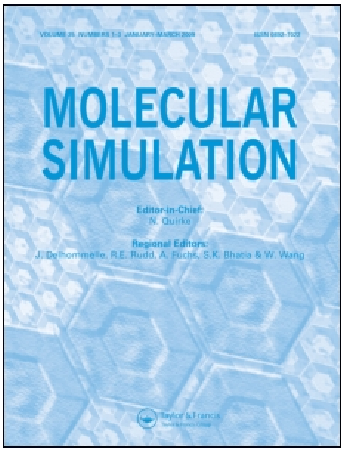


Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

The Surface Structure of CaF_2; A Comparison of Techniques

Shyam Vyas[a]; Robin W. Grimes[bc]; Vladimir Bulatov[bd]; M. Abramowski[b]
[a] Molecular Simulations INC., Parsippany, New Jersey, USA [b] Dept. of Materials, Imperial College, London, UK [c] Los Alamos National laboratory, Los Alamos, New Mexico [d] Dept. of Physics, Oregon State University, Corvallis, OR, USA

To cite this Article Vyas, Shyam , Grimes, Robin W. , Bulatov, Vladimir and Abramowski, M.(2001) 'The Surface Structure of CaF_2; A Comparison of Techniques', Molecular Simulation, 26: 5, 307 — 321

To link to this Article: DOI: 10.1080/08927020108023016

URL: http://dx.doi.org/10.1080/08927020108023016

Molecular Simulation, 2001, Vol. 26, pp. 307–321
Reprints available directly from the publisher
Photocopying permitted by license only

THE SURFACE STRUCTURE OF CaF_2; A COMPARISON OF TECHNIQUES

SHYAM VYAS[a,*], ROBIN W. GRIMES[b,†],
VLADIMIR BULATOV[b,c] and M. ABRAMOWSKI[b]

[a]*Molecular Simulations INC., 300 Lanidex Plaza, Parsippany, New Jersey 07054, USA;* [b]*Dept. of Materials, Imperial College, Prince Consort Rd., London SW7 2BP, UK;* [c]*Dept. of Physics, Oregon State University, Corvallis, OR 97331, USA*

(Received May 2000; accepted June 2000)

A nano-crystal of CaF_2, consisting of 3645 ions, was simulated at 300 K for 110 ps using molecular dynamics. After this time, the structures of non-dipolar {111} and dipolar {200} surfaces showed features which were comparable to simulations carried out with a 2D energy minimisation code. Of particular interest was the similarity between defects that appeared on the {200} surface in the MD simulation and the lowest energy configurations determined in the static simulation.

Keywords: CaF_2; Molecular dynamics; DALEC; Marvin simulation

1. INTRODUCTION

Over the past ten years there has been a dramatic increase in the application of atomistic simulation to the prediction of crystal morphologies. This has been facilitated by new surface simulation codes such as MARVIN [1] and PARAPOCS [2], but the arrival of integrated modelling packages [3] and an increase in computing power have also contributed. These surface simulation techniques take advantage of methodologies such as the

---

[*] e-mail: svyas@msi.com

[†] Present address: Los Alamos National laboratory, P.O. Box 1663, MSK765, Materials Science Division Office, Los Alamos, New Mexico, 87545. Tel.: 505-667-1621, Fax: 505-665-2992, e-mail: r.grimes@ic.ac.uk

calculation of attachment energies and the classification of inorganic surfaces [4, 5] which were developed a decade earlier.

Much of the initial work on inorganic surface modelling was carried out by Tasker [4, 6] and Mackrodt [7] on the surfaces of MgO and Al_2O_3, respectively. However, more recently the technique has matured to the point that it has become possible to predict not only the atomic structure of surfaces [8, 9] but also their crystal morphologies [10–12]. Furthermore, this type of approach has been extended by the work of Schluger *et al.* [13] who modelled the interaction of an AFM tip with a surface.

Despite the sucess of surface modelling, a number of fundamental controversies still persist. The most enduring of these is the treatment of so called dipolar surfaces. These surfaces form when a crystal is cleaved along a plane which contains alternating layers of positive and negative charge. The energy of such surfaces increases as a function of crystal thickness (the simulation block), thus the surface energies converge to infinity. Nevertheless, in reality such faces are seen in crystal morphologies. Indeed, for some materials such as spinel, all surfaces are nominally dipolar [9, 14]. The perceived problem is effectively overcome by the introduction of surface defects; *e.g.*, vacancies [15], interstitials or hydroxide groups [16, 17]. However, in a static simulation, it is necessary to specify the type of defect and its position. Consequently, the outcome of the calculation will depend on details defined by the user; these include the nature of the defects specified, their arrangement, and the size of the surface repeat unit to be considered. Thus, even with a fairly small simulation box the number of options can quickly lead to many hundreds of calculations.

