

Ionic-charge modification at the surface of polar crystals

R. E. Watson and J. W. Davenport

Physics Department, Brookhaven National Laboratory, Upton, New York 11973

(Received 6 December 1982)

A simple variational principle has been applied to obtain a bound on the change in ionic charge of a polar crystal between the surface and the interior. Central to the estimate is the assumption that the energy involves terms analytic in the ionic charge q and that these may be treated as a sum of Madelung, intra-atomic, and interatomic (overlap and hybridization) contributions. The Madelung terms are calculated explicitly, the intra-atomic contributions are obtained from the following paper [Phys. Rev. B **27**, 6428 (1983)], and the change in interatomic terms on going from the bulk to the surface is estimated by scaling with coordination number. The results do not replace detailed quantum-mechanical calculations but they are simple computationally, and they suggest trends in the competition between the Madelung potential, which encourages ion charging, and hybridization, which discourages ionic charging, both at the surface and in the interior of a crystal. Nonpolar surfaces are of principal concern but one polar surface is considered indicating that the charge disturbance penetrates much further in from the surface than it does in nonpolar cases where the effect is largely limited to the first layer of atoms.

I. INTRODUCTION

Ions in the surface of a polar crystal are in general charged differently from ions in the interior. Traditionally, it has been believed that the crystalline potential and bonding effects which drive the crystal to be ionic in the first place are weaker at the surface and therefore the ionic charge at the surface is less. In any case, such charge differences, surface multipole effects, and surface reconstruction (which is often observed to occur) influence the physical and chemical properties of surfaces; for example, valence electron energy levels are shifted, leading to "band-bending" effects. Work functions are also affected by such factors and, while data is sparse, it would appear that work functions change by tenths of an electron volt from one surface to another on some crystals while calculation indicates^{1,2} that the changes would most often be of the order of 1 eV, i.e., an order of magnitude greater than experiment, in the absence of such surface modifications. Concerning the change in ionic charge at the surface, it has been recognized that the Madelung potential at an ion site in the crystal surface differs from the potential at the site of a like ion in the bulk. This difference is a significant driving force encouraging a difference in charge states at the surface. In a previous Communication³ we considered the modification in charge which would arise if all intra-ionic and interionic interaction terms, other than the Madelung term, held to their bulk values at the crystal surface. This was done for nonpolar surfaces,

where individual planes of ions are neutrally charged, and a bound was found indicative that the fractional reduction in ionic charge,

$$\frac{\Delta q}{q} \equiv \frac{q(\text{surface}) - q(\text{bulk})}{q(\text{bulk})},$$

is less than half in magnitude. The purpose of this paper is to include other terms in the model and to consider the case of polar surfaces.

Charge transfer attends compound formation, and the transfer makes a substantial contribution to the heat of formation when the heat is large. Unfortunately, there is no unique, well-defined, value for the charge q associated with the transfer⁴ and different estimates, for a particular polar compound, tend to vary by a factor of 2 or greater. It is not the purpose of the present paper to estimate q but instead, granting that there is ionic character in the crystal bulk, to estimate whether that character is enhanced, or as is more traditionally thought, reduced at the surface. In doing this, Δq will be estimated as a function of q , including the competition of Madelung, intra-atomic, and hybridization terms. Certain factors, such as the transfer which would attend the occurrence of surface states, are neglected.

Central to these estimates is the assumption that the free energy of a crystal and of its face is an analytic function of the charge q of the ions. This assumption, which may be viewed as a mean field theory approach, is not necessarily valid in systems where electron correlation effects are important. Also, there must be substantial hybridization and

overlap of states on the cation and anion so that the charge on either one is a continuous variable. In the limit of no hybridization the charge on the anion would be 0 or -1 . In such a case the surface could be neutral while the bulk is ionic. Hybridization allows for a smooth interpolation between these two limits. The model does not replace detailed quantum-mechanical calculations for surfaces but it has the virtue of yielding relatively transparent results which are often of a general nature. Granted the above assumption, the change in energy associated with a set of anions and cations changing the magnitude of their charge from q to $q + \Delta q$ is

$$\Delta E = \Delta q E_1(q) + (\Delta q)^2 E_2(q) + O((\Delta q)^3), \quad (1)$$

where E_1 and E_2 are made up of Madelung potential energy, intra-atomic, and interatomic overlap and hybridization terms which, it is assumed, can be treated additively. If the charge in the bulk of the crystal is q , then, for the bulk, E_1 is zero and E_2 is greater than or equal to zero from variational considerations. Knowing the linear and quadratic Madelung terms for the bulk, one knows the linear and has a bound on the quadratic contributions from the other terms. Assuming the latter to keep the same values at the surface and by calculating the Madelung terms for the surface, Eq. (1) can be used to estimate the bound on Δq . This was shown previously³ to yield

