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Theoretical modelling of steps and surface oxidation on $CaF_2(111)$

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Abstract

The atomic and electronic structure of several low index surfaces of CaF_2 were calculated using the Hartree–Fock method, a slab model and the CRYSTAL-95 computer code. The calculated value of the (111) surface energy is 0.47 J m^{-2}. Two types of stepped surfaces have been considered, namely the (331) and (211) surface. These surfaces have 3.2 Å high steps with different atomic configuration. The step energy was found to be different for these two types of steps. The structure of the $CaF_2(111)/CaO(111)$ interface was calculated using the same method. The O(2p) band of CaO was found 2.7 eV above the F(2p) band edge of CaF_2.
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1. Introduction

Laser ablation and the resistivity of optical materials against laser pulses with sub-bandgap photon energy strongly depend on the purity of the crystal and the quality of its surface [1]. Surface defects and adsorbed species induce local electronic states in the insulator band gap initiating optical absorption. The absorbed energy is transferred to the lattice and may cause thermoelastic fracture and emission of material from the surface. Information about the atomic and electronic structure of particular surface defects is required in order to understand the basic mechanism of this process in more details.

Cleaved crystalline surfaces always have steps [2]. A recent scanning force microscopy study [3] of $CaF_2(111)$ surfaces cleaved in a vacuum shows that a typical distance between the steps may be 100 Å but varies with cleavage conditions. Often, their height is 3.4 Å, corresponding to one F–Ca–F triple layer. When an intense laser beam hits a step, damage may occur at intensities much lower than the threshold found for a flat (111) terrace [4]. Surface contamination with oxygen or water is expected to further reduce laser resistivity.

In recent UPS measurements of cleaved and polished $CaF_2(111)$ surfaces [5] it was found that a defect induced tail in the density of states extends into the band gap up to 6 eV above the valence band for an air cleaved surface that is most probably related to an oxidation or hydroxidation of the surface. A surface cleaved in a vacuum exhibits a pronounced peak in the density of occupied states above the valence band edge when dosed

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with oxygen [6]. Hence both cleavage and oxidation have been found to introduce occupied states in the band gap of CaF_2.

The purpose of the work partly presented here is to obtain a reliable atomic and electronic structure of the CaF_2 surface using modern ab-initio methods of quantum chemistry and to study the modification of the density of states induced by common surface defects, such as steps and surface oxidation.

The electronic structure of the ideal $CaF_2(111)$ surface has previously been calculated using the semi-empirical LCAO method [7], however surface relaxation effects were neglected. Earlier calculations of the surface structure and dynamics in the framework of the shell model [8] predicted a 19% decrease in the distance between the topmost F and next Ca layers. As an example of the defective surface, the electronic structure of $CaF_2(111)$ with completely removed topmost F layer has been calculated [9]. An additional half filled band was found in the middle of the band gap.

2. Method of calculation

To obtain results presented here, the electronic structure of CaF_2 surfaces was calculated using the Hartree–Fock method and a slab model as implemented in the CRYSTAL95 computer code [10]. The Gaussian basis sets for Ca, F and O ions optimized for bulk CaF_2 and CaO crystals were taken from Ref. [11]. Some calculations were done with additional polarization d-functions on Ca. The surface energy (E_{ijk}) was calculated as the difference between the total energy per unit cell of the slab (E_s) parallel to the (ijk) crystallographic plane and the bulk crystal (E_b) divided by 2, because the slab always has two surfaces:

$$E_{ijk} = (E_s - nE_b)/2.$$

Here n is the number of CaF_2 molecules in the slab unit cell. The step formation energy was estimated as the difference per single step between the surface energy of the stepped surface (E_{ijk}) and that of the flat (111) surface taking into account the difference in the slab unit cell areas:

$$E_{st} = (E_{ijk} - E_{111}\cos\alpha)d/\sin\alpha$$

where d stands for the step height and α is the angle between the (ijk) and (111) planes. The equilibrium structure of the slabs corresponding to the minimum of the total energy with respect to the displacements of atoms has been calculated using a least squares fit of the multidimensional adiabatic potential energy surface by the quadratic form.

