

## Structure of the $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> (0001) surface: An *ab initio* total-energy study

C. Rehbein

*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

N. M. Harrison

*Central Laboratory of the Research Councils, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*

A. Wander

*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

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The structure of the basal plane of the  $\alpha$  phase of Cr<sub>2</sub>O<sub>3</sub> has been investigated using periodic *ab initio* Hartree-Fock theory. The Cr-terminated surface, which is nonpolar but is charged, is found to be stable. However, a large-scale relaxation of the surface layer away from the ideal bulk-terminated structure has been found. The top layer Cr<sup>3+</sup> ions move inward toward the second-layer O<sup>2-</sup> ions by nearly 50% of their original interlayer spacing. This results in a slight lowering of the Cr ionicity in the surface layer, but no large-scale changes in bond character have been found. We therefore propose that the mechanism behind this dramatic reconstruction is purely electrostatic in origin. [S0163-1829(96)01943-1]

### I. INTRODUCTION

The study of transition-metal-oxide surfaces is of fundamental importance to the field of surface science, but has, until recently, been neglected by the majority of workers in the field. The reasons for this are twofold; first, experimental studies have been hampered by the fact that it is very hard to produce well-ordered surfaces from bulk oxide crystals. In addition, these crystals are often insulators which inhibits the use of standard electron-based experimental probes, although progress has been made in this direction.<sup>1</sup>

Progress has been made of late in the use of model oxide systems consisting of well ordered thin-film oxide layers grown epitaxially on metallic supports. The metallic support of such systems allows the use of electron-based techniques, provided the film thickness is relatively small. One surface that has been the subject of a number of studies is thin-film Cr<sub>2</sub>O<sub>3</sub> grown on Cr(110).<sup>2-4</sup> However, the structure of this film is not clear, although on the basis of high-resolution electron-energy-loss spectroscopy on Al<sub>2</sub>O<sub>3</sub> films grown on NiAl(110), a tentative assignment of the surface as the  $\gamma$  phase has been made.<sup>5</sup> The  $\gamma$  phase is a disordered phase in which the tetrahedral and octahedral holes in the oxygen lattice have fractional occupancy,<sup>6</sup> while the  $\alpha$  phase is a well-ordered bulk crystal showing a corundum structure. This consists of an hcp array of O<sup>2-</sup> ions with the metal ions occupying two-thirds of the octahedral interstices in the ordered array. The surface unit cells of the  $\alpha$ -(0001) and  $\gamma$ -(111) surfaces are very similar, and hence it is impossible to separate them on the basis of the observed low-energy electron-diffraction patterns, although the  $\alpha$  phase results in a closer match with the experimentally observed lattice parameters, leading to the identification of the thin film as the  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> (0001) surface in the original study.<sup>7</sup>

The use of periodic boundary conditions in theoretical calculations makes studies of the disordered  $\gamma$ -(111) surface impractical. However, a detailed examination of the two pos-

sible surfaces shows many similarities in their structure (Fig. 1). Hence, although the thin-film system may turn out to be the  $\gamma$  (111) surface, theoretical studies of the  $\alpha$ -(0001) surface, which is amenable to the use of periodic boundary conditions, can still play an invaluable role in helping to elucidate the surface properties of the Cr<sub>2</sub>O<sub>3</sub>-Cr(110) system, as well as being an important study of a bulk oxide surface.

Use of periodic unrestricted Hartree-Fock (UHF) theory has recently been shown to be very successful in dealing with crystalline systems which contain many open shell ions, and in dealing with the spin-dependent ground-state properties of such systems.<sup>8-13</sup> For many of these properties, the use of UHF theory has given results comparable to, or better than, the more usual choice of density-functional theory, or nonperiodic embedded cluster studies. The study of transition-metal compounds is further complicated, since they show a variety of electronic effects ranging from being strong charge transfer insulators [hematite  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Ref. 11) through to metalliclike behavior at the opposite end of the first transition period. Eskolaite ( $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>) is somewhat intermediate between these two extremes, so that borderline characteristics can be expected in its electronic behavior, making this a potentially rich field of investigation. However, like hematite, eskolaite shares a simplifying feature in that no orbital degeneracy or related Jahn-Teller<sup>12</sup> effects are expected to be shown by its metal ions. We have therefore begun our study of this interesting, and important system by attempting to find the stable, lowest-energy structure of the  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> (0001) surface using *ab initio* total energy calculations within the spin unrestricted Hartree-Fock formalism.

