Crystal Structures of Zirconia from First Principles and Self-Consistent Tight Binding

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The origin of the relative stability of the cubic, tetragonal, and monoclinic phases of zirconia (ZrO_2) is investigated. To obtain accurate energies we adopt a new all-electron bandstructure approach within the local density approximation, based on muffin tin orbitals. We also develop a self-consistent tight-binding model with which to study the energies for different structures. The tight-binding model enables us to analyze *ab initio* and experimental phase stabilities in terms of ionic versus covalent effects, including polarization of the anions, and promises to be useful for rapid simulation of more complex systems. [S0031-9007(98)07811-9]

Our primary aim is to understand the stability of the crystalline phases and associated electronic structures of zirconia, ZrO_2. It exhibits three structures in different ranges of temperature at atmospheric pressure, and these have been extensively studied for both their scientific and technological importance [1–3]. The high temperature phase has the cubic fluorite structure (c). As the temperature is reduced, the symmetry lowers to tetragonal (t), Fig. 1, and finally monoclinic (m). We have developed a new tool to help elucidate the driving forces in this process. This is a self-consistent, tight-binding (TB) model which combines covalent and ionic features of the system including polarizability and crystal field splitting. It is remarkable that the model reproduces the energetic and structural properties of the crystal phases of ZrO_2 compared to precise calculations in the local density approximation (LDA) to density functional theory. Moreover, the ingredients of the model are such as to allow us to unravel the underlying physics that drives the observed phase transitions.

Within the classic ionic model, the crystal structures of many dioxides can be rationalized in terms of the radius ratio of the ions. This criterion places ZrO_2 on the border of stability between sixfold coordinated cations (as in rutile, TiO_2) and eightfold coordinated cations, as in UO_2 which has the fluorite structure [4,5]. However, such a simple ionic model is inadequate to explain the c, t, and m structures observed in ZrO_2. The ionic model has been extended to include compressible and polarizable oxygen ions, and an explanation of the relative stability of the phases at 0 K has been offered within this picture, the dipole and quadrupole polarizabilities of the O^{2-} ion induce the symmetry breaking distortions of the lattice [4]. We will see though that in fact the stability of

the m phase can be attributed to *covalency* rather than *polarizability*. A particular difficulty with the classical model for ZrO_2 [4] is that it predicts the rutile structure (r) to be of lower energy than the m structure, although the r structure is never observed experimentally in ZrO_2. This is overcome in the present TB model.

The need for electronic structure calculations also becomes apparent when we consider the phase stability of doped zirconia. It is well known that the phase boundaries are shifted to lower temperatures by doping with suitable impurities, and it is believed that oxygen vacancies play the key role in this (see, for example, Ref. [6]). However, there is little firm knowledge about the nature of the point defects in ZrO_2 [7], which are also crucial to the operation
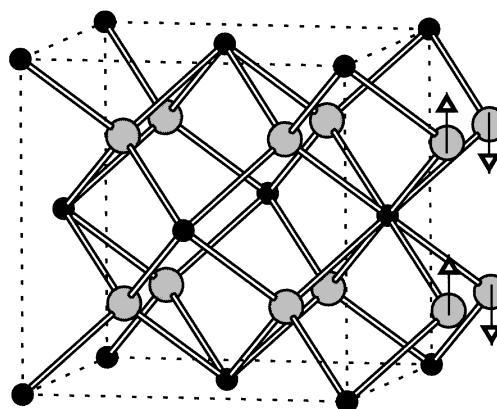

FIG. 1. Atomic positions in the c and t modifications of ZrO_2. Large gray circles are O atoms and small black circles Zr. The cubic, *fluorite* structure shows the eightfold Zr (see on the right) and fourfold O coordination. The symmetry breaking distortion to the tetragonal phase occurs as a spontaneous displacement of the O atoms as shown for four atoms on the right.

of this material as a sensor and in fuel cells. The complex solid state chemistry of ZrO_2 must derive in part from the ease of reduction of the Zr^{4+} ion. An understanding of these aspects demands a treatment of electron transfer within ZrO_2, which is of course beyond the scope of classical ionic models. Several *ab initio* calculations have been published, e.g., Refs. [8–10] for bulk phases, but these approaches become unmanageable for large systems containing defects. We have made accurate *ab initio* LDA calculations on bulk phases in order to parameterize and benchmark the TB model, which we anticipate will be of use for studying more complex systems.

