Revised charge redistribution on semiconductor III–V (110) surfaces

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Abstract
Using *ab initio* calculations we have been able to show that the traditionally assumed charge redistribution on III–V semiconductor (110) surfaces has to be modified. The use of *ab initio* local ionicity calculations confirms that the relative polarity of the cation and anion increases but that the valence charge density locally decreases on both types of site at the surface. The decrease in charge is continuous as a function of atom radius and the overlap with the core levels diminishes. For small radii the cation loses less charge than the anion, which gives a positive electrostatic shift of the surface core level relative to the anion. Hence the traditional explanation for part of the surface core-level shift in terms of initial-state electrostatic effects is not satisfactory. Instead we believe the observed core-level shifts to be related to screening effects stemming from the dangling bonds in the final-state picture.

1. Introduction

Attempts to achieve an understanding of the physical mechanisms behind the structural and electronic properties of semiconductors have attracted much interest during the last few decades, and the understanding of the bulk systems has been well established for more than a decade [1]. Since the III–V (110) surfaces are both non-polar and unreconstructed in nature, they soon became the focus of a large number of investigations both theoretically and experimentally. In the early 1990s, most of the III–V (110) surfaces were thoroughly theoretically investigated [2–4] and the electronic and geometrical structures well established.

For a long time one of the more fundamental results [5–7] for these systems has been that the cation loses electrons on the surface relative to the bulk situation while the anion gains electrons and so the polarity increases on the surface. This fact can be understood in terms of the dangling bonds: the anion bond is well known to attract charge, while the cation dangling bond gives up charge [2–4]. This is a well established result, and little questioned, despite an early parametrized calculation leading to a brief discussion of the lack of redistribution of charge density at the surface [8]. A more recent work that concentrates on comparing theory and scanning tunnelling microscopic (STM) results gives a detailed account of the different

decays of back bonds, bridge bonds and dangling bonds into vacuum [9]. It does not, however, treat the question of total charge density in the vicinity of the ion cores, or the 'ionic charges' (i.e. within typically 1–2 Å of the nucleus), although it provides vital information. Still, the indirect conclusion of the results in [9] supports a non-traditional charge redistribution. Hence it is of vital interest to closely investigate the charge profile of these surfaces by the means of modern theory. Since this includes ground states only, it can be implemented in a relatively straightforward manner too.

In this context it is also important to point out that the traditionally assumed charge redistribution is expected to account at least partly for the surface core-level shift (SCLS) observed [6, 7]. A modern theoretical investigation of the GaAs(110) 3d core-level shifts found reasonable agreement with the initial-state picture, while the final-state (relaxed) picture was not borne out [10]. Physically speaking, this is less than satisfactory, since the initial-state picture is based upon the assumption of frozen orbitals, i.e. one uses the ground-state configuration to calculate the SCLS, while the final-state picture includes the charge relaxation due to the core hole. This is all the more serious since the same numerical methods as were used in [10] returned very good results for the SCLS of the Ge(001) and Si(001) dimers [11] as well as the Sb overlayer in the Sb/GaAs(110) system [12] in the final-state picture. This is especially true when it comes to the relative shift of the different atoms: the results agreed well with the experimental ones within errors [11, 12], while the calculations based on the initial-state picture alone failed [11] as they should be expected to do. The conclusion reached by the authors in [10] is that the relaxation timescales must be widely different for the valence band electrons and the core hole. This is a reasonable explanation, but one that is complicated by the good results for the 3d SCLS of Ge [11] which, electronically speaking, is close to Ga and As. Also the results for the Sb/GaAs(110) system indicate a possible different source of error. Furthermore, is it important to point out that the SCLS is to a large extent made up of the geometrical factor in the Madelung potential [13]. Together with the traditionally assumed charge redistribution, this will result in relative shifts that are not physically consistent with the initial-state picture. When taking into account the proper charge distribution found below, however, the initial-state picture will be adjusted towards a physically sound situation, which explains the shortcoming of the initial-state picture in [10].