In the present study we compare established energy minimisation studies of surfaces with a more holistic approach based on molecular dynamic (MD) studies of nano-crystalline materials. During an MD simulation the crystallite ions are permitted to rearrange themselves dynamically throughout the whole system, subject to forces and interactions from all the other ions in the crystallite. As such, the MD study is able to test the concept that it is necessary, in a finite crystal, to construct defects that remove surface dipoles and how extensive the defect formation may be. However, to provide a realistic sized crystal many hundred of ions must be considered and the crystallite needs to be equilibriated over long timescales. Consequently, the MD study is much more computationally expensive than a single static simulation. Thus it would be very valuable if it were possible to validate, or at least support, certain approximations that are made in the static simulation.

2. METHODOLOGY

2.1. Simulation Techniques

The static energy minimisation simulations of CaF_2 surfaces were carried out using the MARVIN code. This code treats the surface as a block repeated infinitely in two dimensions. The block is divided in two regions. Region I contains the free surface and the ions within it are treated explicitly and their positions minimised using Newton-Rhapson techniques. Region II marks the begining of the bulk, and is kept static. It is required to model the effect of the bulk on the surface. A more detailed discussion of this methodology can be found in numerous reviews and papers [18–20].

The molecular dynamics (MD) studies were carried out using the PENICILLIN code [21], which employs a Gear 5th order predictor corrector algorithm. Two different nano-clusters were studied to examine the finite surface relaxation and rearrangement; a large 3645 atom cluster and a smaller 1665 atom cluster (results from the latter are presented elsewhere [22]). The initial starting geometries of the clusters where chosen such that their morphologies were as close as possible to being spherical, while using only two low index faces, {111} and {200}. In practical terms, such a morphology ensures the variation of the electric field around the unrelaxed cluster is not too great. This prevents ions at low coordinate sites from acquiring too much energy and leaving the cluster. Although there is presently no way of choosing an optimum geometry systematically, a suitable geometry for both clusters was found to be a truncated octahedron (a {111} surface dominated morphology) with large {200} surface facets cut onto it. These faces are seen in the morphology of other fluorite structures [15, 23].

2.2. Potential Parameters

The potentials employed in the present study, use a modified Buckingham form;

$$S_{ij} = A_{\exp}\left(\frac{-r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^{6}} + \frac{D}{r_{ij}^{12}} \tag{1}$$

The D/r^{12} term, not usually used in static minimisation studies, prevents unphysical relaxations at short inter-atomic seperations which can occur at high temperatures, where it is possible for individual ions to have very high

TABLE I Short-range interatomic potential parameters

Interaction	*A (eV)*	ρ *(Å)*	*C* ($eVÅ^{-6}$)	*D* ($eVÅ^{-12}$)
$Ca^{2+}-Ca^{2+}$	44898.1	0.169	0.00	0.00
$Ca^{2+}-F^{-}$	1273.8	0.2997	0.00	0.00
$F^{-}-F^{-}$	1127.7	0.2753	15.83	15.83

instantaneous energies. The potential parameters are listed in Table I, and were derived by fitting to both the CaF_2 crystal structure and the triatomic CaF_2 molecule [21].

2.3. α-shapes

Visualisation of the surface relaxation and rearrangement proved to be impossible using conventional atomic models as too many atoms were present in the cluster to develop an overall view of relaxation. A more general picture can be developed by using a visualisation technique known as the α-shape method [24]. This entails the representation of the atoms as vertices of tetrahedra. Those tetrahedra which are larger than a given radius are removed. A two dimensional example is shown in Figure 1. The resulting shape (the α-shape) captures the 'intuitive' form of the cluster. The

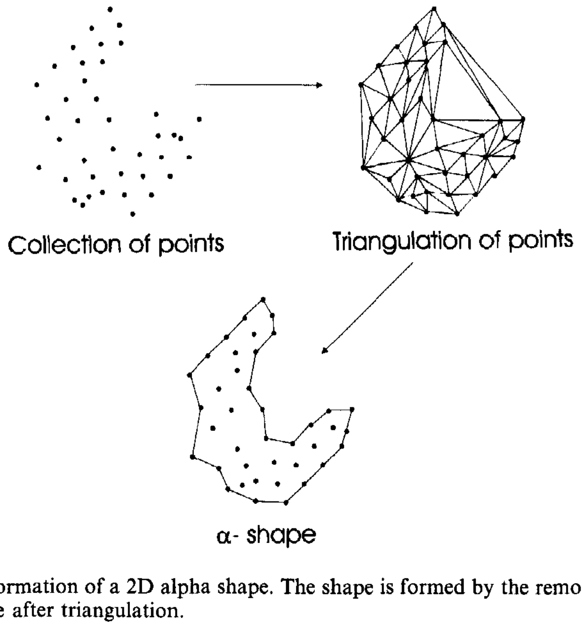


FIGURE 1 Formation of a 2D alpha shape. The shape is formed by the removal of triangles of a specific size after triangulation.