$$0 > \frac{\Delta q}{q} > -\frac{1}{2}$$

for a type of nonpolar surface. The derivation of this is repeated in Sec. II. In the present paper we extend the calculations by estimating the intra-atomic terms in the energy, employing the fits of atomic spectra which are made in the accompanying paper. This yields an "electronegativity" term which is linear in q and a quadratic term which resists charging and which is often overlooked in considerations of charge transfer. Given explicit estimates of the intra-atomic and Madelung terms entering Eq. (1) for either the surface or the bulk, the remainders, associated with overlap and hybridization, are assumed to scale with the number of nearest unlike neighbors (i.e., the coordination number). As described in Sec. II, this allows bounds to be estimated for $\Delta q/q$ which are now specific to a particular compound, to the atomic configurations of the constituents, to the class of valence electrons assumed to be involved in the charge transfer, and to the value of q appropriate to the bulk material. Results are reported in Sec. III for the unreconstructed (110) and (100) surfaces of the NaCl structure, the (110) of zinc blende, and the (110) of CsCl and for a

reconstructed zinc-blende (110) surface characteristic of a number of III-V compounds. For reasons which will be discussed, the charge changes are local to the surface, that is, Δq of measurable magnitude are expected to be limited to one, or at most a few, surface planes of atoms on nonpolar surfaces. The situation is quite different for polar surfaces as will be seen in Sec. IV.

II. CALCULATION OF A BOUND ON $\Delta q/q$ FOR NONPOLAR SURFACES

For the purposes of the present paper we will consider 50-50 compounds consisting of equal numbers of anions and cations of charge $-q$ and $+q$, respectively, in the bulk. Further, let us consider a "prismatic" or nonpolar plane in which there are equal numbers of anions and cations so that it is electrically neutral; (110) planes of the zinc-blende, of the NaCl, and of the CsCl structures are examples of this. The Madelung potential at an anion site in a plane in the bulk of the crystal may be written

$$V_m^- = +q(V_p + V_a + V_b), \quad (2)$$

while the sign is reversed at cation sites. V_p , V_a , and V_b are the contribution from ions in the plane, from ions above and from ions below the plane, respectively, and they have been defined so that V_p (and q) is a positive quantity. If the plane has mirror symmetry in the crystal, the contributions from above and below are equal, i.e., $V_a = V_b$. If the crystal is cleaved so that the ions above the plane are removed and the ions on the surface maintain their charges and positions unchanged the Madelung potential at a surface site is

$$V_s^\mp = \pm q(V_p + V_b). \quad (3)$$

V_s is typically 90% of the bulk Madelung potential. If the ions in the surface suffer a change in the magnitude of their charge from q to $q + \Delta q$, there is an energy, per AB molecule in the surface of

$$\begin{aligned} \Delta E &= -[(q + \Delta q)^2 - q^2]V_p - 2q \Delta q V_b \\ &\quad + 2\Delta q qF + (\Delta q)^2 G + O((\Delta q)^3) \\ &= 2\Delta q q(F - V_p - V_b) + (\Delta q)^2(G - V_p) \\ &\quad + O((\Delta q)^3). \end{aligned} \quad (4)$$

Since all the charges change in the plane, the in-plane V_p term is quadratic in the charge while the V_b term involves the ions in the interior at fixed q interacting with the ions in the plane whose charge is changing. F and G are terms linear and quadratic in Δq arising from overlap, hybridization, and

intra-atomic terms. Keeping quadratic terms and setting the derivative of ΔE with respect to Δq equal to zero, one obtains

$$\frac{\Delta q}{q} = -\frac{F - V_p - V_b}{G - V_p} \quad (5)$$

Let us obtain F and G by assuming the values appropriate to surface sites are equal to those for the bulk. Consider the change in energy associated with changing the magnitude of the charge of the ions in some region (such as an ion pair, a plane of ions, or the whole crystal) from q to $q + \Delta q$. In analogy to Eq. (4), the energy per AB molecule sustaining the change in charge is

$$\begin{aligned} \Delta E_B &= -[(q + \Delta q)^2 - q^2]V_i + 2q \Delta q (V_m - V_i) \\ &\quad + 2 \Delta q q F + (\Delta q)^2 G + O((\Delta q)^3) \\ &= 2 \Delta q q (F - V_m) + (\Delta q)^2 (G - V_i) + O((\Delta q)^3), \end{aligned} \quad (6)$$

where V_i is that part of the full Madelung term V_m associated with the region of the crystal undergoing the charge change while $V_m - V_i$ is that due to the region of fixed q . The fact that the bulk ion charges are stable at the values $+q$ implies

$$\left. \frac{d\Delta E_B}{d\Delta q} \right|_{\Delta q=0} = 0$$

and

$$\left. \frac{d^2\Delta E_B}{d(\Delta q)^2} \right|_{\Delta q=0} > 0,$$

or, in turn

$$F = V_m = V_p + V_a + V_b \quad (7a)$$

and

$$G > V_i. \quad (7b)$$

One is interested in the maximum value of the bound in Eq. (7b). While it may be possible in some structures to define a region such that $V_i > V_m$ this is in general not the case and the maximum value of V_i is obtained by setting it equal to V_m . In such a case, Eq. (6) is written for *all* sites in the crystal interior changing from $+q$ to $+(q + \Delta q)$. Then

