

## Charge transfer in multicomponent oxides

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The transfer of charge between different ions in an oxide plays an essential role in the stability of these compounds. Since small variations in charge can introduce large changes in the total energy, a correct description of this phenomenon is critical. In this work, we show that the ionic charge in oxides can strongly depend on its atomic environment. A model to assign point charges to atoms as a function of their atomic environment has recently been proposed for binary alloys [C. Wolverton, A. Zunger, S. Froyen, and S.-H. Wei, *Phys. Rev. B* **54**, 7843 (1996)] and proven to be very successful in *screened* solids such as semiconductors and metals. Here, we extend this formalism to multicomponent oxides and we assess its applicability. The simple point-charge model predicts a linear relation between the charge on an atom and the number of unlike neighbors, and between the net value of the charge and the Coulomb field at a given site. The applicability of this approach is tested in a large-supercell self-consistent tight-binding calculation for a random Zr-Ca-O alloy. The observed fluctuations of the ionic charge about the average linear behavior (as a function of the number of unlike neighbors) was larger than 0.25 electrons even when many shells of atomic neighbors were considered in the fit. This variation is significant since it can introduce large errors in the electrostatic energy. On the other hand, for small absolute values of the charge, the ionic charge varied linearly with the Coulomb field, in agreement with previous findings. However, for large Coulomb fields, this function *saturates* at the formal chemical charge. [S0163-1829(98)04207-6]

### I. INTRODUCTION

The electrostatic energy plays an important role in determining the structural stability of ionic solids since it represents a large contribution to the total energy.<sup>1</sup> The electrostatic energy of a system of point charges is strongly affected by changes in the values of these charges. In previous work,<sup>2</sup> we studied different calcia-doped zirconia compounds and showed that an important redistribution of charge around each ion was present for different atomic arrangements. These changes considerably affected the formation energy of the compounds in the system. For many applications, such as the determination of phase diagrams, it is essential to compute these energy differences very accurately. Consequently, a correct representation of the dependence of the atomic charge on its environment is necessary. This will be the focus of the present work.

In principle, the charge density in a solid can be determined by solving Schrödinger's equation self-consistently. Often, when modeling complex oxide unit cells or geometries, much simpler descriptions for the bonding are used. Empirical or semiempirical energy methods can be several orders of magnitude faster than self-consistent quantum-mechanical approaches, but at the expense of accuracy in the description of the energy of the system. Usually, two major approximations are introduced in empirical models for oxides: (1) the continuous electron density is replaced by point charges and (2) these point charges are considered to be independent of the environment. This is the cornerstone of the empirical pair-potential models that have been very popular for oxides.<sup>3-5</sup> In these models, the energy is described as the sum of two terms: an electrostatic contribution coming from the point charges and a short-ranged repulsive interaction that represents the overlap of the ionic electron clouds. Ionic

polarization is, to a limited extent, accounted for by representing an ion as a dipole of charge (shell model).<sup>6</sup> Although this method is widely used and has been reasonably successful in predicting properties of oxides, some basic limitations of its description of the electrostatic energy have recently been presented: As we showed in Ref. 2, mixing energies in multicomponent oxides are very sensitive to even small variations in ionic charge. Models with frozen point charges tend to overestimate the mixing energy as they essentially deprive the mixed state of a mechanism (charge transfer) by which it can lower its energy. In other cases, such as the study of metal-oxide surfaces, a correct description of bonding in the system also requires an adequate treatment of the dependence of the charge on the atomic environment.<sup>7</sup> The charge on the metal atom is zero in the bulk metal and increases gradually towards the interface (the metal ion is usually highly ionized in the bulk oxide).