technique is analogous to using polyhedra to represent SiO_4^{2-} units in silicious materials or using space filling diagrams to represent the electron clouds of molecules. Unfortunately, our experience suggests that an α-shape alone will not easily convey important information concerning the atomic distribution of surface ion species. Thus atoms, which intersect the α-shape, were superimposed onto the α-shape surface. The resulting hybrid visualization technique, called DALEC (Direct Atomic Location of Elemental Configurations) was succesful in being able to show clearly the changes to surface atomic structure that resulted from ions being displaced or moved from their perfect lattice positions.

3. RESULTS

3.1. Two Dimensional Surface Simulations: Energy Minimisation

Static infinite 2D surface studies were carried out on those low index faces subsequently cut onto the nano-crystals *i.e.* {111} and {200} (see Tab. II). By comparison with other studies of compounds with the fluorite structure, it is unlikely that surfaces other than the {200} will appear in predicted morphologies [15, 23]. This is supported by observations on naturally occuring minerals which show only {111} surfaces as cleavage and {200} faces as growth planes [25].

The {111} Surface

This Type II (*i.e.*, non-dipolar) surface (Fig. 2) shows very little relaxation as all the ions are symmetrically coordinated. This is clear from the values given in Table II, which show that the unrelaxed surface energy is very similar to the energy of the relaxed surface. As this might indicate, the surface is thermodynamically very stable. This mirrors previous studies of

TABLE II Predicted surface energies using static simulations

		Energy (Jm^{-2})	
Surface	*Configuration*	*Unrelaxed*	*Relaxed*
(111)	–	0.51	0.49
(200)	A	1.46	0.74
	B	2.15	1.12
	AB	1.79	0.80
	C	3.08	1.83

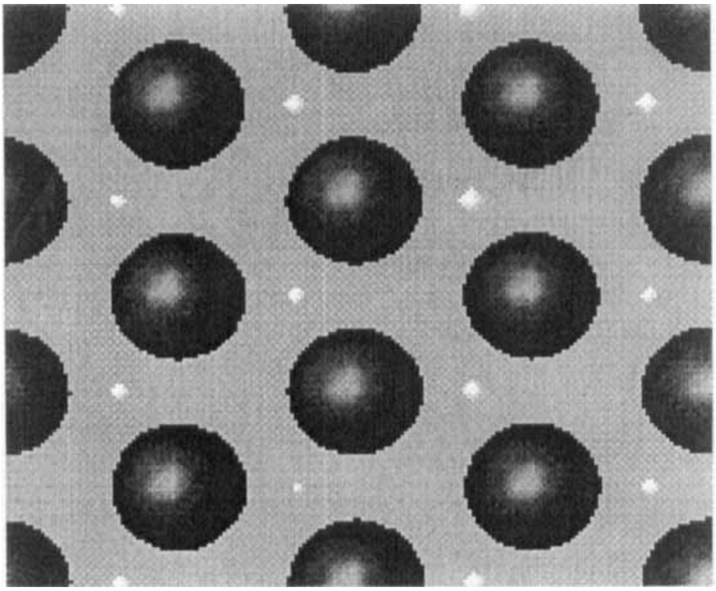


FIGURE 2 Surface structure of the (111) faces. The dark ions are fluorine. Also in evidence are white spots which are calcium ions in the layer below, protruding slightly through the α-shape.

{111} surfaces in other fluorite surfaces [15,23]. Consequently, {111} would be the dominant face in morphology predictions.

