

Theory of the Chemical Shift at Relaxed (110) Surfaces of III-V Semiconductor Compounds

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Surface core-level shifts for many semiconductor compounds are calculated in a tight-binding treatment, and with a local-charge-neutrality approximation. Both ideal and relaxed (110) surfaces are considered. Taking into account first-layer atomic displacements strongly modifies the values of calculated surface core-level shifts and provides a good agreement with experimental values.

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Some years ago photoemission experiments have allowed the determination of core-level binding energies on IV^{1,2} and III-V³⁻⁵ semiconductor surfaces. The observed shifts for covalents (Si) are very sensitive to surface orientation and reconstruction. For the (110) surfaces of III-V compounds experiments yielded shifts of 0.2 to 0.4 eV towards higher (lower) binding energies for surface cations (anions). The purpose of this paper is to present a calculation of these core-level shifts. We consider eight different III-V compounds and study the influence of surface reconstruction. Our theoretical approach is based on the tight-binding approximation. We first propose a simple molecular picture which allows a clear physical understanding. We then present a complete calculation performed on the basis of a local-charge-neutrality condition.

First, let us describe the physical origin of the sign and order of magnitude of the core-level shift. For this we use the molecular or bond orbital^{6,7} picture of these materials. The model consists of pairs of sp^3 hybrids of energies E_C (cation) and E_A (anion) belonging to the same bond and coupled by a hopping integral V . In this way one gets the usual bonding and antibonding states. The contribution of each bond to the electron population of the atom is $1+f$ on the anion and $1-f$ on the cation, where f characterizes the ionicity and is given by

$$f = [(E_C - E_A)/2] / \{[(E_C - E_A)/2]^2 + V^2\}^{1/2} \quad (1)$$

(we can note that f is always positive and lower than unity).

In the same picture the creation of the nonpolar (110) surface corresponds to breaking such bonds, leaving an array of alternate cation and anion dangling bonds. The neutral surface corresponds to two electrons per pair of dangling bonds. As $E_C > E_A$ these two electrons will populate the anion dangling bonds so that the excess population δn_A on the anions relative to the bulk will be equal to $2 - (1+f)$, i.e.,

$$\delta n_A = 1 - f \quad (2)$$

with the opposite $\delta n_C = -\delta n_A$ on the cations.

This electron transfer induces shifts $U_A \delta n_A$ and

$U_C \delta n_C$ of the anion and cation valence intra-atomic levels. From electrostatic arguments one can show⁸ that the core levels will experience a shift of the same sign and order of magnitude. The Coulomb terms U_A and U_C are the difference between an intra-atomic contribution and an interatomic one which, in a point-charge limit, is given by the surface Madelung term. As expected, we have found that the numerical values of U_A and U_C are always positive and lie between 2 and 4 eV depending upon the spatial extension of the atomic orbitals. Thus we get a positive shift $U_A \delta n_A$ on the anions and the reverse on the cations in agreement with experiment. With previously published values of f (Ref. 7) we get $\delta n_A \sim 0.4$ so that the order of magnitude of the shifts should lie between 0.8 and 1.6 eV. These values are much larger than measured ones (~ 0.3 to 0.4 eV) but they will be reduced by screening effects (discussed below) which will bring them into the correct range.

Of course this treatment is too simple to be really quantitative but it provides the basic understanding of the chemical shift for the (110) faces. It shows clearly that these shifts are not directly related to the net charge on the anion and cation in the bulk material [in the simple molecular model these are $1-4f$ and $-(1-4f)$, respectively, whose sign changes for $f=0.25$ while Eq. (2) always keeps a constant sign, in agreement with experiment]. This conclusion contrasts with the one of Mönch,⁹ who related chemical shifts to bulk interatomic charge transfers.

We now describe the complete tight-binding treatment performed for eight semiconductor compounds. We use the first-nearest-neighbors tight-binding parametrization of Vogl, Hjalmarson, and Dow.¹⁰ To study the effect of surface reconstruction we use a d^{-2} scaling law (where d is the interatomic distance) for the interatomic parameters, as proposed by Harrison.¹¹ We choose the atomic geometries of zinc-blende semiconductor surfaces reviewed in by Kahn¹² and, for simplicity, only consider displacements of atoms belonging to the surface plane. We also assume that the Coulomb potential due to charge redistribution has only the diagonal element on each atom. Finally, we calculate the atomic charges near the surface by using a decimation technique^{13,14}