$$G > V_m. \quad (7b')$$

Substituting Eqs. (7) into (5)

$$0 > \frac{\Delta q}{q} > -\frac{V_a}{V_a + V_b}. \quad (8a)$$

For planes having mirror symmetry in the bulk, V_a equals V_b and

$$0 > \frac{\Delta q}{q} > -\frac{1}{2}. \quad (8b)$$

For the unreconstructed $(10\bar{1}0)$ surface of wurtzite which does not have mirror symmetry, V_a and V_b are such¹ that

$$0 > \frac{\Delta q}{q} > -0.32. \quad (8c)$$

When nonpolar surfaces do not have mirror symmetry, the preferred surface is made up of atoms having the maximum number of nearest-neighbor bonds. A consequence of this is that V_a is less than V_b and Eq. (8a) gives a limit for $-\Delta q/q$ whose magnitude is smaller than $\frac{1}{2}$.

The above are the results of the previous communication.³ The F and G of Eqs. (7) involve intra-atomic, overlap, and hybridization terms. The intra-atomic terms F_i and G_i are not expected to change on going from bulk to the surface, but the overlap and hybridization contributions F_h and G_h do. Crudely, the F_h and G_h —which are the charge-dependent and *not* the total contributions to the energy due to overlap and hybridization—can be expected to be proportional to the number of nearest neighbors. Knowing the F_i and G_i from the spectroscopic considerations of the accompanying paper, these can be subtracted from Eqs. (7) to yield the F_h and a bound on the G_h appropriate to the bulk, i.e.,

$$F_h = V_m - F_i \quad (9a)$$

and

$$G_h > V_m - G_i. \quad (9b)$$

These can then be scaled by the ratio of the number of surface nearest neighbors to those of the bulk, N_s/N_b , and inserted into Eq. (5) yielding

$$\frac{\Delta q}{q} = -\frac{F_i + (N_s/N_b)F_h - V_p - V_b}{G_i + (N_s/N_b)G_h - V_p}, \quad (10a)$$

or if the surface is unreconstructed,

$$\left| \frac{\Delta q}{q} \right| < \left| \frac{V_a - F_h(1 - N_s/N_b)}{G_i + (N_s/N_b)(V_m - G_i) - (V_m - V_a - V_b)} \right|. \quad (10b)$$

It is our experience that the denominator always remains positive and the sign of $\Delta q/q$ depends on whether the reduction in the Madelung potential in the numerator, V_a , is larger or smaller than the reduction $(1 - N_s/N_b)F_h$ in intersite terms. In other words, there is a reduction in ionic charge, after the manner of Eqs. (8) when

$$V_a > (1 - N_s/N_b)F_h$$

TABLE I. Geometric surface-dependent factors (see text).

Surface	N_s/N_b	V_p/V_m	V_b/V_m
Unreconstructed NaCl(110)	$\frac{2}{3}$	0.762	0.119
Unreconstructed NaCl(100)	$\frac{5}{6}$	0.924	0.038
Unreconstructed CsCl(110)	$\frac{3}{4}$	0.871	0.065
Unreconstructed zinc blende (110)	$\frac{3}{4}$	0.820	0.090
Zinc blende (110) with the GaAs reconstruction	$\frac{3}{4}$	0.787	0.092

and increases in ionic charge are obtained when V_a is smaller. This competition depends on factors associated with a particular surface as well as on the specific elements forming the compound. The surface-dependent factors are summarized in Table I and consist of the ratios N_s/N_b , the in plane V_p/V_m and the below plane V_b/V_m . For all but one case $V_a = V_b$ and

$$(V_p + 2V_b)/V_m = 1.$$

The exception is the reconstructed GaAs(110) of which more will be said later. Among the unreconstructed surfaces, the largest values of V_a (in units of V_m) and of $(1 - N_s/N_b)$ occur for the NaCl(110), intermediate values occur for NaCl(100) and CsCl(110), and the smallest appear for zinc blende (110). As might be expected, there is a correlation between the reduction in coordination and in the Madelung potentials on crystalline surfaces.

In the following paper,⁵ free-ion spectra are employed to obtain estimates of the energies associated with the charging of ions. For a long time it has been noted that ionization energies vary linearly with ionic charge. To the extent that this is true, the energy of an ion can be written

$$E(q) = E_0 + \alpha q + \beta q^2, \quad (11)$$

where α and β are positive quantities. Here α is the Mulliken electronegativity Φ_m , which is simply the average of the electron affinity and the first ionization potential, i.e., the one-electron energies of the neutral atom and the ion charged -1 . The experimental ionization energies do show deviations from strict linearity, in which case there are higher-order terms in Eq. (11) and Φ_m does not strictly equal α . For many cases of interest, these higher-order terms are experimentally inaccessible and we will assume Eq. (11) as it stands for all elements of concern here. The intra-atomic energy associated with a cation-anion pair changing charge from values of $\pm q$ to $\pm(q + \Delta q)$ is then