The {200} Surface

This is a Type III surface which can be terminated by either a layer of calcium or a layer of fluorine. If calcium ions form the uppermost layer, the surface can be stabilised (*i.e.*, the dipole removed) by either creating F^- interstitials (Figs. 3–5) or Ca^{2+} vacancies (Fig. 6). Additionally, if the surface is formed from a *single* unit cell periodically repeated, the two F^- interstitial ions can be arranged in two possible ways; either diagonally to each other (Fig. 3) or next to one another (Fig. 4). Table II and Figures 3–5 show the energetics and surface structures of such systems. The most thermodynamically stable configuration on a (200) surface is where the defects are anion interstitials which are arranged diagonally opposite each other (Configuration A) . This is similar to the results for other fluorite surfaces [15,23]. Note, that for all these configurations, {200} surfaces contains 50% defects, so that – whether we start with a

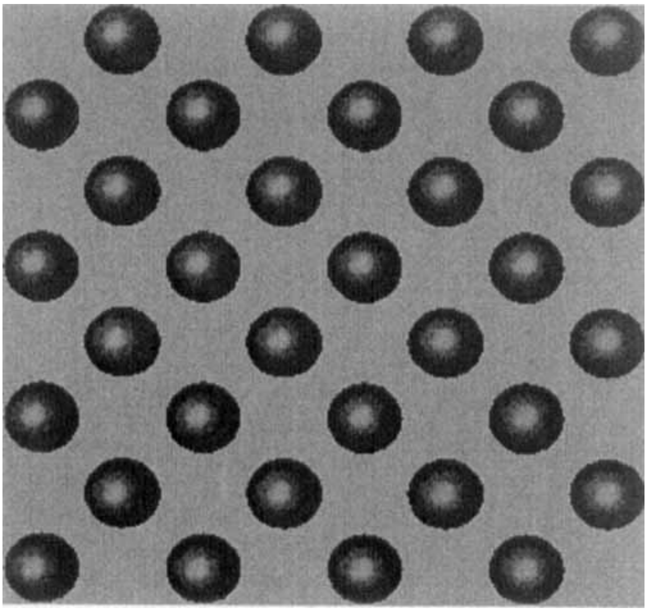


FIGURE 3 "A" configuration of a 3 × 3 cubic unit cell of the (200) surface in a MARVIN simulation after relaxation.

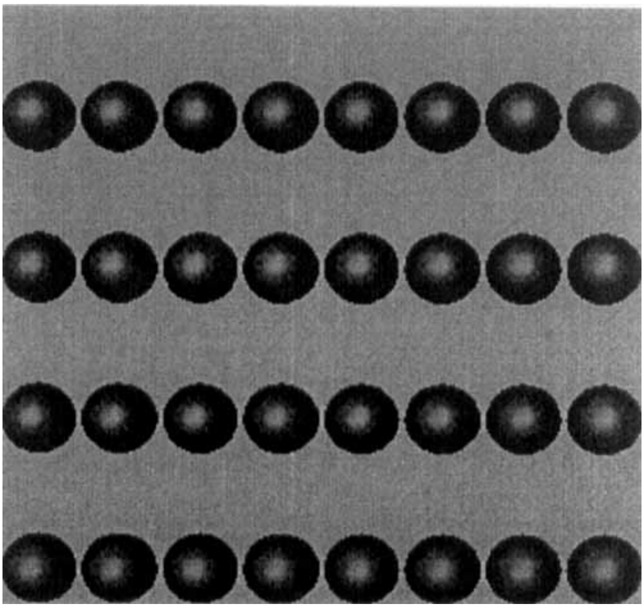


FIGURE 4 "B" configuration of a 3 × 3 cubic unit cell of the (200) surface after relaxation.

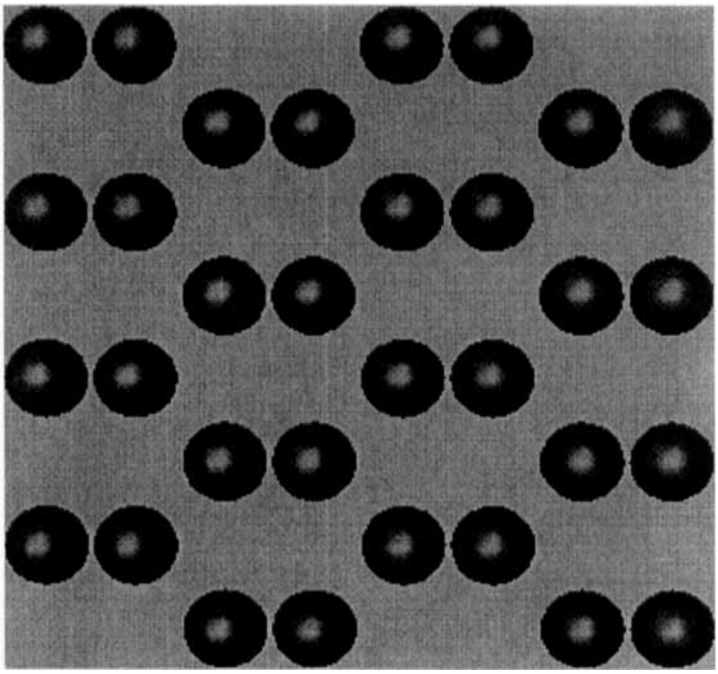


FIGURE 5 "AB" configuration of a 3 × 3 cubic unit cell of the (200) surface after relaxation.

calcium or fluorine terminated surface – the same defective surfaces will be formed.