### II. METHODOLOGY

All calculations were performed with CRYSTAL95 (Ref. 8) codes based on the use of the periodic *ab initio* LCAO (linear combination of atomic orbitals) Hartree-Fock method, with the option of an unrestricted treatment of the spin-

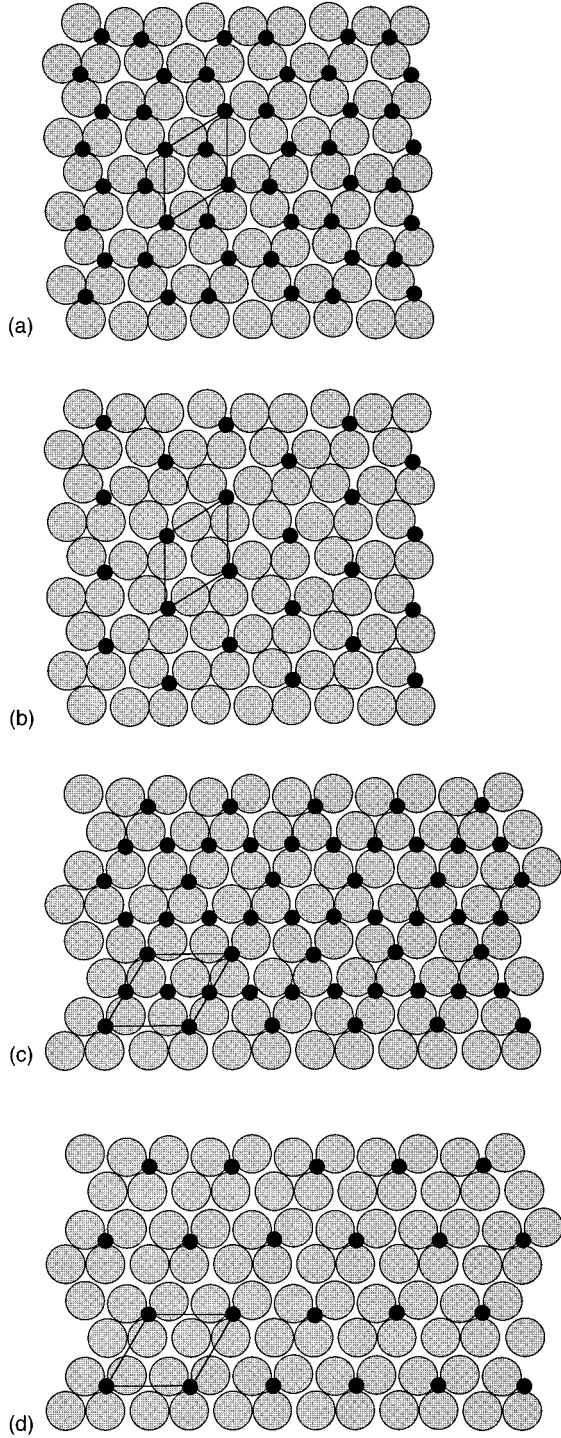


FIG. 1. Possible surface terminations of  $\alpha$  and  $\gamma$  Cr<sub>2</sub>O<sub>3</sub>. (a)  $\alpha$  phase terminated by a Cr<sup>3+</sup> bilayer. (b) The stable (0001) surface terminated by a single layer of Cr<sup>3+</sup>. This is the surface optimized in this study. (c) The  $\gamma$  phase with *all* possible Cr<sup>3+</sup> sites occupied for clarity. (d) A possible termination of the  $\gamma$  (111) surface. Note the similarities in local structure between this diagram and (b) above.

dependent wave functions in open-shell systems.<sup>9</sup> This is necessary to obtain spin-polarized eigenfunctions of the Fock Hamiltonian, since the Cr<sup>3+</sup> ion contains three unpaired electrons. The radial factors of atomic orbitals are expressed as linear combinations of Gaussian-type functions. Basis sets

TABLE I. Summary of results for bulk  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>.