$$\begin{aligned} E_+(q + \Delta q) - E_+(q) + E_-(-q - \Delta q) - E_-(-q) \\ = \Delta q[(\alpha_+ - \alpha_-) + 2q(\beta_+ + \beta_-)] \\ + (\Delta q)^2(\beta_+ + \beta_-), \end{aligned} \quad (12)$$

where the $+$ and $-$ subscripts refer to cations and anions, respectively. From this it follows that

$$G_i = \beta_+ + \beta_- \quad (13)$$

and

$$F_i = G_i + \frac{1}{2q}(\alpha_+ - \alpha_-) \quad (14)$$

in Eqs. (9) and (10). G_i is positive while, if the anion is more electronegative than the cation as it ought to be, the second term of F_i is negative, implying that F_i is smaller than G_i . This contributes to the fact that the numerator of Eq. (10) is numerically sensitive, even changing sign, whereas the denominator does not. More important, the presence of q in Eq. (14) implies that a value of $\Delta q/q$ obtained with Eq. (10b) is a function of q .

The electronegativities α and the accompanying β terms, which are generally overlooked in considerations of charge transfer, depend on what type of electron, valence s , p , or d , is being transferred on or off a site and on what type of atomic configuration, say s^2p^2 vs sp^3 for carbon, is involved. Some of the choices are easy: For III-V compounds in the tetrahedrally coordinated zinc-blende structure one would choose the sp^n configuration while for Sn in a highly coordinated "metallic" environment or for O or Cl, one would choose the s^2p^n configuration. We will assume p -electron transfer for these particular elements though there is no problem defining α and β for some combination of s - and p -electron transfer providing one has an opinion of what that combination is. These choices represent a significant complication to the estimates over and above any shortcomings in the model leading to Eq. (10b). Trends, rather than detailed values of $\Delta q/q$ for par-

TABLE II. $\Delta q/q$ for unreconstructed surfaces of the NaCl Structure.

Compound	Configurations ^a	for $q = \frac{1}{2}$	$\Delta q/q$	
			1	2
(110) surface				
NaCl	$(s^n)(s^2p^n)$	$< +0.87$	$< +0.26$	
LiI	$(s^n)(s^2p^n)$	$< +0.89$	$< +0.33$	
LiF	$(s^n)(s^2p^n)$	$< +0.94$	$< +0.32$	
RbH	$(s^n)(s^n)$	$< +0.33$	> -0.08	
MgO	$(s^n)(s^2p^n)$		> -0.02	> -0.21
BaTe	$(s^n)(s^2p^n)$		$< +0.07$	> -0.14
ZnO	$(s^n)(s^2p^n)$		> -0.27	> -0.39
AgCl	$(d^{10}s^n)(s^2p^n)$	$< +0.34$	> -0.04	
NiO	$(d^8s^n)(s^2p^n)$		> -0.11	> -0.25
FeO	$(d^6s^n)(s^2p^n)$		> -0.03	> -0.20
TiO	$(d^2s^n)(s^2p^n)$		$< +0.07$	> -0.10
α -MnS	$(d^5s^n)(s^2p^n)$		> -0.12	> -0.24
PdH	$(d^9s^n)(s^n)$	$< +0.31$	$< +0.07$	
	$(d^8s^n)(s^n)$	> -0.09	> -0.19	
VN	$(d^3s^n)(s^2p^n)$	$< +0.07$	> -0.14	
	$(d^4s^n)(s^2p^n)$	$< +0.19$	> -0.09	
	$(d^4s^n)(sp^n)$	$< +0.08$	> -0.16	
VC	$(d^3s^n)(s^2p^n)$	$< +0.11$	$< +0.03$	
TiB	$(d^2s^n)(s^2p^n)$	$< +0.12$	$< +0.10$	
(100) surface				
NaCl	$(s^n)(s^2p^n)$	$< +2.2$	$< +1.0$	
RbH	$(s^n)(s^n)$	$< +0.83$	$< +0.17$	
MgO	$(s^n)(s^2p^n)$		$< +0.36$	$< +0.03$
ZnO	$(s^n)(s^2p^n)$		> -0.14	> -0.34
NiO	$(d^8s^n)(s^2p^n)$		$< +0.20$	> -0.05
VN	$(d^3s^n)(s^2p^n)$	$< +0.57$	$< +0.18$	

^aThe exponent n indicates the valence electron assumed to be involved in charge transfer.

ticular compounds, are to be read out of the results of the next section.