For a larger repeat unit, the 50% density of the top anion layer leads to a rapidly increasing number of possible atom configurations. An expansion of the repeat unit from a single unit cell to a 2 × 2 unit cell area results in 153 configurations of fluorine atoms that cover the surface periodically [23]. While such larger repeat unit calculations yield the same energies as the single unit cell simulations for configurations "A" (see Fig. 3) and "B" (see Fig. 4), the hybrid "AB" configuration (see Fig. 5) proves to be slightly more stable for some materials such as UO_2. The AB configuration cannot be simulated with a single repeat unit. Interestingly, in contrast to UO_2, the "AB" configuration for CaF_2 yields a slightly less stable surface energy (see Tab. II) than configuration "A". This means that the anion arrangement on a (200) surfaces differs between different flourite structured materials.

It is also interesting to note how relaxation of the various possible {200} surface configurations drastically changes their energies. This is due mainly

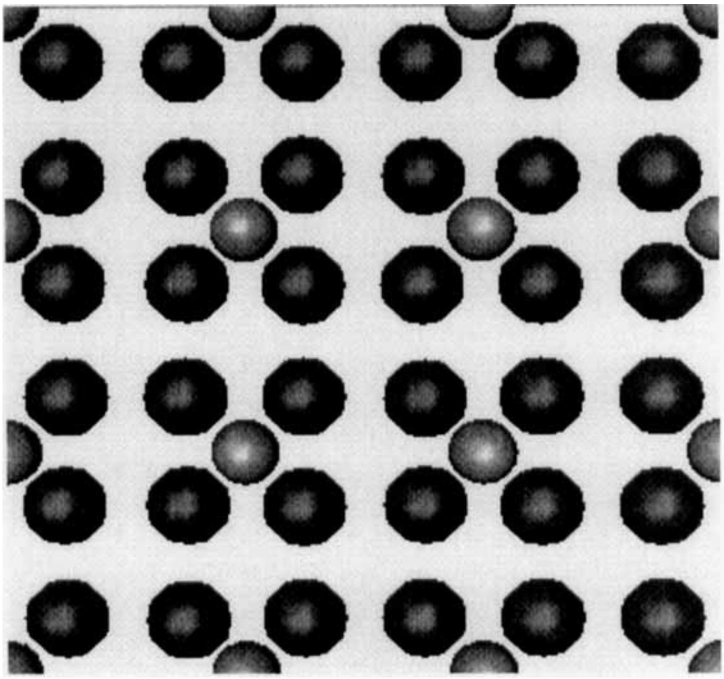


FIGURE 6 "C" configuration of a 3 × 3 cubic unit cell of the (200) surface after relaxation. This surface configuration is terminated by a half-layer of Ca-ions (light spheres). Due to relaxation of the Ca ion top layer, the larger fluorine ions in the layer beneath (darker spheres) project through the α surface to a considerable extent.

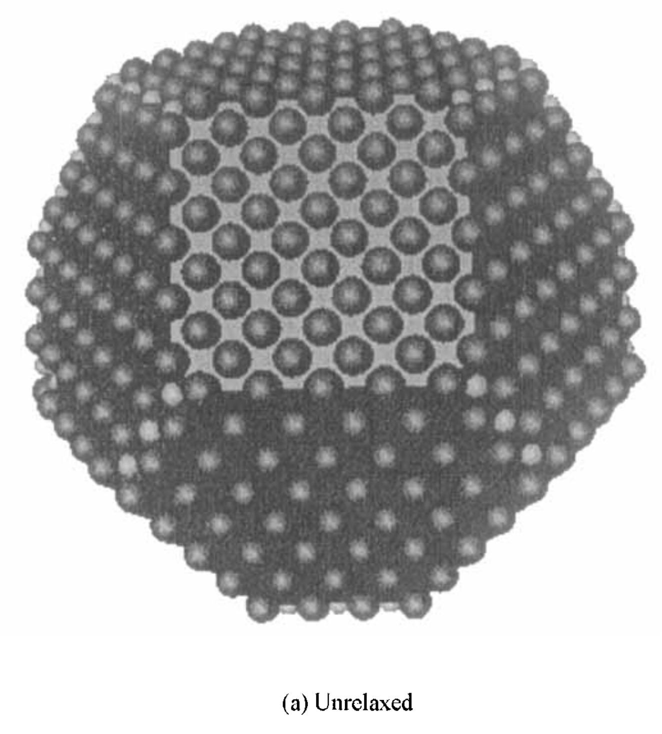
to relaxation in the z-direction. However, relaxation in the $x-y$ plane also occurs, although it is restricted by the periodicity of the repeat unit. Of course, there is no restriction of $x-y$ relaxation in the MD nanocluster simulation.