The *c* phase has just one degree of freedom, its unit cell volume. The *t* phase has two additional degrees of freedom: besides the axial c/a ratio of the unit cell, the symmetry breaking displacement of the oxygen atoms δ is a variable (Fig. 1). The *r* phase also has two additional degrees of freedom. The *m* structure has 12 additional degrees of freedom. We have varied the size of the unit cell in each case, so as to obtain energy versus volume curves, and in each case we have completely relaxed all internal degrees of freedom. To calculate the band structures and total energies, we use an accurate method using density functional theory within the LDA. It is a new variant of the full potential linear muffin tin orbitals (FP-LMTO) method [11], in which the charge density is no longer matched at arbitrary sphere radii and which removes the need for defining "empty" spheres. An additional benefit is the existence of an analytic force theorem. For the highest precision, we use a rather complete basis of *s*, *p*, *d*, and *f* smooth Hankel functions

[11] with zero kinetic energy and additional *s*, *p*, and *d* functions with kinetic energy -2 Ry. These are augmented within muffin tin spheres of radius 2 a.u. (Zr) and 1.7 a.u. (O). We use Zr 4*p* rather than 5*p* orbitals in the basis since the former cannot be treated as core states [8,10] and the latter are too high in energy to contribute significantly to the energy bands. The Zr 4*s* dispersion is treated in a frozen, overlapping core approximation [11].

Our TB approach uses a minimal basis of *s* and *p* orbitals on oxygen and *d* orbitals on Zr. An entirely new feature of our model compared to more conventional self-consistent TB approaches [12–14] is the inclusion of off-diagonal, on-site matrix elements in the Hamiltonian, which are calculated from the crystal fields generated by the charge distribution. This feature allows the oxygen ions to polarize to the dipole and quadrupole levels, thus incorporating for the first time in a *quantum mechanical* model the effects which the *classical* polarizable ion model [4] predicts to be essential in discussing the relative stability of the phases. We are therefore combining in a single model the essential physics of *ionicity* and *covalency* and of polarizability which have previously only been treated within conceptually separate models.

We describe here the essential features of our TB approach; details have been published elsewhere [15]. A good theoretical starting point for this and all TB models is the Hohenberg-Kohn-Sham (HKS) total energy functional in which the exchange and correlation energy $E_{xc}[n]$ has been expanded to second order in the electron density $n(\mathbf{r})$ [16]:

$$E^{HKS} = \sum_i^{occ.} \langle \Psi_i | H_0 | \Psi_i \rangle$$
$$- \frac{1}{2} \int \frac{n_0 n_0'}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} \, d\mathbf{r}' + E_{xc}[n_0] - \int V_{xc}[n_0] n_0 \, d\mathbf{r} + E_{ii}$$
$$+ \frac{1}{2} \iint \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta^2 E_{xc}}{\delta n \, \delta n'} \bigg|_{n=n_0} \right) \delta n \, \delta n' \, d\mathbf{r} \, d\mathbf{r}'. \quad (1)$$

$n_0(\mathbf{r})$ is a reference electron density and H_0 is a reference one-electron Hamiltonian, in which the effective potential is generated from the reference electron density n_0. $\delta n = n - n_0$ is the difference between the actual and the reference charge density. We use the shorthand notation of [14]; a prime on the charge density indicates that it is evaluated at $\mathbf{r}'$. The summation is over all occupied states (occ.). The Kohn-Sham equation, a single particle Schrödinger equation, is simply obtained from (1) by variational minimization with respect to $n(\mathbf{r}) = \sum_i^{occ.} |\Psi_i(\mathbf{r})|^2$ subject to the normalization constraints on the wave functions $\langle \Psi_i | \Psi_i \rangle = 1$. As in traditional TB models, we treat the second line of (1) as a repulsive pairwise potential of Born-Mayer form, the two parameters of which are fitted to approximately reproduce our *ab initio* energy-volume curves for the *c* and *r* structures [15].

Without the last term of (1), this functional is the Harris-Foulkes one, which would have $\mathcal{O}(\delta n^2)$ errors. To do self-consistent TB we introduce a two-center approximation both for the Hamiltonian and the electrostatic terms, so that H_0 couples local orbitals between two sites and the last term of (1) involves on-site and intersite interactions between atom-centered, nonspherical charges. The TB representation of the term in $\delta^2 E_{xc}/\delta n \, \delta n'$ is purely on-site, and combines with the on-site Coulomb term to give an effective Hubbard U, which we set to 1 Ry.