Recently, new energy models that relax the ionic charge have been presented and applied to empirical potential schemes. In the model of Streitzieller and Mintmire, the charge is determined from local atomic electronegativities and long-ranged electrostatic interactions.<sup>7</sup> In another model, introduced by ourselves and based on the work of Majewski and Vogl,<sup>8</sup> a tight-binding Hamiltonian that allows for charge transfer is solved self-consistently.<sup>8,9</sup> The latter approach has been shown to give excellent results for the mixing energy in oxide systems.<sup>9-11</sup>

In this paper, we will investigate variations of the ionic charge for a prototype system, CaO-ZrO<sub>2</sub>, and we will identify the parameters that strongly affect its value.

The definition of ionic charges is not unique as there is a level of arbitrariness in how to divide a continuous quantum-mechanical electron density among ions. Sometimes, this density is simply integrated within regions of a specific

shape (e.g., spheres) while in other cases the projection of the charge density on a set of basis functions localized at the ions is used.<sup>12–14</sup> Such ambiguity makes absolute values of the ionic charge meaningless. However, their *variation* within a consistent scheme for assigning charge is a good indication of how the electron density around ions changes. In this work, we will determine ionic charges, by taking the projection of the solid wave functions onto a local tight-binding orthogonalized basis set.

Studies of charge redistribution in screened alloys, such as semiconductors and transition metals, indicate that point charges extracted from LDA calculations can be well reproduced with a very simple analytic model, in which the charge on a given ion only depends on the *number of unlike* neighbors it has.<sup>15,16</sup> In this paper, we will investigate if a similar set of rules can be applied to oxide systems, where large charge transfers and long-ranged interactions are present. We characterize both the effect of local environment (by counting the number of unlike neighbors) and the effect of the long-ranged Coulomb field. In screened alloys, the charge was found to depend linearly on the Coulomb field.<sup>17</sup> We will study whether the same behavior holds for oxides. This fact can make the evaluation of the Madelung energy easier, especially in extended systems.<sup>17</sup>

In Sec. II, we summarize the point-charge model introduced in Refs. 15 and 16. Section III deals with the generalization of this model to complex oxides and the application to the CaO-ZrO<sub>2</sub> system. Then in Sec. IV, we use a self-consistent tight-binding model to study the dependence of the charge on the environment and Coulomb field. Finally, in Sec. VI, we summarize the results obtained.

## II. POINT-CHARGE MODEL

The charge of an ion is expected to have the smallest absolute value when all its neighbors are of its same kind. The justification is that if the system is screened enough, an atom surrounded by like neighbors will behave as if it were part of a pure *elemental* solid and, consequently, its charge will be close to zero.<sup>18</sup> This idea was used by Magri and collaborators to express the charge in a binary alloy, as a *linear* function of the number of unlike atoms in the nearest-neighbor shell.<sup>15</sup> This was later extended to any number of shells by Wolverson *et al.*<sup>16</sup> Using notation of this previous work, the charge  $q_i$  at site  $i$  is expressed as

$$q_i = \lambda_1 \sum_s \frac{\lambda_s}{\lambda_1} \sum_{k_s} [S_i - S_{k_s}], \quad (1)$$

where  $\lambda_s$  are constants and the first sum goes over the desired number of shells.  $S_i$  is 1(0) if an  $A(B)$  atom is located at site  $i$  and the last sum is over all sites in the shell  $s$ . Note that the latter sum counts the number of unlike neighbors in the  $s$  shell. From the information over various shells, a *generalized number of neighbors*  $\tilde{N}$  can be defined as

$$\tilde{N} = \sum_s \frac{\lambda_s}{\lambda_1} \sum_{k_s} [S_i - S_{k_s}]. \quad (2)$$

Expression (1) was tested, for example, in large supercell local-density approximation (LDA) calculations (256–432

atoms) for the Cu<sub>1-x</sub>Zn<sub>x</sub> random alloy.<sup>16,17</sup> These calculations were performed at fixed lattice parameters. The total charge at site  $i$  was defined in terms of the muffin-tin approximation used in the evaluation of the Coulomb field.<sup>17</sup> It was found that the accuracy of Eq. (1) depends on the number of shells considered. Taking the first two (three) nearest-neighbor shells was sufficient to reproduce the LDA results for a fcc (bcc) Cu<sub>1-x</sub>Zn<sub>x</sub> lattice very closely.<sup>16</sup>