We show in this investigation of the GaAs(110), AlAs(110), GaP(110), InP(110) and InAs(110) surfaces that the traditional charge distribution is wrong and that both the anion and cation generally lose charge density. Only relative to each other do the anions become more ionic with the result that the local polarity increases. Using *ab initio* calculations we investigate both the spatial charge distribution and the atomic valence charges as functions of the radius and find significant differences for the surface atoms as compared to the bulk situation. Charge density is lost relative to the bulk for *all* radii, although the loss is modest close to the nuclei. This directly implies an electrostatic SCLS opposite to what was qualitatively assumed earlier. Instead we propose a time-dependent model where the filled dangling bond on the anion overcompensates for the electrostatic shift by means of efficient screening in the final-state picture. Detailed investigations of this final-state model are planned for the future and will be presented later.

2. Theory

All wavefunctions and energy eigenvalues were calculated *ab initio* within density functional theory [14, 15] (DFT) using the local density approximation (LDA) as implemented by Ceperley and Alder [16] and Perdew and Zunger [17, 18]. For the electron–ion interaction, fully separable, non-local pseudopotentials (PP) were used [19, 20], based on self-consistent

solutions of the relativistic Dirac equation for free atoms [20–22]. The calculations were performed using the plane-wave band-structure code fhi94md.cth[1], which is a version of fhi93cp heavily modified [23] as regards the computational methods. The geometries were described by the slab supercell method, using the theoretical lattice constants for GaAs (5.56 Å), AlAs (5.61 Å), GaP (5.38 Å), InP (5.87 Å) and InAs (6.06 Å). A plane-wave cut-off energy of 16 Ryd and 12 special Monkhorst–Pack k-points in the irreducible Brillouin zone (IBZ) were used to sample the wavefunctions in the supercells, corresponding to 96 points in the full zone. For the bulk calculations we used the same parameters with the exception of the number of k-points: we employed 19 and 125 points in the IBZ and the full zone respectively.

Slabs consisting of eleven atomic layers, suspended in eight layers of vacuum, modelled the (110) surfaces. All atomic positions were completely relaxed. The equilibrium geometries were considered established when all forces were smaller than 0.005 eV Å^{-1}, corresponding to an estimated numerical uncertainty of $\leqslant$0.05 Å. The charge was integrated inside the central vacuum region and was found to be negligible. Both the electrostatic and full potentials go rapidly to zero in the vacuum region. To explicitly test the quality of the slabs, we investigated the partial density of states (PDOS), the effective potential, the electrostatic potential and the electronic charge distribution within each slab. Inside a central region of five atomic layers, all of these characteristics took on their ideal bulk values within the numerical uncertainty, which clearly indicates the quality of the model. The atomic positions of the five most central planes were furthermore found to coincide with the bulk positions within numerical uncertainty, which lends further credibility to the results.

The PDOS was produced by extracting each wavefunction $\phi_{k,\varepsilon}(r)$ for a certain eigenvalue ε at the specified k-point from the total wavefunction. By projecting the plane-wave representation of $\phi_{k,\varepsilon}(r)$ onto atomic orbitals, the s, p and d contributions from each atom were subsequently found and the charge taken as the sum of the integrated s-, p- and d-electronic charges. For every calculation except the reference computations carried out to test the slab quality, the atomic orbitals were cut off at $|r| = r_0$ to ensure that the projection only took place inside the spheres centred at each atom with radius r_0. By repeating the calculations for different values of r_0 we were able to interpolate smooth results for the atomic valence charge $C(r)$ with a numerical accuracy better than 5‰ of the absolute value. Comparison between the charge results for the bulk calculations and those for the middlemost atomic planes of the slabs displayed a difference of well below 1‰. The remaining numerical details were identical to those in reference [24]. Special care was taken to ensure that the s, p and d contributions constituted the entire charge for a given radius in the case of the surface atoms since they tend to lose charge relatively to the bulk. To test this, we considered the surface As and Ga atoms of the GaAs(110) system and integrated the total charge (no s, p and d resolution) in real space for different radii (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 Å) using a Monte Carlo-based method with ten million sampling points in each integration. The charge-density values were three-dimensionally interpolated from the real-space charge grid using a second-degree 3D Taylor expansion. All differences were well within numerical errors for all radii. Hence any charge redistributions found should be expected to be of physical nature.