3.2. MD Simulation of the 3656 Atom Cluster

The two pairs of Figures 7(a) and (b), 8(a) and (b) show the cluster before and after it has been equilibrated at 300 K for approximately 110 ps. In each figure, one $\{200\}$ face and four $\{111\}$ faces are visible. The lighter colours are due to calcium atoms, while the darker colours are due to the presence of fluorine atoms. Thus, the lighter coloured areas in the α-shapes are where the calcium atoms are at the surface and the dark areas are where fluorine atoms are at the surface.

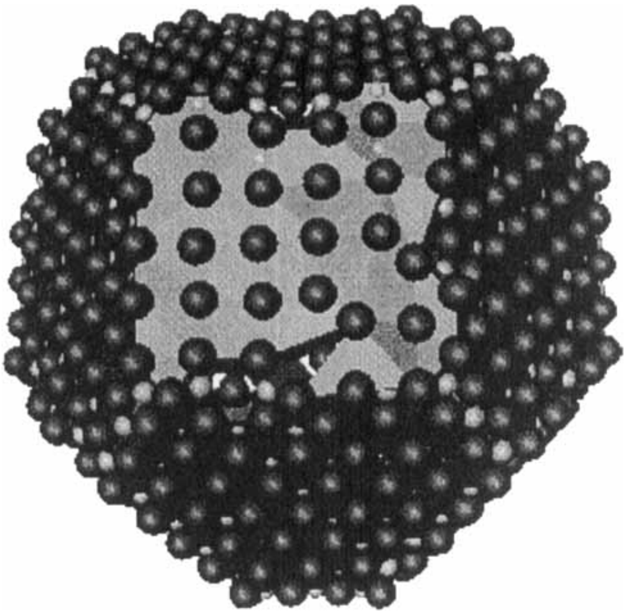
The images show some striking similarities with the results from the static simulations (see Figs. 2–6). However, the finite nature of the surfaces is also evident. For example, the centres of the {111} faces show a very smooth surface structure with a uniform relaxation analogous to that seen in the 2D infinite surface simulations (Fig. 2). However, the ions at the edges of the surface are slightly higher than those in the centre and thus, to a slight extent, form ridge like structures. This edge effect is a result of these ions being under-coordinated, compared with those ions at the centre of the face.

An unrelaxed F^- terminated {200} surface (see Fig. 7(a)) shows the formation of F^- vacancies after equilibriation (see Fig. 7(b)). These are equivalent to the F^- interstitials imposed on the static simulation to stabilise the Ca^{2+} terminated surface. Furthermore, the remaining fluorine ions show a high degree of order. The ordering in Figure 7(b) is primarily that of the lowest surface energy arrangements of the F^- ions in the MARVIN simulations, with the anions being diagonally opposite to each



(a) Unrelaxed

FIGURE 7 The 3656 atoms cluster, seen from the F-terminated (200) face before and after (see next page) simulation for 110 ps at 300 K.



(b) Relaxed

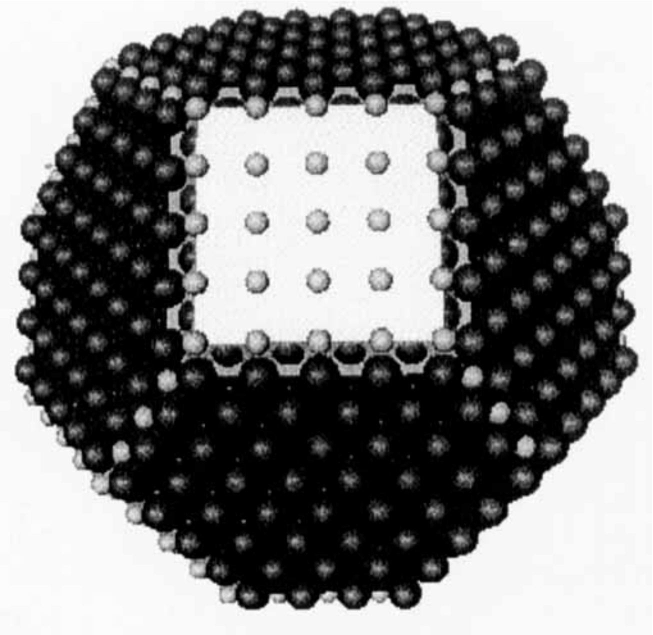
FIGURE 7 (Continued).