The results of this investigation also showed a remarkably linear relation between  $q_i$  and the long-ranged Coulomb field  $V_i$ , at site  $i$ .<sup>17</sup> This behavior can be predicted from the simple charge model when enough neighboring shells are considered.<sup>16</sup>

## III. POINT-CHARGE MODEL IN MULTICOMPONENT OXIDES: DOPED ZIRCONIA

To describe oxide materials, the model of Eq. (1) has to be extended, as most oxide systems of interest have at least three or more different species. We will generalize Eq. (1) by separately specifying the number of neighbors of each possible type. We will illustrate this procedure for the case of calcia-doped zirconias within the fluorite structure.

The fluorite structure can be thought of as formed by two interpenetrating sublattices: a fcc-like one for the cations (e.g., zirconium and calcium) and a simple-cubic one for the anions (e.g., oxygen and vacancies). The oxygen vacancies are introduced into the structure to compensate for the different nominal charge of the Ca and Zr ions.<sup>19</sup> Because there is no intermixing between the cation and anion sublattices, the first-neighbor shell of the cations contains only oxygen atoms or vacancies and the first-neighbor shell of the anions only contains cations. Similarly, the second-neighbor shell of the cations (anions) is made up exclusively out of cations (anions). Equation (1) can then be written for each species, up to two neighbor shells, in the following way,

$$\begin{aligned} q_i(\text{Zr}) &= \lambda_1 N_{\text{Ca}} + \lambda_2 N_{\text{O}} + C_{\text{Zr}}, \\ q_i(\text{Ca}) &= -\lambda_1 N_{\text{Zr}} + \lambda_3 N_{\text{O}} + C_{\text{Ca}}, \\ q_i(\text{O}) &= -\lambda_2 N_{\text{Zr}} - \lambda_3 N_{\text{Ca}} + \lambda_4 N_{\text{O}} + C_{\text{O}}, \end{aligned} \quad (3)$$

where  $\lambda_i$  and  $C_\alpha$  are constants, and  $N_\alpha$  is the number of neighbors of type  $\alpha$  ( $\alpha = \text{Ca}, \text{Zr}, \text{or O}$ ). Overall *charge neutrality* imposes both the symmetry in the  $\lambda_i$  parameters and a constraint on the coefficients  $C_\alpha$ ,

$$x_{\text{Zr}} C_{\text{Zr}} + x_{\text{Ca}} C_{\text{Ca}} + x_{\text{O}} C_{\text{O}} = 0. \quad (4)$$

Here,  $x_{\text{Zr}}$ ,  $x_{\text{Ca}}$ , and  $x_{\text{O}}$  indicate the atomic fraction of zirconium, calcium, and oxygen ions, respectively. Equations (3) can be written to include any number of shells. Note that when more than two species are present,  $\lambda_i$  will not only depend on the shell, but also on the identity of the central ion. As indicated in Eq. (3) not all the  $\lambda_i$  corresponding to a given type of shell (e.g., nearest neighbor) are independent but they are related by imposing charge neutrality.

Similar to what was done in Ref. 16, a generalized number of neighbors for each ion can be defined from Eqs. (3),

$$\begin{aligned}
q_i(\text{Zr}) &= \lambda_1 \left( N_{\text{Ca}} + \frac{\lambda_2}{\lambda_1} N_{\text{O}} \right) + C_{\text{Zr}} \\
&= \lambda_1 \bar{N}^{\text{Zr}} + C_{\text{Zr}}, \\
q_i(\text{Ca}) &= -\lambda_1 \left( N_{\text{Zr}} - \frac{\lambda_3}{\lambda_1} N_{\text{O}} \right) + C_{\text{Ca}} \\
&= -\lambda_1 \bar{N}^{\text{Ca}} + C_{\text{Ca}}, \\
q_i(\text{O}) &= -\lambda_2 \left( N_{\text{Zr}} + \frac{\lambda_3}{\lambda_2} N_{\text{Ca}} - \frac{\lambda_4}{\lambda_2} N_{\text{O}} \right) + C_{\text{O}} \\
&= -\lambda_2 \bar{N}^{\text{O}} + C_{\text{O}}. \tag{5}
\end{aligned}$$

The charges for the different ions can then be expressed as a function of these  $\bar{N}$ .