3. Results and discussion

As noted above, the geometrical and electronic structures of the different III–V (110) ideal surfaces are very well known today. The topmost anion moves outwards, while the cation

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[1] fhi94md.cth is based on fhi93cp, purchased from the Computational Physics Communications Library in 1995. While the basic computational physics is the same, the changes of computational nature are extensive.

in the surface plane is displaced inward in order to achieve an effective sp hybridization; see figure 1. The dangling bonds of the atoms in the first atomic plane result in surface states (resonances) in the vicinity of the fundamental bandgap while back bonds and the anion s orbitals produce more low-lying surface states and resonances; see e.g. [2–4, 25]. Because of the excellent knowledge of these systems, however, we will not pursue the presentation of these surfaces, although the structural parameters are included in table 1 for comparison.
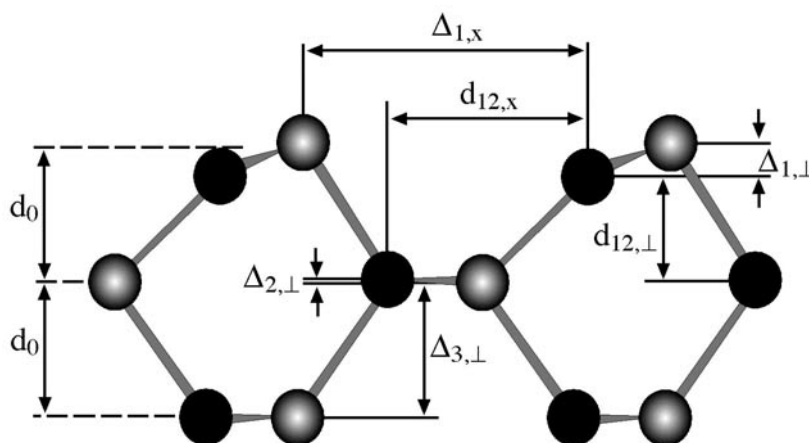

Figure 1. The principal atomic geometry of the relaxed III–V (110) surfaces. Black circles represents the cations and grey circles the anions.

Table 1. The geometrical parameters of the different III–V (110) surfaces as defined in figure 1. All values are in Å.

Surface	$\Delta_{1,x}$	$\Delta_{1,\perp}$	$\Delta_{2,\perp}$	$\Delta_{3,\perp}$	$d_{12,x}$	$d_{12,\perp}$
GaAs(110)	4.38	0.67	0.10	1.95	3.18	1.47
GaP(110)	4.26	0.58	0.08	1.88	3.06	1.44
InP(110)	4.62	0.66	0.11	2.04	3.34	1.57
InAs(110)	4.77	0.74	0.13	2.09	3.48	1.57
AlAs(110)	4.46	0.71	0.11	1.94	3.26	1.41

Turning to the more specific results for the valence charge, we find that both the cation *and* the anion locally lose charge at the surface; see figures 2(a), 2(b) and 3. It should especially be noted that the spherically integrated charge is smaller for *all* radii. This should also be intuitively expected from the diminished overlap with surrounding atoms, the expansion of orbitals into vacuum and the geometrical change; see below for details. The relatively large insensitivity furthermore implies that the qualitative result of lost charge density for both types of surface ion is valid regardless of the exact definition of 'atomic radii'. Although this is not a 'true' loss of charge—only of local charge density—this will still directly affect the SCLS. This is so since within the initial-state picture, the charge distribution is considered to be frozen and no relaxation is taking place. Charge 'lost' to the background, such as interstitial charge and charge in orbitals extending into the vacuum, will still affect the absolute values of the SCLS through the Madelung potential. Because of the $1/R$ dependency, it will, however, lose part of its contribution; charge moved e.g. four times its normal distance from the core will lose 3/4 of its effect on the local electrostatic potential. At the same time, the difference in effect on
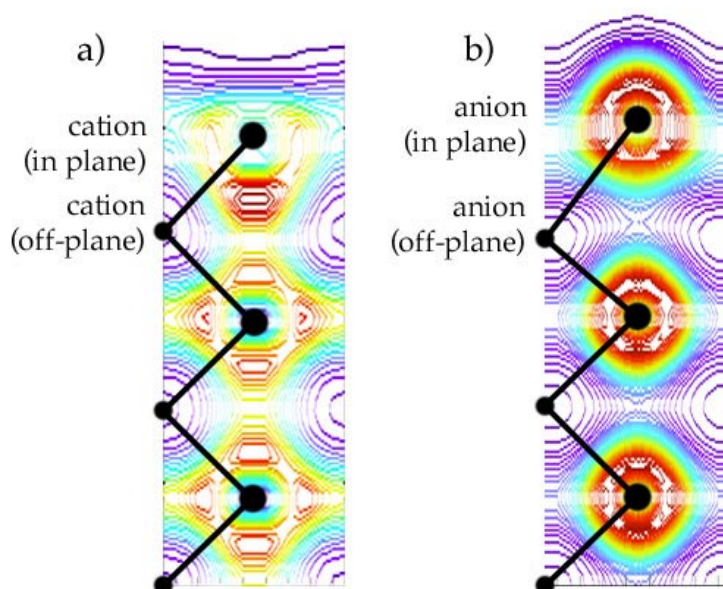
Figure 2. A contour plot of the total valence charge distribution of GaAs(110) for (11$\bar{1}$) planes (i.e. planes perpendicular to the surface and the surface Ga–As bond) cutting through: (a) the cations; (b) the anions. Units are 1/40 of the bulk peak value in both cases. Warm colours indicate higher values. The results for the other systems are very similar.

