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## The structure and properties of fluorite crystal surfaces

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**Résumé.** — Les énergies, les tensions et les structures cristallographiques des surfaces (111) et (110) de  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  et  $\text{UO}_2$ ,  $\text{ThO}_2$ ,  $\text{PrO}_2$ ,  $\text{PuO}_2$ ,  $\text{CeO}_2$  sont calculées en utilisant un modèle de *coquille* ionique. Les énergies trouvées dans le cas de la surface de clivage (111) sont en bon accord avec les données expérimentales dont on dispose. Dans tous les cas, les valeurs des tensions superficielles correspondent à l'existence de contraintes de compression en surface. Les structures cristallographiques déterminées montrent que la relaxation augmente avec le rayon ionique et l'étude de la distorsion de la surface (110) met en évidence une différence qualitative entre  $\text{CaF}_2$ ,  $\text{SrF}_2$  et les autres cristaux étudiés.

**Abstract.** — The surface energies, tensions and structures of the (111) and (110) surfaces of  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  and  $\text{UO}_2$ ,  $\text{ThO}_2$ ,  $\text{PrO}_2$ ,  $\text{PuO}_2$ ,  $\text{CeO}_2$  have been calculated using an ionic shell model. The surface energies for the natural cleavage plane (111) are compared with the available experimental data and agree well. The surface tensions indicate a compressive stress in both surfaces. The surface structures show increasing relaxation with increasing ion size and the rumpling of the (110) surface indicates a qualitative difference between  $\text{CaF}_2$ ,  $\text{SrF}_2$  and the other crystals studied.

1. **Introduction.** — The surface energy is an important physical property of a material and its calculation requires the relaxation of the ions in the surface to equilibrium. This gives the surface structure that may be important for the interpretation of LEED and ion scattering spectra. In recent years, much work has been done calculating the properties of defects in ionic crystals and the application of the interionic potentials derived for these studies should enable more reliable calculations of surface properties to be made. The fluorite crystals described in this paper have a number of commercial applications that require knowledge of the surface properties. The alkaline earth fluorides are used as optical windows and their fracture strength has been studied by crack propagation methods [1-3]. When this occurs slowly and without plastic deformation the critical fracture energy is the same as the surface energy. Among the applications of the metal oxides studied here, is their use as a nuclear fuel material. The surface energy affects the growth of bubbles and voids in the material and is a necessary parameter for modelling of fuel behaviour under irradiation. Values for the surface tension are also reported and refer to the energy required to stretch the surface. The surface tension is related to the trace of the surface stress tensor and is often measured by lattice parameter changes in small crystallites. The surface geometry of the alkaline earth fluorides has not been studied since the free surfaces strongly adsorb water [4] but uranium dioxide has been studied by a number of techniques [5]. The results are pre-

sented here since the relaxed geometry may be important for studies of the mechanism of adsorption and other surface properties.

2. **The calculation.** — A crystal can be considered as a stack of planes parallel to any surface. The region of crystal for which the ionic relaxations are calculated consisted of eighteen planes for the (111) orientation and six planes in the (110) orientation. This stack is matched to a further static and unpolarizable block representing the bulk crystal whose presence is included to ensure convergence of the lattice sums. The forces on all the ions in the explicit crystal region were calculated with periodic boundary conditions parallel to the surface. The ions were relaxed to equilibrium and the energy of the block before and after relaxation was determined. Comparison of this energy with that for a region of perfect, bulk crystal gave the surface energy. The surface tension was determined, by differencing, from

$$\gamma = E_s + A \frac{dE_s}{dA}$$

where  $E_s$  is the surface energy and  $A$  the area [6]. The Madelung and other lattice sums were carried out over planes. A full description of the method has been given elsewhere [7].

A fully ionic model is assumed with  $\text{M}^{2+}\text{F}_2^-$  for the alkaline earth fluorides and  $\text{M}^{4+}\text{O}_2^{2-}$  for the oxides. This is certainly a good approximation for the fluorides and has been used successfully in many

calculations for oxides [8]. The ionic polarizabilities are described by the shell model and a short-range potential acts between the ions. The shell parameters and short-range potential were obtained from the work of Catlow, Norgett and Ross [19] and Catlow and Vail [10] who fitted in most cases to the elastic and dielectric properties of the material. Where these data were not available for  $\text{PrO}_2$ ,  $\text{PuO}_2$ , and  $\text{CeO}_2$  the potentials were obtained from those for  $\text{UO}_2$  and  $\text{ThO}_2$  by extrapolation while requiring crystal equilibrium at the observed lattice constant [10]. Some approximation is made in using these potentials, derived from bulk data, at a surface and this will be more severe for the oxides than the fluorides. Also, due to better experimental data and a more flexible form for the analytical potential, the fluoride potentials should be considered more reliable than those for the oxides. Previous estimates of the surface energy have ignored surface relaxations or used potentials that do not reproduce the range of bulk and defect properties of those used here [11]. This led to substantial variations in surface energy between calculations sometimes leading to unrealistic results, and focussed debate on the validity of various ionic radii [2]. It has also been asserted that cleavage energies should be compared with unrelaxed and unpolarized surface energies since relaxation occurs after the passage of the crack [2, 12]. However, for slow crack velocities the relaxation of the surface

can be considered to occur concurrently with the breaking of the bonds and should therefore be included.