III. RESULTS FOR NONPOLAR SURFACES

As already noted, Eq. (10b) yields bounds on the magnitude of $\Delta q/q$, whether the ratio is positive or negative, representing enhancement or reduction in ionic charge at the crystal surface. The NaCl structure is perhaps the best to consider because a number of ionic compounds are represented which involve constituents for which there is some consensus as to the atomic configuration in which they occur and as to what valence electrons are involved in charge transfer. Results for ions in the outermost layer of the (110) surface appear in Table II for a number of such compounds and $\Delta q/q$ are reported for ionic charges q equal to the formal valence of the constituents and to half that value. Positive $\Delta q/q$ are obtained for the alkali halides and negative $\Delta q/q$ prevail for the divalent chalcogenides. For the most part, the magnitude of the ratios is less than a

third. Results are also tabulated for some transition-metal compounds for which there is some question as to the electrons involved in charge transfer: We have assumed s transfer for transition-metal ions with monovalent or divalent d^n shells. The resulting $\Delta q/q$ are quite small. Results are also listed in Table II for the (100) surfaces of some of the compounds. Atoms on a (100) surface sustain Madelung potentials and near-neighbor coordinations which are closer to bulk behavior (see Table I) than on the (110) surface. The resulting $\Delta q/q$ show a greater tendency to be positive, implying that hybridization effects are prevailing, and the bounds are larger in magnitude [largely due to smaller denominators in Eq. (10b)].

Results for the (110) surface of some compounds in the CsCl structure appear in Table III. Again, the $\Delta q/q$ for the monovalent compounds are substantial and positive while the polyvalent systems have small or negative values. A large number of systems involving a transition element alloyed with noble-, transition-, or main-group elements (such as

TABLE III. $\Delta q/q$ for the CsCl(110) surface.

Compound	Configurations	$\Delta q/q$		
		for $q = \frac{1}{2}$	1	2
CsCl	$(s^n)(s^2p^n)$	$< +1.5$	$< +0.53$	
CsI	$(s^n)(s^2p^n)$	$< +1.5$	$< +0.52$	
HgMg	$(s^n)(s^n)$		> -0.10	> -0.25
HgSr	$(s^n)(s^n)$		$< +0.10$	> -0.15
TlBi	$(sp^n)(sp^n)$	$< +0.02$	> -0.19	
	$(s^2p^n)(s^2p^n)$	$< +0.34$	$< +0.04$	
TlCl	$(sp^n)(s^2p^n)$	$< +0.65$	$< +0.06$	
	$(s^2p^n)(s^2p^n)$	$< +1.0$	$< +0.25$	
AuCs	$(d^{10}s^n)(s^n)$	$< +1.9$	$< +0.90$	
AuMg	$(d^{10}s^n)(s^n)$		$< +0.17$	0
AuZn	$(d^{10}s^n)(s^n)$	> -0.10	> -0.22	> -0.24
CuBe	$(d^{10}s^n)(s^n)$	$< +0.32$	$< +0.23$	$< +0.20$

Al) form in this structure. While a certain degree of polar character is associated with such compounds, metallic bonding is involved where d transfer on or off a transition-metal site is accompanied by s - p conduction-electron transfer in the opposite direction. The net charge transfer is a small fraction of either. Given an opinion of the ratio of d to non- d transfer one could extend the considerations of the following paper to estimate the intra-atomic terms

for such a case. Then, assuming that the ratio of d to non- d transfer is the same at the surface as in the bulk one could estimate $\Delta q/q$. Granted the various uncertainties, this has not been attempted.

Results for the unreconstructed (110) faces of compounds in the zinc-blende structure are represented in Table IV. The monovalent and divalent compound results are much like those already seen for the (110) NaCl-structure face: Modest posi-

TABLE IV. $\Delta q/q$ for the zinc-blende (110) surface.

Compound	Configurations	$\Delta q/q$		
		for $q = \frac{1}{2}$	1	2
Unreconstructed surfaces				
AgI	$(d^{10}s^n)(s^2p^n)$	$< +0.28$	> -0.03	
CuF	$(d^{10}s^n)(s^2p^n)$	$< +0.55$	$< +0.09$	
ZnS	$(s^n)(s^2p^n)$	> -0.05	> -0.22	> -0.31
ZnO	$(s^n)(s^2p^n)$	$< +0.07$	> -0.19	> -0.32
HgSe	$(s^n)(s^2p^n)$		> -0.40	> -0.42
BeS	$(s^n)(s^2p^n)$		> -0.11	> -0.21
β MnS	$(d^5s^n)(s^2p^n)$		> -0.12	> -0.23
β SiC	$(sp^n)(sp^n)$	$< +0.43$	$< +0.24$	
GaAs	$(sp^n)(sp^n)$	$< +0.02$	> -0.17	
GaP	$(sp^n)(sp^n)$	$< +0.43$	$< +0.11$	
InSb	$(sp^n)(sp^n)$	$< +0.23$	0	
AlAs	$(sp^n)(sp^n)$	$< +0.05$	> -0.18	
BN	$(sp^n)(sp^n)$	$< +0.38$	$< +0.16$	
BP	$(sp^n)(sp^n)$	$< +0.27$	$< +0.04$	
Surfaces with GaAs reconstruction ^a				
GaAs	$(sp^n)(sp^n)$	> -0.17	> -0.31	
GaP	$(sp^n)(sp^n)$	$< +0.11$	> -0.13	
InSb	$(sp^n)(sp^n)$	> -0.03	> -0.20	
BP	$(sp^n)(sp^n)$	0	> -0.19	

^aThese are surfaces with the GaAs reconstruction in the surface layer, scaled to the appropriate lattice constant.