Value	This study	Previous theory (Ref. 13)	Experiment
$a_0$	5.04 Å (+1.8%)	5.05 Å	4.95 Å
$c_0$	13.72 Å (+1.1%)	13.735 Å	13.566 Å

at the all-electron level were used throughout. The basis sets used were taken from a previous study of bulk  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>.<sup>13</sup> The oxygen basis set, denoted as 8-411 G\*,<sup>14</sup> was based on an earlier study of Al<sub>2</sub>O<sub>3</sub>,<sup>15</sup> with the exponents of the 4*sp* shell and polarization function reoptimized to minimize the energy of crystalline Cr<sub>2</sub>O<sub>3</sub>. Chromium was represented by an 8-6-411 G contraction with two *d*-type 41 G shells variationally optimized to an isolated Cr<sup>3+</sup> ion. The exponents of the 5*sp* and 4*d* shell of Cr were refined by a minimization of the crystal energy of Cr<sub>2</sub>O<sub>3</sub> as in the case of the oxygen functions. The relative charges on atoms and the bond overlap populations were calculated using a Mulliken partition of the charge density. This is a somewhat arbitrary choice, since there is no unique method of performing the partition of the charge density. However, the choice of a given scheme is still extremely useful in comparing the results of calculations performed using similar basis sets.<sup>16</sup>

In CRYSTAL the convergence of the real-space summations of the Coulomb and exchange contributions to the Fock matrix are controlled by five overlap criteria (*T1–T5*). The control of these approximations is described in detail elsewhere.<sup>8</sup> The values used in this study were 10<sup>−6</sup>, 10<sup>−6</sup>, 10<sup>−7</sup>, and 10<sup>−13</sup>, which result in a numerical error in the binding energy of order 1 and/or 0.01 m Hartree in relative energies of different structures.

The validity of these values was tested by application of the method to a calculation of the bulk lattice parameters for  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>, which has the corundum structure of space group  $R\bar{3}c$  with hexagonal close-packed (0001) layers of O atoms and two-thirds of the octahedral interstices in between filled by Cr atoms. Below the Néel temperature of between 32 and 42 °C (according to sample purity), the stable phase is antiferromagnetic,<sup>17</sup> and consists of alternating planes of Cr ions in the *c* direction which are antiferromagnetically coupled.<sup>18,19</sup> The results of these calculations are displayed in Table I along with the corresponding experimental values, and the results from the earlier study. As can be seen, the lattice parameters are correctly reproduced to better than a 2% error. The energy difference between the antiferromagnetic and ferromagnetic crystal at the relaxed geometries in this study is found to 0.03 eV, which agrees reasonably well with the experimental Néel temperature. Consequently, we can have confidence in the methodology and parameters used in this investigation.

### III. RESULTS

The surface was studied using an infinite two-dimensional slab geometry. The unit cell consists of a (1×1) surface, and a block of material six layers thick. The surface was terminated by a layer of Cr<sup>3+</sup>, giving a slab geometry of Cr<sup>3+</sup>-3×O<sup>2-</sup>-Cr<sup>3+</sup>-Cr<sup>3+</sup>-3×O<sup>2-</sup>-Cr<sup>3+</sup>. This geometry is shown schematically in Fig. 2. A surface terminated by a single layer of chromium ions is chosen, since this gives rise

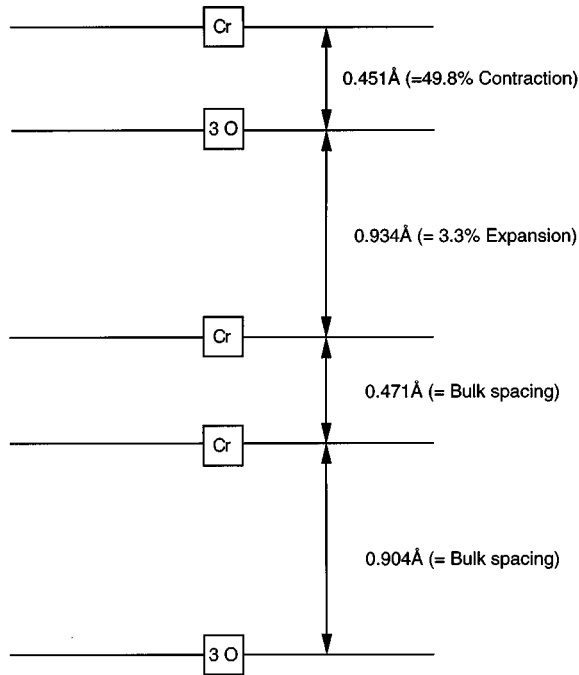


FIG. 2. A schematic side view of the optimized  $\text{Cr}_2\text{O}_3$  structure showing the large relaxation between the first and second layers of the crystal.

to a nonpolar slab geometry, and has been found as the stable termination in earlier studies of  $\alpha$  alumina and  $\alpha$  chromia.<sup>20,21</sup> Other possible terminations of the slab can be produced by a cyclic permutation of the individual layers of the unit cell (Fig. 3). As shown in the figure, stoichiometric slabs, which are required due to the constraint of charge neutrality, all display a nonzero dipole moment across them, and hence are unstable surface geometries.