#### IV. COMPARISON OF THE CHARGE MODEL AND THE TIGHT-BINDING PREDICTIONS

To test Eq. (5) in an ionic solid, we performed a large supercell calculation for a Zr-Ca-O alloy in an unrelaxed  $3 \times 3 \times 3$  (324 sites in total) fluorite cell. The lattice parameter corresponds to the cubic zirconia structure (5.05 Å). An equal number of calcium and zirconium ions was randomly distributed in the cation sublattice. The number of vacancies was the same as the number of Ca ions, ensuring charge neutrality when formal charges are assigned to the ions. Because of the large size of this cell, many different crystallographic sites and local environments can be sampled in a single calculation. Similar results were obtained by using smaller cells with different atomic configurations (to sample a significant number of atomic environments).

The self-consistent tight-binding method described in Ref. 9 is used to compute the charges. This method offers a full quantum-mechanical description of bonding and a natural way of incorporating charge transfer, oxygen breathing,<sup>20</sup> and nonspherical charge relaxations. Although slower than pair-potential models, it is still orders of magnitude faster than other quantum-mechanical techniques because the various time-consuming integrals of the first-principles tight binding are replaced by suitable parametrizations. As a result, the Hamiltonian matrix elements are described as distance-dependent functions that are determined by fitting to several physical properties.

The tight-binding approach is capable of handling the large supercell calculation required in this study in a reasonable computational time. We already demonstrated that this method accurately reproduces formation energies in doped zirconias.<sup>2</sup> Since the accuracy of these predictions critically depends on the correct description of the ionic charge, it is reasonable to assume that the tight-binding model will also provide correct values for the charges. The charge is defined as the projection of the electron wave function in the solid onto the basis orbitals. This is the same value of the charge used to compute the Madelung energy within the tight-binding model.

For CaO-ZrO<sub>2</sub>, the solid wave functions are expanded in atomiclike  $2s$  and  $2p$  orbitals localized at the oxygen ions,

$4s$  and  $4p$  centered at the calcium ions, and  $4s$ ,  $4p$ , and  $4d$  for the zirconium ions. We independently fit the overlap and hopping integrals to the bands and lattice constants of pure CaO and ZrO<sub>2</sub> and one compound with composition CaZrO<sub>3</sub>. The properties of these structures were calculated (see Ref. 2) with the *ab initio* pseudopotential method.<sup>21</sup> Both the valence and the lower levels of the conduction band were used. For the latter, a much lower weight (0.01) was assigned in the fit of the tight-binding matrix elements. The initial values for the parameters were taken as the CaO and ZrO<sub>2</sub> sets found in Refs. 9 and 10, respectively (the O-O being an average of both results). For the Ca-Zr second-nearest-neighbor coefficients, only the  $s\sigma$  integrals were included. We also tested adding  $s$ - $s$  and  $s$ - $p$  integrals but the results did not improve appreciably. The integrals were assumed to obey Harrison's distance dependencies.<sup>22</sup> The root-mean-square difference between the pseudopotential and the tight-binding bands was of the order of a few hundredths of an eV. The lattice constants differed by less than 0.5%.

$\vec{K}$ -space integrations in the  $3 \times 3 \times 3$  supercell were tested both with a  $2 \times 2 \times 2$  uniform grid and with only the  $\Gamma$  point. The charges were already converged within 0.01 electrons in the latter case. Consequently, all the calculations were done with the  $\Gamma$  point.