The matrix elements of H_0 are determined with respect to the *c* structure as follows. The on-site *s*-level in oxygen is modeled as a nominal 3*s* state to allow the ions to polarize. In oxygen, the intersite parameters $ss\sigma$, $sp\sigma$, $pp\sigma$, and $pp\pi$ and their distance dependence

are fitted to the *ab initio* O-2p band and the volume dependence of its bandwidth. The other intersite matrix elements are chosen to approximately reproduce the *ab initio* bandwidths, with the usual canonical scaling [17], and only nearest neighbor (i.e., Zr-O) interactions are included. The diagonal elements are fitted to the *ab initio* band gaps.

Motivated by the successes of classical polarizable ion models, we approximate the intersite Coulomb terms by representing δn as a sum of point multipoles Q_L up to $\ell = 2$, where L stands for the combined angular momentum index (ℓ, m). Previous self-consistent TB has included the monopole terms (analogous to rigid ions [12]).

We include the higher multipoles as the expectation values of the operator $\hat{Q}_L^e = e\hat{r}^\ell Y_L(\mathbf{r})$ at a given site in the self-consistent wave function:

$$Q_L^e = \sum_{L'L''} \sum_i^{\text{occ.}} \bar{c}_{L'}^i c_{L''}^i \langle L'|\hat{Q}_L^e|L''\rangle. \quad (2)$$

The $c_{L'}^i$ appearing in (2) are the wave function expansion coefficients at the site in question in terms of the localized orbitals $\langle \mathbf{r}|L\rangle = f_\ell(r)Y_L(\mathbf{r})$. The index i subsumes the band and $\mathbf{k}$-point indices. The matrix elements have the form

$$\langle L'|\hat{Q}_L^e|L''\rangle = e\Delta_{\ell'\ell''\ell}C_{L'L''L}, \quad (3)$$

in which the strength of the ℓ tupole created on a site by combining orbitals of angular momentum ℓ' and ℓ'' is

$$\Delta_{\ell'\ell''\ell} = \int r^{\ell+2} f_{\ell'} f_{\ell''}\, dr.$$

The symmetry and selection rules in (3) are taken care of by the Gaunt coefficients $C_{L'L''L}$. The one-electron potential, including crystal field splitting up to $\ell = 4$, is then obtained from (2) by a straightforward structure constant expansion [15,17].

For our choice of minimum basis there are just two independent Δ's on each site. On the Zr sites, the most important is Δ_{ddg}, which provides the cubic splitting of d states into the t_2 and e manifolds. We find a value $\Delta_{ddg} = 65$ *a.u.* gives good agreement between TB and *ab initio* bands for c and r structures, which have opposite signs of the splitting. The other parameter on Zr is Δ_{ddd} which we simply set equal to $\sqrt{\Delta_{ddg}}$. On oxygen, the parameters are Δ_{spp} and Δ_{ppd}. These have no influence at sites of cubic symmetry, but in the rutile structure, for example, we have found that Δ_{ppd} controls the width of the oxygen $2p$ band due to a splitting of the O $- 2p$ levels by field gradients. The final crystal field parameter, Δ_{spp}, has little effect on the bands, but the dipole it creates on the anions effects the force on them in the symmetry breaking $c \to t$ distortion, so we have adjusted it to fit the *ab initio* energy versus δ curve [15]. These results reproduce the soft phonon mode at the X point which is associated with the transition from the c structure.

Calculating forces on atoms within our TB model presents no difficulties after the self-consistent solution has been obtained by iteration. From the variational prop-

erty of the total energy E^{HKS}, if we slightly displace an ion, the first-order change in energy can be obtained by keeping the c_L^i and hence the δn unperturbed. The force is therefore the sum of three contributions, corresponding to the three lines of (1): first the terms from the derivatives of the matrix H_0 evaluated in the unperturbed wave function, second the repulsive potential, and third the classical electrostatic force between the unperturbed multipoles. The first two terms are the same as in elementary non-self-consistent TB, while the third is a surprisingly straightforward application of classical electrostatics, the simplicity of which is a result of charge self-consistency and the variational principle.

The energy volume curves we have calculated with *ab initio* and TB are displayed in Fig. 2. The axial ratio q and tetragonal distortion δ are also shown as a function of volume in Fig. 2. Note that at small volumes, there is no symmetry breaking in the c phase, and that as the volume is increased, the single energy well in q and δ splits into a double well. This is a second-order phase transition, in which δ is the order parameter proportional to the amplitude of the soft phonon mode. If V_0 is the volume at the transition, Landau theory predicts that $\delta \sim (V - V_0)^{\frac{1}{2}}$ and $q \sim (V - V_0)$. This is reflected in Figs. 2(c) and 2(d).