tive $\Delta q/q$ are obtained for the noble-metal halides while reduced ionic character is obtained for the divalent systems. Of the systems reported, ZnO and MnS form in both the NaCl and zinc-blende structures, and the $\Delta q/q$ for both are essentially identical in the two structures. Results are also shown for SiC and a number of III-V compounds assuming the sp^n atomic configurations. A q of less than $\frac{1}{2}$ is appropriate for the III-V compounds, implying that $\Delta q/q$ is positive. While the sp^n is consistent with tetrahedral bonding, the actual valence charge is expected to be intermediate between this and the s^2p^{n-1} configuration. Results for the latter configuration are the same, within ± 0.2 , for all but the As compounds. The bounds are smaller in magnitude for SiC, essentially identical for InSb, BP, and BN, and increased for GaP. Owing to the substantial change in β (see Table I of Ref. 5) for the two As configurations, the bounds on $\Delta q/q$ increase by 0.5 for both compounds. In cases such as this, details of the fits for α and β are important to the results.

The (110) faces of the III-V compounds are known to reconstruct. The (110) face consists of zigzag cation-anion chains which initially lie in the (110) plane. These tilt and shift inwards slightly.^{6,7} Assuming the GaAs reconstruction applies (apart from scaling due to varying lattice constant) to the III-V compounds in general, results for several of these compounds appear at the bottom of Table IV. Going to the reconstructed surface has made the $\Delta q/q$ more negative or less positive. This has arisen from a competition in what reconstruction has done to V_p and V_b . The unreconstructed surfaces dealt with here had the separation, between the surface layer and the next plane of ions beneath, equal to the separation in the bulk. However, electrostatic considerations indicate that the surface layer should normally contract in towards the substrate beneath, as it has. V_b , the interaction between the layer and the substrate, thus increases in magnitude and this would imply a shift in $\Delta q/q$ to more positive values. However, the tilting of surface chains has reduced V_p to such an extent that $V_p + V_b$ is smaller in magnitude (see Table I) and, being in the numerator of Eq. (10a), leads⁸ to more negative $\Delta q/q$. Surface reconstruction can shift $\Delta q/q$ in either direction depending on whether reconstruction modifies the arrangement of atoms in the surface layer. Such reconstructions will, of course, also affect the hybridization matrix elements. One of the most interesting features of reconstruction is that it causes the second plane of ions to be much more severely affected by the presence of the surface than it would be in the unreconstructed case.

The calculations represented in Tables II–IV assumed charge transfer only within the surface layer.

If reconstruction causes surface anion and cation sites to be inequivalent, there can be charge transfer between the surface and the interior. There are other factors outside the model, such as the occurrence of surface states, which will also cause transfer. None of these will be considered here. There can also be transfer within interior layers but this is expected to be small. The difference in the Madelung potential at a surface site as against that in the bulk is of the order of 10% as can be seen in Table I. This difference is typically an order of magnitude smaller^{1,6} for the first plane of ions inside. In addition, these ions have their full complement of nearest neighbors. As a result, ions as close as one layer in from the surface barely “see” the surface. The largest contribution in the change in potential sampled by such ions then comes from the change in charge in the surface layer, and this is not great. As a result, the Δq are small in the interior of nonpolar surfaces and have little effect on the surface ions. The situation is different on polar surfaces.

IV. CHARGE MODIFICATION ON POLAR SURFACES: GaAs(111)

The polar surfaces of concern here involve alternating planes of cations and anions and ionic charge modification within the outermost layer of ions involves charge transfer to one (or more) layer(s) to the interior. Consider that the transfer Δq involves the two outermost layers of ions. Associated with this transfer is a dipole potential which, in the interior of the crystal, is the same at anion and cation sites and therefore does not encourage any change in ionic charge there. However, the potential induced at sites in either of the two surface planes is quite different from that at the next plane inside, and thus charge transfer within the outermost two layers encourages transfer with the next layer. Charge transfer within the three then encourages transfer with the fourth and so on into the interior of the crystal. Equations (10) can be replaced by a set of coupled equations for transfer between successive pairs of layers. To do this it is convenient to rewrite the bound defined in Eq. (9b) as

$$G_h = V_m - G_i + \Omega, \quad (9b')$$

where Ω is unknown and zero or positive valued. Whatever its value, Ω is characteristic of the bulk material and is common to each of the coupled equations and thus results can be obtained as a function of Ω . Ω is also common to different surfaces causing Δq to be smaller than the bounds Δq_{\max} reported for nonpolar surfaces in Tables II–IV, the relationship being

$$R \equiv \frac{\Delta q}{\Delta q_{\max}} = \frac{D}{\Omega + D}, \quad (15)$$

where D is the denominator of Eq. (10b).