the cation and anion from that particular charge will be drastically reduced since the relative difference in distance between the charge at hand and the different cores grows smaller. Thus it should be clear within the initial-state picture that lost (redistributed) charge density inside the 'atomic spheres' directly affects the electrostatic core-level shifts in a way similar to a true loss of charge. This similarity should be understood from now on.

Because of this effect, the electrostatic core-level shifts will work in the opposite direction to what is usually assumed for the anions. The findings also properly explain the relatively larger error of the Ga 3d SCLS within the initial-state picture in [10]. For small and modest radii, the charge-density loss is substantially smaller for the Ga ion than for the As ion; see figure 3. Adding this electrostatic effect to the surface Madelung potential for fixed charge [13] (i.e. calculated before charge redistribution) yields a higher-situated 3d level in the Ga ion than first expected, which is exactly the result of [10]. Hence the energy of the emitted photon will be lower than predicted from the cation, and on the high side for the anion. See figure 4 for a sketch of the different contributions to the core-level shifts in the case of the anion.

From the point of view of valence charge, the effect is the reverse though. Using any of the common ionic radii, the cations lose more electrons than the anions relatively speaking and the polarity increases. Although the concepts of ionic/atomic charge, polarity and ionicity are somewhat vague, a systematic use of the definition in [24] yields a clearly increased local ionicity at all III–V (110) surfaces; see table 2. This is so since the cations outside the core region tend to redistribute more charge than the anions relative to their initial valence number, something that can be directly connected to the surface-state transfer. Hence the statements of increased polarity of the surface ions turn out to be correct, although in a different way to what was originally envisaged [5–7]. It is very important though to point out that both types of ion *lose* charge density at any distance from the nucleus and that the polarity increase is only
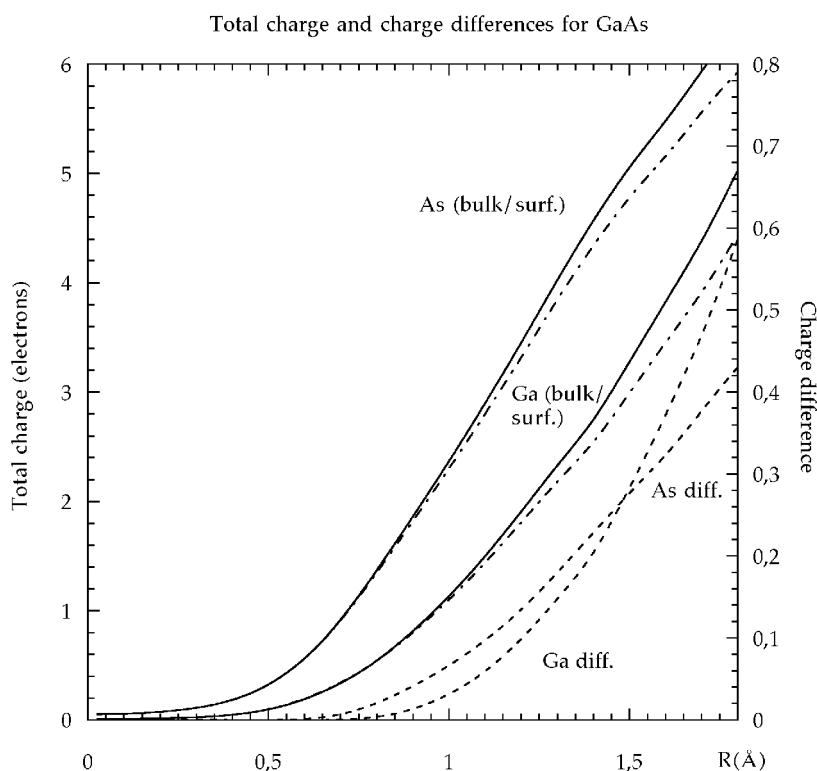
Total charge and charge differences for GaAs