If we do not enforce charge neutrality, each of the Eqs. (5) can be fit *independently* providing the best *linear* match to the data set. The results of this procedure are shown in Fig. 1 as a function of  $\bar{N}$  for two-, four-, and ten-neighbor shells, respectively (i.e., one cation and one anion, two-cation and two-anion, and five-cation and five-anion shells, respectively). Relation (5) predicts the straight line plotted in the figures. Clearly, even when not imposing the extra constraint of charge neutrality [Eq. (4)] the fit is poor. The dispersion around the linear behavior is of the order of 0.25 electrons. As we showed in Ref. 2, this variation can produce large errors in the formation energy values.

The dependence of the charge at a given site on the Coulomb field at that site is shown in Fig. 2. The charge exhibits a linear behavior with respect to the Coulomb field for small values of this field. A similar situation was observed for the Cu<sub>1-x</sub>Zn<sub>x</sub> random alloy (only small charges were involved in these studies).<sup>17</sup> However, in our case the charge levels off at the formal valence charge for large fields. This is not unexpected since those values correspond to closed-shell electronic configurations. [The Coulomb field would have to be increased (decreased) considerably more in order to start adding (removing) electrons to (from) the following (previous) electronic shell.]

#### V. DISCUSSION

The tight-binding results in Fig. 1 indicate an important effect of the atomic environment on the charge. Differences of more than 2.5 electrons are present between ions of the same species. Consequently, simple energy models that assume *fixed* charges are bound to fail as they will lead to large errors in the Coulomb energy. The variation of charge with structure in zirconias has also been suggested by other experimental and theoretical work.<sup>23,24</sup>

The calcium ions are shown to be almost completely ionized, independently of the structure or the symmetry of the