Not all possible crystal surfaces are stable in an ionic material and those that are unstable for electrostatic reasons cannot be described in terms of a simple termination of the bulk structure [13]. The (100) fluorite surface is of this type [14] and so the calculations here are limited to the stable (111) and (110) surfaces.

**3. Results and discussion.** — Table I summarizes the potential parameters for the fluorite oxides from the work of Catlow [8] and Catlow and Vail [10]. The potentials for the fluoride crystals have been published elsewhere [9]. The potentials and results for uranium dioxide are included here for comparison with the other oxides but the surface calculation has been described in more detail previously [14]. The results from this calculation are the same as the earlier calculation apart from the surface tension. This is due to a better handling of the outer crystal region that exposes small residual bulk strains present with this potential at the observed lattice spacing. The surface energies are unaltered and this emphasizes that the surface tensions are the least reliable numbers calculated by this method since they are very sensitive to the relaxation.

Table II shows the calculated surface energies

Table I. — Potential parameters for the fluorite oxides [8, 10]  $r_0$  is the nearest anion-anion separation. There is no cation-cation short-range potential, the anion-cation potential is  $V_{+-}(r) = A_{+-} \exp(-r/\rho_{+-})$  and the anion-anion potential is  $V_{--}(r) = A_{--} \exp(-r/\rho_{--}) - C_{--}/r^6$ .  $Y$  is the shell charge and  $k$  the corresponding force constant.

Potential parameter	$\text{UO}_2$	$\text{ThO}_2$	$\text{PrO}_2$	$\text{PuO}_2$	$\text{CeO}_2$
$r_0$ (Å)	2.734 1	2.799 85	2.734 7	2.698 0	2.705 5
$A_{+-}$ (eV)	1 217.8	1 116.8	1 226.0	1 166.2	1 178.1
$\rho_{+-}$ (Å)	0.387 1	0.401 25	0.387 1	0.387 1	0.387 1
$A_{--}$ (eV)	22 764.3	22 764.3	22 764.3	22 764.3	22 764.3
$\rho_{--}$ (Å)	0.149 0	0.149 0	0.149 0	0.149 0	0.149 0
$C_{--}$ (eV Å <sup>6</sup> )	112.2	114.193 6	112.2	112.2	112.2
$Y_+  e $	6.54	6.093 65	6.54	6.54	6.54
$Y_-  e $	- 4.40	- 3.857 17	- 4.40	- 4.40	- 4.40
$k_+$ (eV Å <sup>-2</sup> )	103.38	76.827	103.38	103.38	103.61
$k_-$ (eV Å <sup>-2</sup> )	292.98	333.43	292.98	292.98	292.98

Table II. — Calculated surface energies for relaxed (111) fluorite surfaces compared with experimental cleavage measurements and other theoretical estimates.

Crystal	Calculated $E_s$ ergs cm <sup>-2</sup>	Experimental cleavage energy ergs cm <sup>-2</sup> [1]	Experimental cleavage energy ergs cm <sup>-2</sup>	Other theoretical [11]
$\text{CaF}_2$	476	510	450 [3]	364, 543
$\text{SrF}_2$	407	420	356, 260 [2] 465, 430	332, 437
$\text{BaF}_2$	349	350	280 [3]	355, 393

for the alkaline earth fluorides compared with experiment and other theoretical estimates. The deduction of cleavage energies from the experimental data depends on the relation between the energy and the crack propagation data with the elastic constants of the material. The deduced energy also depends on the crack velocity. Kraatz and Soltai [2] give four energy values for SrF<sub>2</sub> depending on the theoretical relationship governing crack propagation and the crack velocity. They prefer the lowest value of 260 ergs cm<sup>-2</sup> since this gives least scatter to the experimental results, although the more sophisticated theoretical treatment yields the higher value for this crack velocity. The results of Gilman [3] and Becher and Freiman [1] are based on the simpler theoretical interpretation of the data. The cleavage energy at zero crack velocity should be compared with the surface energy but experimental measurements at low velocities are confounded by an increase in irreversible processes [2]. Similarly, the calculations should be compared with experiments at absolute zero temperature but the lower temperature experiments also suffer from an increase in irreversible energy losses. However, it has been suggested [2] that the error in comparing with higher temperature results should only be a few per cent as indicated by the small change in the elastic constants. The theoretical calculations recorded for comparison [11] are unrelaxed lattice with two choices of ionic radii. Table III summarizes the surface energy for the