Figure 3. The total charge as a function of the radius R for the Ga and As atoms in bulk GaAs (full lines) and in the surface top layer of GaAs(110) (dash–dotted lines). The differences in total charge are also displayed (dashed lines). The results for GaP, InP, InAs and AlAs are very similar.

relative. Differently stated, we do not find any region in space around the surface ions where the total charge density (i.e. all states included) is larger than in the corresponding bulk case, taking the numerical uncertainty into account. Also in absolute numbers there are only one or two regions 0.1–0.2 Å wide for the different systems where the charge density is comparable to that of the bulk. These findings are true outside as well as within the pseudopotential cut-off radii (between 0.8 and 1.1 Å) for the different species. Neither is it trivial in any way that surface-state charge redistribution should overcome the difference in charge density due to the movements of the ions (see below). This does, however, imply that the vacuum leakage, and not the geometrical expansion, is the dominant factor for the charge loss of the anion.

Looking more carefully at the spatial distributions (see figures 2(a) and 2(b)), we notice essentially three effects: vacuum leakage, geometrical compression/expansion and charge exchange in the surface states. Vacuum leakage—or, more rigorously formulated, expansion of orbitals into vacuum as compared to the extension into the bulk—has been well known for a long time and generally tends to diminish the local charge density at the surface, something that is clearly seen in figure 2. Alternatively put, any atomic layer inside the bulk will experience overlap of charge with atomic layers on both sides, while the surface layer only has neighbouring atoms on one side. Hence the charge density of the surface atomic layer should generally be expected to be less than in the bulk case. Furthermore, different electronic states experience different vacuum leakages, something that should be expected on the basis of e.g. the directionality and character of the different states. In principle, it is not possible in a
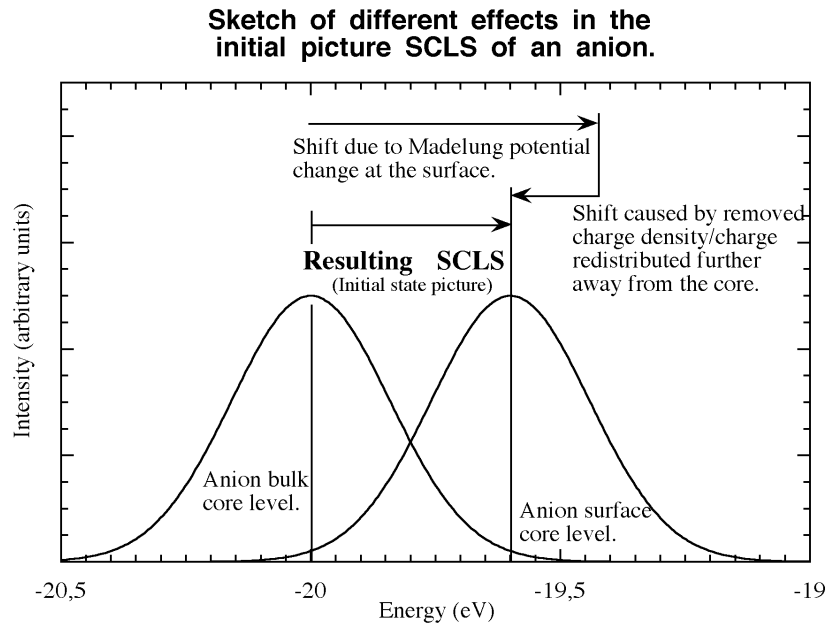
Sketch of different effects in the initial picture SCLS of an anion.

Figure 4. A sketch of the different contributions to the core-level energy for an anion in the bulk and at the surface respectively. Note that the Madelung shift indicated here is based on a fixed anion charge; see reference [13].