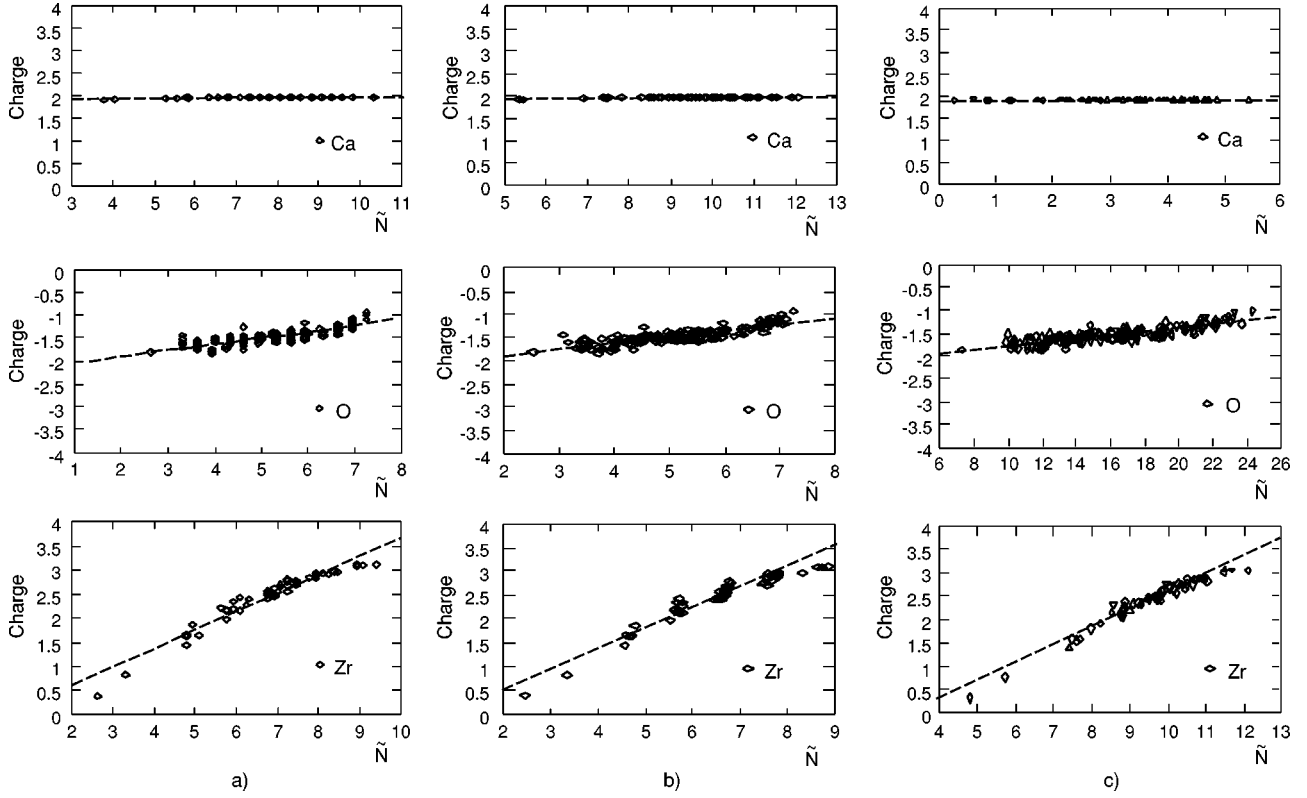


FIG. 1. Charge (in electrons) versus generalized number of neighbors  $\tilde{N}$ . The straight line is the prediction of the charge model of Eq. (5) when two-, four-, and ten-neighbor shells are included [(a), (b), and (c), respectively]. The  $\lambda$  parameters were fit without imposing charge neutrality. The dots correspond to tight-binding large-supercell calculations.

site that they occupy. This behavior was confirmed by our pseudopotential calculations.<sup>2,10</sup> Electronic density plots with virtually no valence electron density in the Ca ions (Fig. 3) were obtained for different arrangements of the atoms on the fluorite lattice.

As Fig. 2 shows, dispersion of the ionic charge as a function of the Coulomb field is smaller than as a function of  $\tilde{N}$ . There is almost a one-to-one correspondence between charge and Coulomb field for the zirconium atoms. The same is true for oxygen up to an absolute charge of  $\sim 1.4$ . For larger values, the dispersion starts increasing considerably. This may be related to the weak binding energy of the second electron on the oxygen atom. The  $O^{2-}$  configuration is actually not stable in the free ion but it is stabilized in the solid by the Coulomb field.<sup>25</sup> Consequently, this second electron can be considerably affected by the particular local environment of the ions. We believe this effect is responsible for the increase in the dispersion of the values of the oxygen charges beyond the 1.4 electron absolute charge.

The relation between point charges and Coulomb fields can be understood within perturbation theory. As was shown in Ref. 22, the reduction of charge between closed-shell ionic species (“the softening of the ion”) can be approximated by  $(H_{ij}/H_{ii} - H_{jj})^2$  to first order in the Hamiltonian matrix element  $H_{ij}$  between orbitals  $i$  and  $j$  (on different atoms). For the fixed lattice used in the present work, the  $H_{ij}$  can be assumed to be constant, while  $H_{ii} - H_{jj}$  can be taken as a constant plus a term linear in the difference in Coulomb fields on  $i$  and  $j$ .<sup>26</sup> Thus, the limiting behavior in Fig. 2 is reproduced: For large Coulomb fields, the softening of the

ions decay as the inverse of the square of the fields and formal chemical charges are obtained. By doing a Taylor’s expansion of  $(H_{ij}/H_{ii} - H_{jj})^2$  for small values of the Coulomb field, the softening of the ion becomes proportional to this field and, consequently, a linear relation between the charge and the Coulomb field is predicted.

## VI. CONCLUSIONS

The self-consistent tight-binding results show that the ionic charge depends quite strongly on its environment. For a random CaO-doped zirconia alloy, variations of more than 2.5 electrons were detected in the Zr ions. Any empirical or semiempirical total-energy method that assumes these charges to be fixed may introduce large errors in the evaluation of the electrostatic energy.