Our *ab initio* calculations are in excellent agreement with experimental results, and incidentally confirm the satisfactory accuracy of the pseudopotential method used by Stapper, and Kralik *et al.* We find the energy differences between t and c, and m and c, to be 3.6 and 7.7 mRy/ZrO$_2$, compared to 3.3 and 7.5 found by Kralik *et al.* [10]; and 4.6 and 8.2 found by Stapper [9]. Figure 2 shows that our tight-binding model reproduces the relative energetics of these phases as well as the atomic structures. Note that the new TB model reproduces the large volume expansion in the transition from the t to the m phases. It is this that is exploited in the transformation toughening in ZrO$_2$-based engineering ceramics [1,18].

By switching off the Δ's on the oxygen ions, we are able to explore the effect of not allowing the anions to polarize. This reduces but does not eliminate the spontaneous tetragonal distortion of the c phase [15], exposing the important role of polarizability in stabilizing this lower symmetry phase. The energy of the m phase is increased by less than 10 mRy/ZrO$_2$ when the Δ's are set to zero, which places the m and c phases essentially equal in energy. The polarizability is of less consequence in stabilizing the m phase than is the covalency, when we set the TB hopping integrals to zero, reducing our model to a classical electrostatic one, then c is more stable than m by 40 mRy. We may conclude that *covalency* is the controlling effect in stabilizing the monoclinic phase of ZrO$_2$. This is in apparent contrast to the conclusions of the classical polarizable ion model which attributes the stability of the m phase to the anion polarizability [4]. Such a model must capture all covalent effects within its
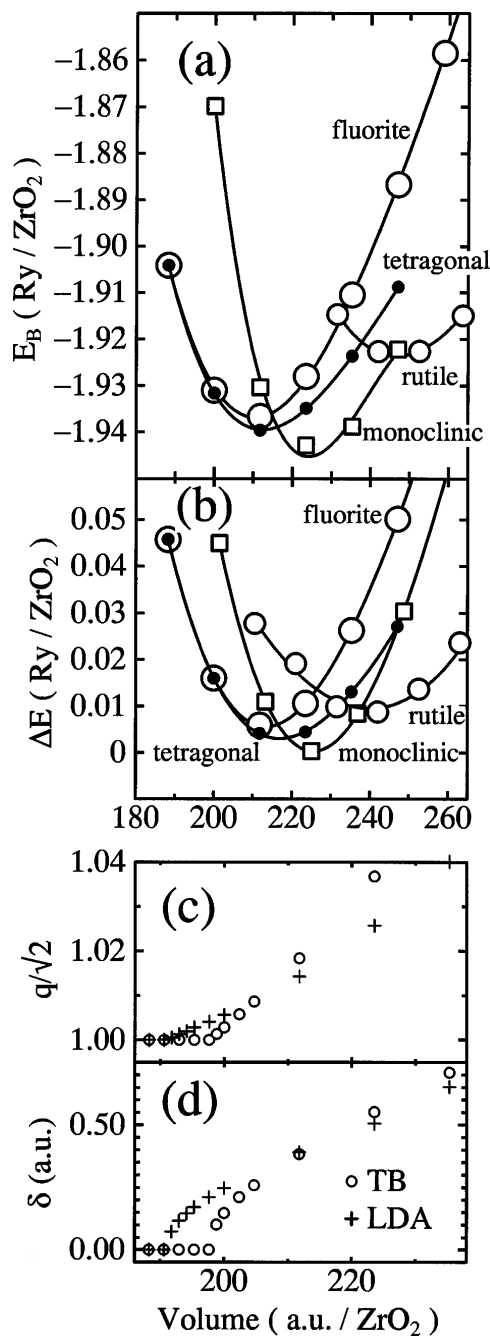
FIG. 2. Structural energy versus volume in four phases of ZrO_2. At each volume, the energy is minimized simultaneously with respect to all the remaining degrees of freedom. (a) *Ab initio* calculations of the absolute binding energy (energy with respect to spin polarized free atoms); (b) TB results referred to the equilibrium energy of the *m* phase. (c) and (d) show the axial ratio q and distortion parameter δ in the *t* modification as a function of volume.

ionic polarizabilities, and it remains to be seen how this limits its transferability between atomic environments.

Future work will use the model to explore the energetics of defect structures in ZrO_2 and apply the same

TB model to other oxides in which anion polarizability is thought to be an important factor, such as Al_2O_3.

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