other, *i.e.*, configuration A (see Fig. 3). Clearly, the vacant sites have formed to counter the dipole of the Type III surface despite the relatively small thickness of the crystallite. This vindicates the approach used in the MARVIN calculations for the stabilisation of the Type III surfaces. However, the ridges between this {200} face and the adjacent {111} faces show a small amount of disorder and the sharp boundaries of the unrelaxed cluster (Fig. 7(a)) have been lost in the relaxed cluster (Fig. 7(b)). Furthermore, in the bottom right of this face there is a departure from the configuration A type ordering which is actually configuration AB type. Note that configuration AB is only slightly less favourable than configuration A (see Tab. II).

In Figure 8(a), the unrelaxed Ca^{2+} terminated {200} face is shown, which is on the opposite side of the cluster from the view shown in Figure 7(a). Again, this has been formed without the type of dipole removing defects needed for a 2D MARVIN simulation. After relaxation, this surface shows the presence of F^- interstitial ions, represented by the presence of darker colours on the surface (see Fig. 8(b)). These interstitial ions also show some degree of ordering, approaching that of configuration A. This result supports the conclusion of the previous static studies which favoured a (200) surface stabilised by the presence of F^- interstitial defects rather than Ca^{2+} vacancies.

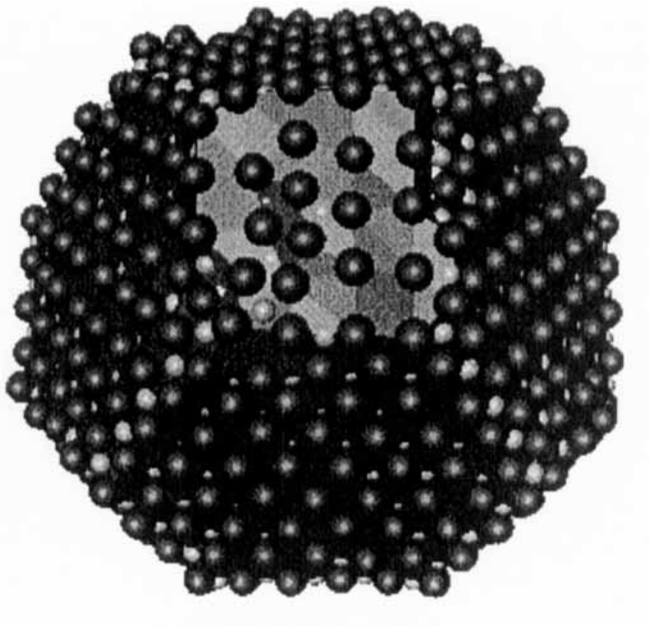
In Figures 8(a) and (b), corners where a {200} and two {111} faces meet, the edge between two {111} faces, and an edge between {111} and {200} faces are all visible. After relaxation, all the edges are covered by F^- ions. The corners are still discernible however, their angularity has decreased. The edges also show a relaxation and lose their sharpness, though they still remain relatively well defined.

Although the results are not presented in the present work, the phenomena seen in the present 3645 ion cluster are reproduced by the smaller 1665 ion cluster [22]. That cluster shows a similar surface relaxation with the formation of defects on the dipolar {200} faces and an even more distinct rounding of the cluster edges.



(a) Unrelaxed

FIGURE 8 The 3656 atoms cluster, seen from the Ca-terminated (200) face before and after 110 ps at 300 K.



(b) Relaxed

FIGURE 8 (Continued).

4. SUMMARY

The primary purpose of this study was to determine if the way in which static 2D energy minimisation simulations are used to determine the surface energies of dipolar surfaces could be justified by MD simulations. In this regard, we found that the fluorine terminated {200} surface predicted as having the lowest energy using the static 2D technique (Fig. 3) was indeed reproduced on the (200) surface of the MD simulated nanocluster. However, there was clearly also a contribution from another fluorine terminated configuration (Fig. 5), the static surface energy of which was calculated to be only slightly less favourable (see Tab. II).

Although further MD calculations involving larger {200} surface areas would be valuable in investigating fluorine ion ordering, it is clear that fluorine ion termination is preferable to calcium ion termination, clearly supporting the prediction of the static simulations. Furthermore, the non-dipolar {111} surfaces of the nanocluster did not develop any defects, as would be expected again from the results of static simulations.

Finally it was noted that the structures of apexes and corners of the cluster showed considerable relaxation from perfect lattice positions. As such, this also merits greater investigation.