Table 2. The ionicity and ionic radii for the bulk and surface atoms respectively, together with the polarity ratio (PR, in parentheses) and total charge (definitions in [24]). The radii are in Å and the charge and ionicity in electron charges; the numerical uncertainties are ±0.01 Å and <5% respectively. The ionicity δ_i equals the normalized charge transfer from cation to anion; see [24] for details.

System	δ_i (PR)	Cation R_i	Anion R_i	Cation charge	Anion charge
Bulk					
GaAs	0.32 (1.98)	1.43	1.58	2.67	5.30
GaP	0.36 (2.03)	1.40	1.50	2.64	5.36
InP	0.47 (2.16)	1.52	1.62	2.48	5.35
InAs	0.41 (2.09)	1.56	1.67	2.58	5.40
AlAs	0.28 (1.94)	1.47	1.56	2.76	5.36
(110) surface top layer					
GaAs	0.33 (2.00)	1.43	1.58	2.53	5.05
GaP	0.39 (2.06)	1.40	1.50	2.49	5.14
InP	0.49 (2.19)	1.52	1.62	2.33	5.10
InAs	0.44 (2.12)	1.56	1.67	2.42	5.13
AlAs	0.31 (1.97)	1.47	1.56	2.59	5.10

plane-wave method to assign different electronic states to specific atoms, but by investigating the weight on the specific atoms at each k-point—a standard method within the field—we have been able to assign the different states with high accuracy. In this particular case we find that

the back bonds, surprisingly enough, in fact seem to extend further out into the deep vacuum than the surface states of the corresponding species. The plane-wave assignment renders this conclusion somewhat weak though, but the result is consistent with the investigation in reference [9]. It should be pointed out though that the absolute charge far into the vacuum is relatively small. This effect is combined with a leakage/extension of the back-bond charge into the bulk, which is similar in size to the vacuum leakage. The back bonds for the cations and anions are in addition of the same type, and since the anion (cation) part of the back bond is proportional to its total valence charge, so also will the charge-density loss from the back bond be in a first approximation. Consequently, this properly explains the relatively similar loss in total charge due to leakage relative to the bulk valence charge for cations and anions.

We also find the local valence charge to be compressed and expanded beneath the cation and anion respectively. That is, the charge density is locally higher beneath the pushed-down cation and locally lower beneath the uplifted anion; see figure 2 for GaAs(110). To investigate this further in detail and prevent any dependency on definitions, we integrated all charge below both cation and anions in cylindrical cones for different angles and radii. Although the absolute numbers were dependent on the exact choice, of course, the qualitative results for compressed (=locally increased for a given radius) and expanded (=locally decreased) charge remained the same for all choices ($10°$, $20°$, $30°$ and $45°$ and 1.0, 1.5 and 2.0 Å.) These results should clearly be expected from simple chemical and electrostatic considerations. While the chemical bonds approximately locate the electrons, the changed electrostatic situation forces a change in local density. This is true both for the vacuum leakage and for the compression and directly implies that while the number of electrons in the bonds is conserved, the shape of the orbitals might be drastically changed at the surface.

Finally we notice a charge transfer (away from the bulk charge ratio) from the cation dangling bond to the dangling bond of the anion, much in agreement with earlier findings [2–4, 25]. The surface band transfer partly depletes the volume above the cation of charge, while it adds extra charge to the upper end of the anion; see figure 2. It is, however, not enough to overcome the loss of charge density due to expansion and vacuum leakage. Thus the total valence charge density of the surface anion is generally less on a local level compared to the bulk situation. Hence it is of utmost importance for the knowledge of the chemistry of the III–V (110) surfaces to include *all* charge, and not only the orbitals connected to the surface states, when investigating these systems.

It should be noted at this stage that the surface atoms do not lose *charge*—only local *charge density*. That is, the charge is redistributed in such a way that electronic charge becomes located further away from the surface ions than in the corresponding bulk case. Just taking the actual charge transfer between dangling bonds into account (i.e. assuming a relatively static distribution of the remaining electrons) may explain earlier statements in the literature. From the viewpoint of the initial-state picture of the SCLS, this finding is equivalent to a true loss though. The overlap with the core levels will be diminished and the average charge be located further out from the core. This directly implies a downward shift of the core levels, just as if some of the charge had been lost. It is, however, important to point out that this is a qualitative result and not a quantitative one. Calculating the exact effect on the core levels within DFT is not entirely to be recommended, though. This is so since DFT-LDA (as well as GGA) is well known not to reproduce energy levels very accurately in the first place (an error of ± 0.5 eV is common, i.e. of the same size as the SCLS itself). Hence it is of little use to calculate the core energy levels within this approach. DFT does, however, return the charge density with a very high accuracy, at least outside the pseudopotential cut-off radius, which ensures that the qualitative results found here are physically sound and should be valid generally. They also in principle form the basis for a possible calculation of the exact core