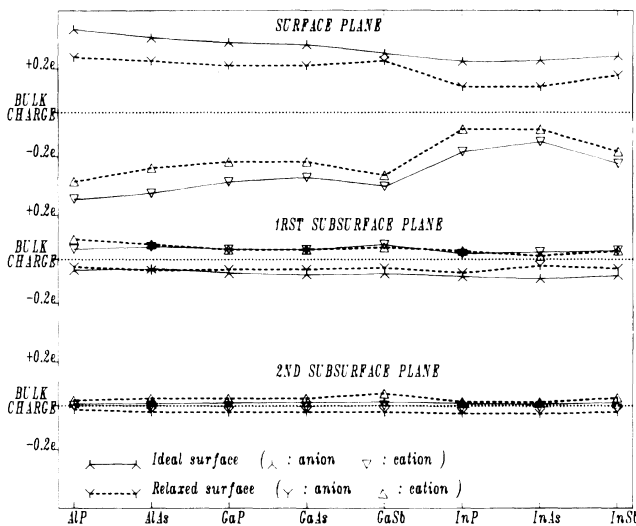


FIG. 1. Excess charges (relative to bulk charges) on the anions and cations for the first three surface planes.

which is the best suited to the required accuracy (better than $0.01e$). To determine the surface core-level shifts we start from a non-self-consistent calculation in which unmodified bulk parameters are used. The charges calculated on each type of atom of the surface and the first two inner planes are plotted in Fig. 1. One finds that the charge disturbance is mainly localized in the surface plane and that it is reduced by the reconstruction. Furthermore, the net excess charge relative to the bulk for surface anions and cations keeps a constant sign independent of the sign and magnitude of the bulk net atomic charges, confirming the simple picture discussed above.

For calculating the core-level shift we use a "local-charge-neutrality condition" identical to the one introduced in the determination of band offsets at heterojunctions.¹⁵ We consider that the "exact" intra-atomic potential is close to the value which ensures local atomic

charges equal to the bulk ones (i.e., local neutrality with respect to the bulk). In principle, this approximation is best when the screening is strong, i.e., essentially for long-wavelength perturbations. This does not seem to be the case here since the charge perturbation is localized on the surface plane and, furthermore, is changing sign from anions to cations. However, it is periodic along the surface and can be expanded in Fourier series involving the reciprocal lattice vectors \mathbf{K}_{\parallel} of the surface plane. In view of the rapid decrease of the atomic orbital form factors the dominant terms in such an expansion correspond to the smallest reciprocal vectors, i.e., $\pm(2\pi/a)(1,0,0)$. This screening effect will mainly correspond to a reduction by a q -dependent dielectric function $\epsilon(q)$ with q close to $2\pi/a(1,0,0)$. This effective dielectric constant turns out to be of order 3 to 4, much smaller than the long-wavelength value. To estimate the accuracy of a local-charge-neutrality criterion under these conditions one can use the arguments given in Ref. 15 to show that the true shift is equal to the zero-charge value minus a corrective term $\Delta_b/\epsilon(\epsilon-1)$, where Δ_b is the "bare" or non-self-consistent shift and ϵ the effective dielectric constant discussed above. For the anions Δ_b is given by $U_A\delta n_A$. With $\delta n_A \sim 0.2$ (Fig. 1) and the values of U_A and ϵ quoted before we get a corrective term smaller than 0.1 eV. Thus we can conclude on general grounds that the zero-charge approximation will overestimate the core shifts by an amount smaller than 0.1 eV.

The predicted core-level shifts are reported in Table I for the unreconstructed and reconstructed surfaces and compared to available experimental data. The predicted values have the correct sign and order of magnitude. They are slightly overestimated which confirms our discussion of the local neutrality approximation. The core shifts do not depend strongly upon the material, their absolute values always lying in the range 0.2 to 0.4 eV (except for one theoretical prediction of 0.69 eV for AlP).

In conclusion, we have developed a simple model and a full calculation of the core-level shifts at the (110) surface of III-V zinc-blende compounds. The complete theory can be readily extended to other cases, such as

TABLE I. Calculated surface core-level shifts for anions, ΔE_A , and cations, ΔE_C . Results of photoemission experiments (Refs. 3-5) are also reported.

Compound	Theory, ideal surface		Theory, reconstructed surface		Experiment	
	ΔE_A	ΔE_C	ΔE_A	ΔE_C	ΔE_A	ΔE_C
AlP	0.68	-0.63	0.69	-0.30	X	X
AlAs	0.53	-0.47	0.40	-0.33	X	X
GaP	0.54	-0.60	0.43	-0.41	X	-0.28
GaAs	0.43	-0.58	0.40	-0.38	0.37	-0.28
GaSb	0.28	-0.40	0.41	-0.35	0.30	-0.36
InP	0.11	-0.56	0.00	-0.34	X	-0.3
InAs	0.06	-0.58	0.28	-0.31	X	-0.26
InSb	0.19	-0.46	0.22	-0.28	0.29	-0.22

ideal covalent surfaces where charge transfer mainly occurs between the first and second surface planes. It can also be applied to Si(111) 2×1 where there are again two inequivalent atoms per unit cell in the surface plane. This is currently being studied.

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