In the initial states of geometry optimization, only the  $\text{Cr}^{3+}$  ions were allowed to move, with their direction of motion being constrained to be perpendicular to the surface. This produces a very large relaxation of approximately 50% in the first-to-second-layer ( $\text{Cr}^{3+}$  to  $\text{O}^{2-}$ ) distance. However, such effects are not unexpected. The topmost  $\text{Al}^{3+}$  layer of the (0001) surface of  $\alpha\text{-Al}_2\text{O}_3$  has also been found to undergo a similar large relaxation,<sup>20,22</sup> while large relaxations of the (0001) chromia surface have previously been predicted on the basis of ionic modeling.<sup>21</sup> Having found an approximate geometry, the second-layer  $\text{O}^{2-}$  ions were then allowed to move vertically as well. This additional degree of freedom results in little change in the optimum structure, although a slight displacement of the  $\text{O}^{2-}$  ions is observed. This is to be expected, since the oxygen ions, due to their large size, are virtually close packed in the ideal crystal, and hence a large vertical displacement gives rise to unacceptably large Coulombic repulsion between the second and fifth layers of the slab. Finally, the oxygen ions were also allowed to move parallel to the surface plane, but maintaining the symmetry of the surface system. The sequence was then cycled, until a self-consistent solution was found in which all four structural parameters were simultaneously optimized. The ferromagnetic and antiferromagnetic (AFM) phases were independently optimized. The geometry of the two

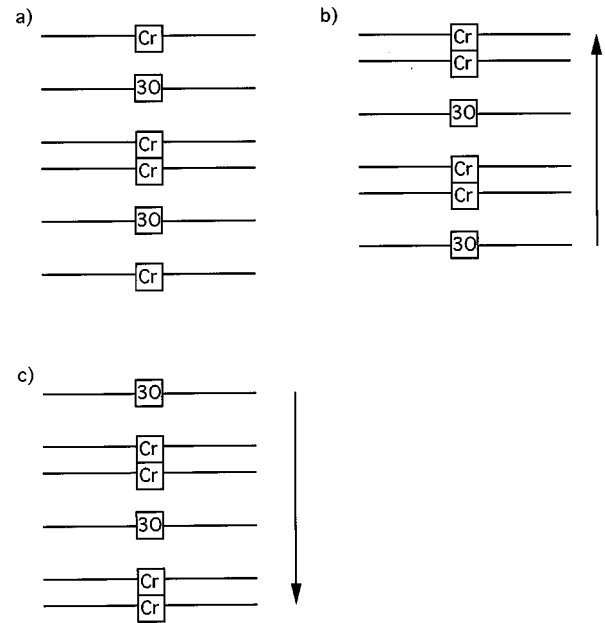


FIG. 3. Possible terminations of the  $\text{Cr}_2\text{O}_3$  slab. (a) Termination by a single  $\text{Cr}^{3+}$  layer. This geometry is the stable ground-state configuration. (b) Termination by a  $\text{Cr}^{3+}$  bilayer. (c) Termination by an  $\text{O}^{2-}$  layer. The constraint of charge neutrality forces the unit cell to contain four  $\text{Cr}^{3+}$  ions and six  $\text{O}^{2-}$  ions. Note that geometry (a) gives rise to a nonpolar unit cell, while terminations (b) and (c) are polar in character, with the arrows showing the dipole moment.

phases is virtually identical (all differences  $\leq 0.02$  Å) but the AFM phase has an energy lower by 0.02 eV, and is hence the stable ground-state structure. The results of this full optimization are displayed in Table II. Throughout the optimization procedure, the charge of the central  $\text{Cr}^{3+}$  ions was monitored. For all optimizations, the charge varies by less than

TABLE II. Summary of results for the geometry optimization of  $\alpha\text{-Cr}_2\text{O}_3$  (0001) in the antiferromagnetic phase.  $z$  is taken to be perpendicular to the surface, and  $x$  is an in-plane displacement.  $\alpha$  and  $\beta$  refer to spin-up and -down electrons respectively. The overlap population is a measure of the degree of covalency contained in an interatomic bond.