levels within the Hartree–Fock approximation if one uses the frozen valence charge found here. The use of such a calculation is quite limited though since the direction of the additional shifts caused by the charge distribution found in this investigation is opposite to what is observed experimentally. Hence the initial picture itself at least partly fails when confronted with these new findings. This is—beside the exact electronic nature of these surfaces—one of our most important findings in this investigation.

Despite the fact that we have only treated the detailed charge distribution of the ground state (initial-state picture) of the different III–V (110) surfaces, we would like to try to address the observed problems in the final-state picture and suggest future investigations. In the initial-state picture the different surface effects result in an electrostatic shift in the opposite direction; see above and figure 4. In the final-state picture, however, the core hole will leave the atom positively charged. In the bulk the valence charge is bound relatively firmly spatially in the bonds between the ions, while at the surface the dangling bond should be expected to be more free to move quickly and screen the core hole much more efficiently. In this respect the total charge—although initially distributed 'far' from the anion—will contribute to the SCLS by overcompensating for the screening relative to the bulk situation. Since the vacuum leakage is relatively limited for the dangling bonds compared to the back bonds [9], there will most probably be different timescales for the electronic relaxation. This would explain the problems in the final-state-picture investigation in reference [10]. It is also important to point out that the topmost III–V (110) surface layer forms a relatively strong dipole due to the tilted geometry and ionic nature of the surface atoms. Although a definite charge transfer is also taking place in the topmost layer in homopolar substances like Si and Ge [11], or the absorbed layer of Sb [12], the effect is smaller in these cases since the atoms are themselves neutral in the bulk and on other surfaces. Hence the suggestion of different relaxation timescales [10] for the core hole and the valence charge can be put on a sound physical footing. If the dangling-bond charge, but not the charge lost from the back bonds to vacuum, has time to relax, the SCLS will generally be lower, and this is especially so for the cation since its dangling bond is virtually empty. Relaxing all charge thus gives an unrealistically high value [10].

Since time-dependent electronic relaxation is extremely hard to perform, we would like to end by suggesting the following qualitative theoretical investigation. Starting with the converged ground-state electronic charge distribution, one introduces a 3d core-level hole. In practical terms this means that the nine remaining d electrons have to be included as 'extra valence electrons' in the calculation in order to include and follow the total electrostatic effect. Having artificially fixed the ground-state s–p valence charge distribution (i.e. identical to the one with ten d electrons with one subsequently removed), it is then possible to gradually relax the electronic system and monitor which electronic states move in to screen the hole first. At each step the 3d core-level shift will also be observed. Although no exact timescale will be established, such a calculation would settle the question of in what order the different valence states will screen the hole and how this affects the core-level shift. Assuming a theoretical/experimental fit for the core level, it would be subsequently possible to approximately determine at which stage the filling of the core hole interrupts the process. A very high accuracy is necessary, however, including a full accounting for the electrostatic effects, in order to make the results quantitatively reliable. Requiring extensive computing power, this will involve the use of a large surface cell as well as additional d electrons being included in the calculations. (Note that a 1×1 surface cell will correspond to 1 ML of excited ions that evidently may affect each other via the s–p valence charge.)

Although extremely approximate, the suggested calculation would give valuable insight into the photoemission process and the detailed mechanisms of the SCLS. Our intention is to implement an investigation of this type and present the results as soon as possible.

4. Conclusions

We have found that the total valence charge density is lower at both the cation *and* anion sites at the surface—contrary to general belief—something that directly implies an electrostatic core-level shift of the wrong sign in the initial-state picture. Only the relative polarity increases due to differences in the exact charge loss. The detailed charge redistribution found also properly explains the recent theoretical findings for the initial-state picture, and a complementary explanation of the final-state-picture results is advanced. A possible test calculation is suggested in addition. These are novel aspects of these otherwise well investigated systems, and revise the physical picture of the III–V (110) systems.

Acknowledgment

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