Since the electrostatic energy plays an important role in determining the structural stability of oxides, it is essential to represent the charge changes very accurately. Unfortunately, our results indicate that the ionic charge is not well captured by characterizing the local neighborhood of the ion, as is the case in small-charge-transfer systems.<sup>16</sup> Rather, we find that the Coulomb field is a better predictor for the ionic charges of the cations. The relation between charge and Coulomb field is linear for small charge transfer, in agreement with the results obtained on screened alloys, but deviates from linearity at larger charge transfer. For the oxygen ion, neither the local environment nor the Coulomb field *separately* is a good indicator for the ionic charge when the ion is strongly negatively charged. Calcium ions were found to be fully ionized,

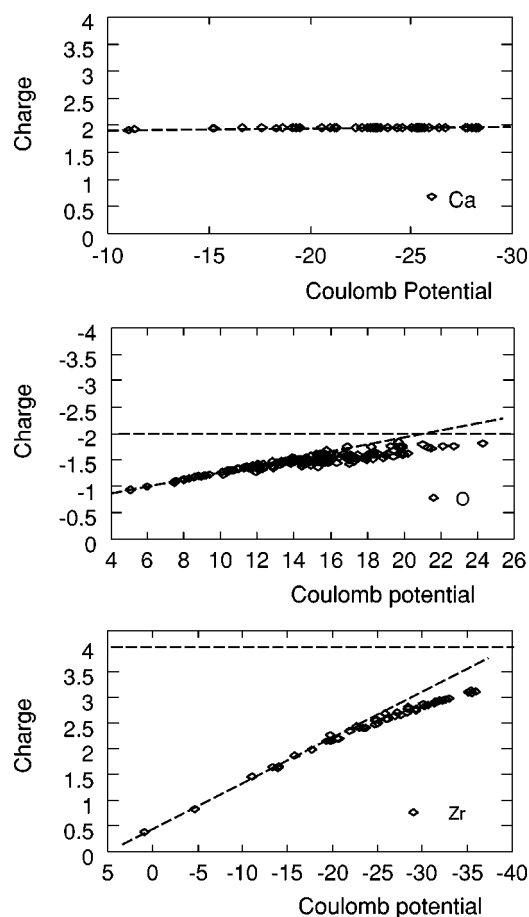


FIG. 2. Charge (in electrons) at site  $i$  vs Coulomb field  $V_i^*e$  (in eV) at that site. The lines indicate the limiting behavior for small and large charge transfer.

independently of the particular environment.

Significant advances could be made in the energetic description of oxides with semiempirical models if they can be made to account for variable charge states. The self-consistent tight binding approach presented earlier<sup>9</sup> may of-

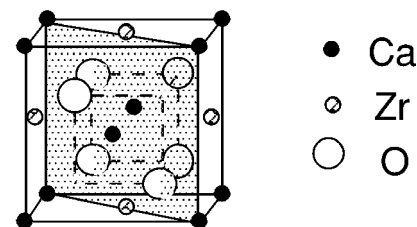
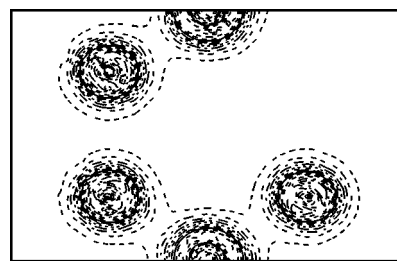


FIG. 3. Valence electron density for the structure and plane shown as computed with the plane-wave pseudopotential method. The difference in electron density between two consecutive lines is of  $5.2 e/\text{\AA}^3$  and the volume of the unit cell is  $135 \text{\AA}^3$ . Note that Ca atoms are fully ionized.

fer a good alternative in this respect, although it does require a tedious fit to *ab initio* band-structure data and equations of state.

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