs and the (111) surface of Ge.] Reference 31 (C-V measurements) reports the values $\Delta E_v = 0.55$ eV (room temperature), Ref. 32 gives $\Delta E_v = 0.56$ eV at room temperature, and $\Delta E_v = 0.60$ eV at 77 K. All these data are in excellent agreement with our value $\Delta E_v = 0.57$ eV for the $\frac{1}{2}$ (Ge + Ga) interface. However, the same Ref. 31 also gives an alternative value $\Delta E_v = 0.9$ eV (from another sample with different doping). In neither of the above measurements is the crystallographic orientation of interface specified. The uncertainty of the experimental results is still larger in the I-V measurements and Ref. 33 (p.110) reports studies on different samples showing ΔE_v varying from 1 to 1.4 eV. The considerable spread in all these data is partly due to an uncertainty in the identity of the interface in question; partly it reflects various assumptions in interpretation of the transport phenomena involved. Understanding of the latter is further complicated by differences in doping causing band bending and by the presence of interface states.

Besides the above-mentioned (static) dipoles the interface can also be characterized by "dynamic" dipoles which are the additional moments that arise from small displacements of the interface; these dipoles reflect the amount of electronic charge around the interface and its "adaptability" (i.e., which part will move rigidly with core and which part will redistribute). As we had to repeat all calculations for various relaxed positions of interface, we found that in the narrow limits of Δ all components $V(\vec{G})$ of the self-consistent potential behave as linear functions of the relaxation Δ. The same is true for the shift of the average potentials $\bar{V}_0^{Ge} - \bar{V}_0^{GaAs}$ which is plotted in Fig. 10. As our relaxation of interface by Δ may be viewed as longitudinal displacements the interface effective charge e^* can be identified with the *longitudinal* effective charge of lattice dynamics. We proceed exactly as in the case of bulk GaAs (Refs. 27 and 34), and use the same geometry in order to extract the charges from the shifts $\bar{V}_0^{Ge} - \bar{V}_0^{GaAs}$. We obtain from Fig. 10 $e_L^* = +0.13\ |e|$ for the $\frac{1}{2}$ (Ge + Ga) interface and $e_L^* = -0.082\,|e|$ for the $\frac{1}{2}$ (Ge + As) interface. These values are close to those which might be estimated by a simple averaging of the values in the bulk: As there is $e_L^* = 0$ in Ge and $e_L^* = 0.198\,|e|$ in GaAs (Ref. 35), and taking the signs[34] of the effective ions to be Ga^+, As^-, we would expect e_L^* to be close to $+0.099|e|$ for the $\frac{1}{2}$ (Ge + Ga) interface, and $e_L^* \approx -0.099|e|$ for the $\frac{1}{2}$ (Ge + As) one; this is the same sign and order of magnitude as e_L^* determined above from our self-consistent calculations. On the contrary, in the simple model of interface given in Ref. 14, where the bare ions are screened by a dielectric constant, we would get $e_L^* = -|e|/2\epsilon = -0.046|e|$ for the $\frac{1}{2}$ (Ge + Ga) interface and $+0.046|e|$ for the $\frac{1}{2}$ (Ge + As) one; the signs would be reversed.

Resulting self-consistent potentials determine also the eigenenergies of interface states predicted by our interface models. Although we do *not* expect all individual values to be exact (as discussed above) we have evaluated them for several wave vectors $\vec{k}$, in particular, for the

points J, K of the two-dimensional Brillouin zone.[8] At the J and K points there are states localized to the interface, however, no states were found with energies in the fundamental gap. The interface states will be treated more completely in the future work II.

V. CONCLUSION

In summary, we have presented calculations of the total energy and the charge density for the Ge-GaAs(100) interface. This is perhaps the simplest possible polar interface in which the question of the interface structure can be clearly posed. First, general considerations[13,14] show that the lowest-energy interfaces are "compensated," which can be accomplished only by mixing Ge and Ga or As atoms on the interface planes. However, the lowest-energy configuration—the stable stoichiometry—is not known. The object of our work is to predict the structure of the interface by calculating the energy directly and, from the resulting interface dipole and interface states, to predict the electronic properties of the interface. To do this we have considered the two simplest models of the compensated interface—ones in which the interface region is only one plane, on which there are either $\frac{1}{2}$ Ge and $\frac{1}{2}$ Ga atoms or $\frac{1}{2}$ Ge and $\frac{1}{2}$ As atoms. From these results we expect to be able to deduce properties of more extended interfaces as combinations of the two considered here.

In this paper we have presented the first calculations for such an interface using a fully self-consistent method. To our knowledge, it is also the first such calculation of the total energy for any interface. In order to carry out the computations efficiently we have divided the problem into two parts. The first part is described in the present paper where we have used the average-atom approximation for the interface plane. This greatly reduces the computations because it allows the interface plane to have the same periodicity as in the bulk. With this approximation we carried out tests (which are essential for all the later work) and showed it was feasible to minimize the total energy. The result was that the energy was minimum with the atoms very close (less than 0.01 Å) to the unrelaxed positions for both interfaces. The dipole discontinuities at the interface were found to be very different in the two cases: +0.57 eV (higher in Ge) for the $\frac{1}{2}$ (Ge+Ga) interface and − 0.03 eV for the $\frac{1}{2}$ (Ge+As) case. The average of 0.27 eV is very close to the value 0.25 eV found for the (110) nonpolar interface[9,11] (using the same pseudopotentials we have used). The values of the dipoles change little with relaxation and are determined primarily by the stoichiometry. Experiments have shown only small variations of the dipoles (in the same sense as given by our calculations but an order-of-magnitude smaller variation), which suggests that there is really only a small variation in stoichiometry in the experimental Ga- and As-rich (100) interfaces. We have also calculated the dynamic effective charge of the interface plane to be $e_L^* = +0.13|e|$ and $-0.082|e|$ for $\frac{1}{2}$ (Ge+Ga) and $\frac{1}{2}$ (Ge+As), respectively. No interface states were found in the fundamental gap, although several localized states were predicted in the valence band. We found a preference for the $\frac{1}{2}$ (Ge+As) stoichiometry [total energy by 360 meV per interface atom lower than with the $\frac{1}{2}$ (Ge+Ga) stoichiometry], however, it is not clear if this is a real phenomenon or artifact of our model of interface or merely a numerical consequence of averaging the atoms. In future work we will consider interface planes with real Ge, Ga, or As atoms instead of the average atoms. Our present results show that such calculations are feasible and should predict accurately the lowest-energy stable interface structure.

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