Parameter	Value
Cr $\Delta z$	-0.423 Å
O $\Delta z$	+0.03 Å
O $\Delta x$ (fractional)	-0.02
Cr-O (bulk)	1.925 Å
Cr-O (surface)	1.786 Å
Cr total $e^-$ population-bulk	21.701
Cr total $e^-$ population-surface	21.889
Cr $\alpha$ - $\beta$ bulk	3.02
Cr $\alpha$ - $\beta$ surface	3.01
Cr $\alpha$ - $\beta$	0.017
Cr-O bond overlap-bulk	0.029
Cr-O bond overlap-surface	0.041
Surface energy (unrelaxed)	9.3J m <sup>-2</sup>
Surface energy (relaxed)	3.1J m <sup>-2</sup>

0.01 of an electron from the expected bulk value, and hence we can be confident that the results show convergence with respect to slab thickness.

#### IV. DISCUSSION AND CONCLUSIONS

Although nonpolar surfaces of transition-metal-oxide surfaces are expected to be stable, crystal faces which terminate in a charged layer of ions can be expected to be less stable than those in which the surface is terminated by a charge neutral sheet. This arises from the high Coulomb energy associated with each layer of (unshielded) point charges. Hence we can expect that such surfaces should undergo relatively large relaxations in an effort to decrease the net charge of the surface plane. This type of relaxation should give rise to a large decrease in the surface energy arising from a decrease in the Coulombic repulsion energy of each charged layer, due to an increased shielding of charged objects.

This mechanism is demonstrated by the current study as shown in Table II. The bulk-terminated surface has a very high surface energy ( $9 \text{ J m}^{-2}$ ), arising from a high Coulombic interaction term. As the topmost charged layer ( $\text{Cr}^{3+}$ ) relaxes inward towards the bulk, the Coulombic interaction decreases dramatically, as does the surface energy, until a minimum value of  $3 \text{ J m}^{-2}$  is reached. This value is still somewhat high, but it should be remembered that the (0001) is not the thermodynamically stable surface of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub>. Studies of dispersed powdered  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> by transmission electron microscopy<sup>23</sup> have shown that the most stable surface configuration is the (011 $\bar{2}$ ) surface, which is the subject of an ongoing study in this laboratory.<sup>24</sup>

However, other effects could also occur at the surface of this material. Chromium, like all transition metals, can exist in a variety of oxidation states. As well as lowering the Coulomb energy by relaxation and increased shielding, the system could also lower its energy by lowering the charge trans-

fer to the surface (replacing  $\text{Cr}^{3+}$  by  $\text{Cr}^{2+}$ ). This would also lead to a lowering of the in-plane repulsive interactions. However, this effect would also lead to a change in the bonding of the surface layer, and should give rise to a partial covalent character in the Cr-O bond system. Examination of the results presented in Table II does indeed show that the surface Cr ions carry slightly less charge than the bulk ions ( $-0.188e^-/\text{ion}$ ). However, the bond overlap populations (a measure of the covalent character of bonding between atoms) shows that both the Cr-O bonds in the bulk and in the surface are effectively ionic in character. There is a slight increase in the bond overlap population at the surface, but this value is still effectively zero. Hence we can conclude that the surface ions are still  $\text{Cr}^{3+}$  in nature, with three unpaired electrons which still reside in the *d* shell of the atom.

The formation of the surface and the associated relaxations of the surface layers does indeed lead to a slight redistribution of charge. The surface Cr ions become slightly more diffuse, shifting charge into the outer *d* shell of the split valence basis set. Again, this is to be expected, since in this manner the Cr ion can further lower its energy. However, the effect is very small being of the order of  $0.01e^-$  per surface Cr ion.

Consequently, we can conclude that the hexagonal (0001) face of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> is stable, but undergoes a dramatic reconstruction of the outermost  $\text{Cr}^{3+}$  layer in which the ions move inward by nearly 50% of their original interlayer spacing. This does not greatly perturb the Cr-O bond system (the Cr-O bond length drops by 7.2%), which remains ionic in nature. The driving force behind this large-scale movement of the surface plane is purely electrostatic in origin, since no change in the character of the Cr-O bond is observed.

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