References

[1] Gay, D. H. and Rohl, A. L. (1995). "MARVIN–a new computer code for studying surfaces and interfaces and its application to calculating the crystal morphologies of corundum and zircon", *J. Chem. Soc. Farad. Trans.*, **91**, 925.

[2] Parker, S. C. and Price, G. D. (1989). "Computer Modelling of Phase Transitions in Minerals", *Adv. Solid st. Chem.*, **1**, 295.

[3] *Cerius2 Software* (1998). Molecular Simulations, Inc., San Diego, California.

[4] Tasker, P. W. (1979). "The stability of ionic crystal surfaces", *J. Phys.: C*, **12**, 4977.

[5] Hartmann, P. and Bennema, P. (1980). "The attachment energy as a habit controlling factor", *J. Cryst. Growth*, **49**, 145.

[6] Tasker, P. W. and Duffy, D. M. (1984). "The structure and properties of the stepped surfaces of MgO and NiO", *Surf. Sci.*, **137**, 97.

[7] Mackrodt, W. C. and Stewart, R. F. (1979). *J. Phys.: C*, **12**, 5015.

[8] Oliver, P. M., Parker, S. C., Purton, J. and Bullett, D. W. (1994). "Atomistic Simulations and electronic-structure of TiO_2 (100) surfaces", *Surf. Sci.*, **307**, 1200.

[9] Binks, D. J. (1994). "Computational modelling of zinc oxide and related oxide ceramics", *Ph.D. Thesis*, University of Surrey.

[10] Oliver, P. M., Parker, S. C. and Mackrodt, W. C. (1993). "Computer-simulation of the crystal morphology of NiO", *Modelling Simul. Mater. Sci.*, **1**, 755.

[11] Allan, N. L., Rohl, A. L., Gay, D. H., Catlow, C. R. A., Davey, R. J. and Mackrodt, W. C. (1993). "Calculated bulk and surface-properties of sulfates", *Faraday Discuss.*, **95**, 273.

[12] George, A. R., Harris, K. D. M., Rohl, A. L. and Gay, D. H. (1995). "Computational investigation of surface structural relaxation in crystalline urea", *J. Mater. Chem.*, **5**, 133.

[13] Shluger, A. L., Rohl, A. L., Gay, D. H. and Williams, R. T. (1994). "Atomistic theory of the interaction between AFM tips and ionic surfaces", *J. Phys. Condens. Matter*, **6**, 1825.

[14] Binks, D. J., Grimes, R. W., Rohl, A. L. and Gay, D. H. (1996). "Morphology and structure of $ZnCr_2O_4$ spinel crystallites", *J. Mater. Sci.*, **31**, 1151.

[15] Vyas, S., Grimes, R. W., Gay, D. H. and Rohl, A. L. (1998). "Structure, stability and morphology of stoichiometric ceria crystallites", *J. Chem. Soc. Farad. Trans.*, **94**, 427.

[16] Saul, P., Catlow, C. R. A. and Kendrick, J. (1984). "Theoretical- studies of protons in sodium-hydroxide", *Phil. Mag. B*, **51**, 107.

[17] Baram, P. S. and Parker, S. C. (1996). "Atomistic simulation of hydroxide ions in inorganic solids", *Phil. Mag. B*, **73**, 49.

[18] Catlow, C. R. A. (1994). "Computational Solid State Chemistry", *Computational Materials Science*, **2**, 6.

[19] Catlow, C. R. A., Bell, R. G. and Gale, J. D. (1994). "Computer Modelling as a Technique in Materials Chemistry", *Special Issue of J. Mater. Chem.*, **4**, 781.

[20] Catlow, C. R. A., Dixon, M. and Mackrodt, W. C. (1982). "Interionic potentials in ionic solids", In: *Computer Simulation of Solids*, Edited by Catlow, C. R. A. and Mackrodt, W. C. Springer-Verlag, Berlin.

[21] Dornford-Smith, A. and Grimes, R. W. (1995). "Novel vaporization mechanisms for NaF and CaF_2 nano-crystallites in vacuo", *Phil. Mag. B*, **72**, 563.

[22] Vyas, S. (1996). "Simulation of ceria: bulk and surface defects", *Ph.D. Thesis*, University of London.

[23] Abramowski, M., Grimes, R. W. and Owens, S. (1999). "Morphology of UO_2", *J. Nuc. Mat.*, **275**, 12.
[24] Edelsbrunner, H. and Mücke, E. P. (1994). "3-dimensional alpha-shapes", *ACM Transactions on Graphics*, **13**, 43.
[25] Frye, K. (Ed.) (1981). In: "*The Encyclopedia of Mineralogy*", Hutchinson Ross, Stroudsburg, Pennsylvania.