Table III. — *Surface energies and tensions for fluorite (110) surface and surface tension for the (111) face calculated for relaxed surface.*

Crystal	$E_s(110)$ ergs cm <sup>-2</sup>	$\gamma(110)$ dynes cm <sup>-1</sup>	$\gamma(111)$ dynes cm <sup>-1</sup>
CaF <sub>2</sub>	760	644	1 632
SrF <sub>2</sub>	630	591	1 242
BaF <sub>2</sub>	492	177	643

(110) surface which is, as expected, higher than for the (111). The surface tensions for each surface are shown indicating a compressive stress in both cases.

Table IV. — *Surface energy parameters for the fluorite oxide surfaces.*

Crystal	$E_s(111)$ ergs cm <sup>-2</sup>	$\gamma(111)$ dynes cm <sup>-1</sup>	$E_s(110)$ ergs cm <sup>-2</sup>	$\gamma(110)$ dynes cm <sup>-1</sup>	Born-Haber cycle estimate $E_s(111)$ ergs cm <sup>-2</sup> [11]
UO <sub>2</sub>	1 064	3 226	1 561	651	1 050
ThO <sub>2</sub>	1 016	4 167	1 451	1 670	1 150
PrO <sub>2</sub>	1 057	4 373	1 571	1 316	
PuO <sub>2</sub>	1 049	4 358	1 509	983	
CeO <sub>2</sub>	1 051	4 369	1 524	1 084	

Table V. — *Ionic displacements for fluorite surfaces (111) and (110) in units of anion-anion nearest distance (cube edge). Relaxation is the decrease in mean distance of the top two planes. Rumple is the separation of sublattices in surface plane.*

Crystal	Relaxation (111)	Relaxation (110)	Rumple (110)	Anion lateral displacement (110)
CaF <sub>2</sub>	0.005	0.038	- 0.054	0.019
SrF <sub>2</sub>	0.014	0.035	- 0.043	0.029
BaF <sub>2</sub>	0.044	0.052	+ 0.020	0.039
UO <sub>2</sub>	0.052	0.066	0.005	0.042
ThO <sub>2</sub>	0.059	0.057	0.022	0.054
PrO <sub>2</sub>	0.051	0.062	0.005	0.042
PuO <sub>2</sub>	0.055	0.069	0.009	0.040
CeO <sub>2</sub>	0.054	0.067	0.008	0.041

Table IV records the surface energy and tension results for the fluorite oxides. The Born-Haber cycle estimates for UO<sub>2</sub> and ThO<sub>2</sub> [11] agree closely with the calculations and the results for all the oxides are similar. The slightly lower energy values for ThO<sub>2</sub> reflect the lower calculated cohesive energy (99.9 eV/unit cell compared with ~ 103 eV/unit cell for the other oxides). It was noted for the alkali halides that the surface energy was proportional to the cohesive energy [7] and this trend is continued here. The alkaline earth fluorides also show an increasing surface energy with cohesive energy. Experimental data is only available for the surface energy of UO<sub>2</sub> and its comparison relies on extrapolation from high temperature and some assumptions about the variation with stoichiometry. The experiments give a value of ~ 1 400 ergs cm<sup>-2</sup> at absolute zero temperature [15].

Table V shows the geometries of the relaxed surfaces. Following Welton-Cook and Prutton [16] these are recorded in a simplified form. Using only the core co-ordinates and so ignoring the electronic polarization, the relaxation refers to the decrease in the spacing of the top two layers and the rumple is the separation of the two sublattices in the (110) surface. This enables comparison to be made between the different crystals. A more complete description of the relaxation is given elsewhere for UO<sub>2</sub> [14].

The results show an increase in relaxation with increasing cation size, and all the results for the oxides are very similar. The most interesting feature is the inversion of the rumpling on the (110) plane as the cation size increases. For the calcium and strontium fluorides the cation relaxes into the surface much more than the anion whereas this is reversed

for barium fluoride and the oxides. If this is not an artefact of the calculation it could cause observable differences in the properties and reactivity of the (110) surfaces.

I should like to thank Dr. C. R. A. Catlow for supplying his unpublished potentials for the fluorite oxides.

## DISCUSSION

*Question.* — M. J. GILLAN.

Could one calculate surface entropies and would it be of any interest ?

*Reply.* — P. W. TASKER.

Surface entropy calculation would be particularly

useful for producing surface energy results at the temperature of the experiments. The most direct way to calculate it is via the surface phonons for the finite crystal slab and we are hoping to do this calculation in the future.

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