Consider the unreconstructed polar (111) surface of GaAs which has the zinc-blende structure. There are alternate planes of Ga and As ions. To one side of a Ga(As) site in some given plane is one of its four nearest-neighbor As(Ga) ions in a plane ($\sqrt{3}a/4$) away (a being the cubic lattice constant). To the other side there are the three other nearest neighbors in a plane one-third the distance away. The stable surface is presumed to occur when the surface layer is triply bonded to the layer below. If the surface planes are kept at full ionic charge, there are long-ranged capacitive Coulomb energy terms built up in the crystal.^{1,2,8} This results in a charge reduction in the outer layer for reasons quite other than those of concern here (zero long-range Coulomb energy occurs when the surface charge is at three-fourths the bulk value for the GaAs here). The reduction can be associated with having a surface layer whose sites are partially occupied by ions at full charge,⁹ with complete coverage by ions at fractional charge^{1,2} or by some combination of the two.¹⁰ The Δq arising from the Madelung and interatomic terms, as plotted in Fig. 1, omit this natural reduction.

Calculations were done as a function of the ratio R defined for the (110) nonpolar surface of GaAs [see Eq. (15)]. In addition, nonzero charge transfer was allowed down to some given depth below the surface, after which Δq was set equal to zero, and results were then obtained as a function of that depth. For well-behaved cases, as are represented in the figure, the Δq converged to zero in the interior of the crystal once the appropriate depth was reached. The range is quite shallow when R is small: The Δq of but four layers deviate significantly from zero when $R = \frac{1}{3}$. The range is increasing rapidly in the vicinity of $R = 0.6$, and at values of 0.62 and greater the calculations are unstable and do not converge. The critical value of 0.62 is common to surfaces with both Ga and As in the outer layer and whether or not the hybridization terms, F_h and G_h , at the surface, are scaled for reduced surface coordination. It does depend on the coupling between layers and would be different for the polar surface of another compound.

The sign of the Δq at the surface have the sign of the terms in the energy which are linear in that Δq [corresponding to the numerator of Eqs. (10)]. They are negative for the Ga surface, positive for the As, and negative for both when F_h and G_h are not scaled (thus not accounting for the reduced near-neighbor coordination at the surface). The Δq are small in

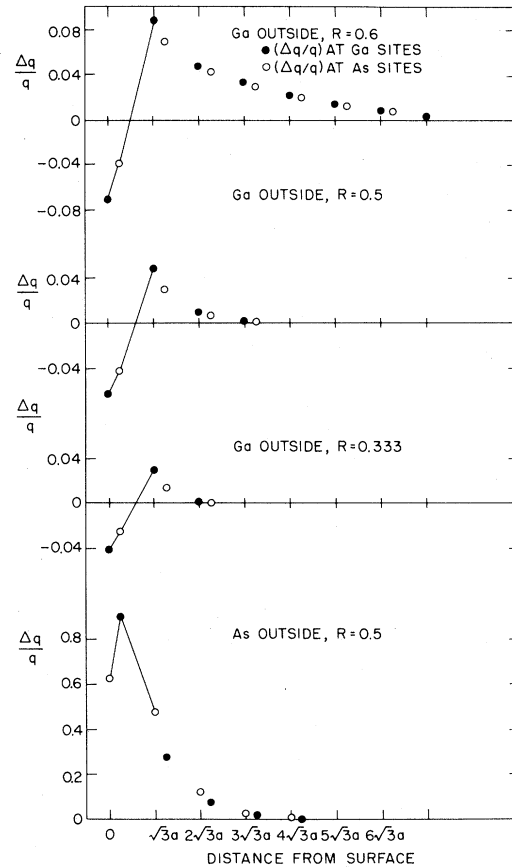


FIG. 1. Deviation in ionic charge from that in the bulk at the unreconstructed polar (111) surface of GaAs (see text). The results $\Delta q/q$ are normalized to the bulk ionicity q and the distances are given in terms of the lattice constant a . Results are shown for one case where As is outermost and three with Ga outermost where the calculations have been done for differing values of R [see Eq. (15)]. R is a measure of how much $[d^3\Delta E_B/d(\Delta q)^2]_{\Delta q=0}$ is greater than zero in the bulk.

magnitude for the Ga surface and reverse sign after the first two layers. In contrast they are an order of magnitude greater for the other three cases and do not reverse sign on going into the interior. The sign reversal appears to be associated with the small magnitude.

V. CONCLUSION

Traditionally chemical intuition has suggested that, at the surfaces of polar crystals, the ionic character is reduced with respect to that in the bulk. Previously, allowing only the Madelung potential to be different at the surface, we obtained the reduction

$$0 > \frac{\Delta q}{q} > -\frac{1}{2}$$

for nonpolar surfaces. In other words, the ionic

charge is reduced in magnitude to somewhere between half and the full bulk value. In the present paper we have employed empirical estimates of intra-atomic terms and, given these, have estimated the extra-atomic hybridization and overlap terms which were then assumed to scale with the reduced coordination number at a surface. Multipole effects have been neglected. The result is values of the bounds on $\Delta q/q$ for nonpolar surfaces which are functions of q and of the compound involved. Such estimates will never replace proper quantum-mechanical calculations for a surface, but they are easily done allowing a survey of a number of compounds which can be compared either with experiment or proper calculation. Given the Madelung potential information of Table I, the estimates are trivial hand calculations. The necessary Madelung potentials may be straightforwardly calculated,^{1,11} and often these calculations are within the means of a programmable hand calculator.

The number obtained as a bound for $\Delta q/q$ for some particular compound and surface should not be taken too seriously, but we believe it appropriate to inspect the trends in the results. Enhancement of the charge at a nonpolar surface, i.e., $\Delta q/q > 0$, tends to be obtained for the monovalent compounds while charge reduction is more likely the case for polyvalent systems. Whether or not the surfaces of the monovalent systems actually suffer an increase in ionic charge, the present calculations would indicate that they are expected to at least undergo *less* of a decrease than do the surfaces of polyvalent systems. This correlates with a trend seen in the accompanying paper. There the ionic charge of a compound, due *solely* to intra-atomic effects, is estimated. The resulting q for the monovalent compounds are of the order of what is expected in the crystal, while the q for polyvalent systems are smaller than expectation. This suggests that the Madelung terms dominate over hybridization in the polyvalent systems and that the two are roughly equal in effect in monovalent compounds. With the Madelung terms being more important in the polyvalent systems, there is more to be lost at the surface and hence a greater tendency for charge reduction at such surfaces.

Some differences in charge change are found in going from one crystal face to another: For the NaCl structure Δq on the (100) surface is greater, i.e., more positive, than that on the (110). In no case were negative bounds in excess of one-half in magnitude obtained for¹² $\Delta q/q$. The above observations are for unreconstructed surfaces. Reconstruction can shift the bound in either direction. As encountered on GaAs(110), it moves the bounds to more negative values. $\Delta q/q$ that are less than one-fourth in magnitude appear typical for the bulk of the systems considered.

Significant deviations from bulk ionicity are limited almost entirely to the surface layer itself on a nonpolar surface. The situation is quite different for a polar surface as was seen in the preceding section. The solutions indicated a tendency for the disturbance to extend a good distance into the crystal. This was associated with the fact that the direction of charge transfer was, of necessity, normal to, rather than within, planes parallel to the surface. This can prove troublesome for *a priori* calculations as well and may explain why there is a dearth of them in the literature. Perhaps a detailed calculation for a nonpolar surface, taken with a model calculation, such as described here, can be used to extrapolate to a description of a polar surface.

One motive for the present investigation was the observation that the change in work function from one crystal face to another is much smaller than what would be expected for unreconstructed faces at full bulk ionic charge. There is insufficient experimental data to determine overall trends to which theory should be compared but it appears clear that some combination of modified ionic charge, of reconstruction and of multipole contributions must be at play. The present investigation may be of a help in defining the role of the first factor.

ACKNOWLEDGMENTS

This work has benefited from our collaboration with Morris Perlman in recent years. We regret that his death prevented his collaboration on this and the following paper. This work was supported by the Division of Materials Science, U. S. Department of Energy under Contract No. DE-AC02-76CH00016.

¹R. E. Watson, M. L. Perlman, and J. W. Davenport, *Surf. Sci.* **115**, 117 (1982).

²R. E. Watson and M. L. Perlman, *Surf. Sci.* **122**, 371 (1982).

³R. E. Watson, M. L. Perlman, J. W. Davenport, and T. K. Sham, *Solid State Commun.* **41**, 151 (1982).

⁴R. E. Watson and L. H. Bennett, in *Charge*

Transfer/Electronic Structure of Alloys, edited by L. H. Bennett and R. H. Willens (Metallurgical Society of the American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1973).

⁵R. E. Watson, L. H. Bennett, and J. W. Davenport, following paper, *Phys. Rev. B* **27**, 6428 (1983).

⁶The GaAs(110) reconstruction assumed here involved

only the surface layer; see J. W. Davenport, R. E. Watson, M. L. Perlman, and T. K. Sham. *Solid State Commun.* **40**, 999 (1981).

⁷For GaAs, see S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. VanHove, *Phys. Rev. B* **17**, 3303 (1978) and C. B. Duke, R. J. Meyer, and P. Mark, *J. Vac. Sci. Technol.* **17**, 971 (1980); recent studies of reconstruction for related compounds include C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and J. Carelli, *Phys. Rev. B* **24**, 562 (1981); C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and G. Scott, *ibid.* **24**, 3310 (1981).

⁸In this case Eq. (10b) does not apply since it was assumed that V_a and V_b in the equation are for the unshifted surface layer.

⁹R. W. Nosker, P. Mark, and J. D. Levine, *Surf. Sci.* **19**,

291 (1970).

¹⁰Either case has repercussions on estimates of the Δq associated with surface Madelung and reduced bonding effects. Here we have assumed the surface layer to consist of complete coverage by fractionally charged ions. This affects the intraatomic energy term of the surface ions since this term depends on q as well as Δq [e.g., see Eqs. (12) and (14)].

¹¹E.g., R. E. Watson, J. W. Davenport, M. L. Perlman, and T. K. Sham, *Phys. Rev. B* **24**, 1791 (1981).

¹²This is numerically possible but likely only if one insists that the more electronegative element [the one having the larger α in Eqs. (12) and (14)] is, despite this, the cation.