The dependence of the results on the slab thickness has been checked for the ideal (111) surface. It was found that the density of states projected to the F ion in the middle of a 9-layer slab (6 F layers and 3 Ca layers) is already the same as in the bulk crystal. The calculated surface energy is the same for slabs containing 6 or more atomic layers. Thus we assume that 6 atomic layers are sufficient to correctly reproduce the surface electronic structure and relaxation.

3. Stoichiometric CaF_2 (111) surface

We found that the perfect $CaF_2(111)$ surface exhibits no atomic relaxation. Calculated displacements of the atoms in the surface layers are less than 0.01 Å. The surface energy was found to be 0.47 J m^{-2} in good agreement with experimental data [12]. The basis set extension with polarization d-function on Ca does not significantly change this result. The surface band gap and the width of the valence band in the slab calculation were the same as those in the bulk. There are no surface states in the band gap of the perfect (111) surface. However, the density of states (DOS) projected to the surface F ion differs significantly from the bulk one. In contrast to the bulk DOS, which has two peaks almost equal in height, the surface DOS has only one peak with a maximum close to the top of the valence band.

We assume that step edges on the (111) surface are aligned along F rows in the [110] direction. Therefore, three equivalent orientations of steps are possible and for each orientation there are two types of steps differing by their direction of descent. Fig. 1 shows (331) and (211) slabs having different

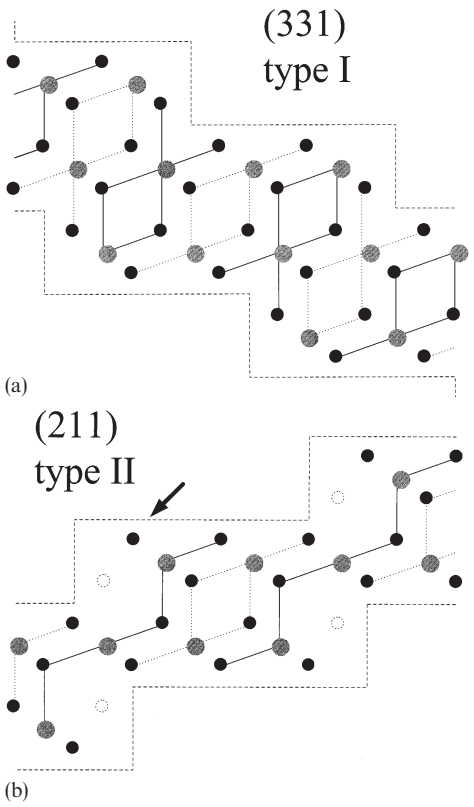

Fig. 1. Cross-section of the CaF_2 slabs simulating the stepped surfaces in the (110) plane perpendicular to the step edge. Black circles denote the positions of F ions. Larger gray circles indicate Ca ions. Ions situated in the drawing plane are connected by solid lines. Dotted lines connect the ions, which are in the next parallel plane. Steps on (331) and (211) surfaces are referred to in the text as type I and type II steps, respectively. Dashed circles denote an alternative position of the topmost F ion (marked by an arrow) for type II steps.

type of steps. Type I steps have only one atomic configuration shown in Fig. 1a. For steps of type II the position of the topmost atom (marked by an arrow in Fig. 1b) is not clear a priori. It could also be situated on the lattice site denoted by the dashed circle making the (211) surface atomically flat. Thus we considered two possible atomic configurations for type II steps. Apparently the type I step has the lowest formation energy of 0.25 nJ m^{-1}. The step energies for two configurations of type II steps are 0.35 and 0.56 nJ m^{-1}, respectively. The higher energy corresponds to the flat (211) surface. In addition, the density of occupied electronic states has been calculated for the type I stepped surface and detailed results will be forwarded in a future communication. Here we note that in contrast to the flat (111) surface, steps induce states in the band gap. The projected density of states for step atoms has one peak located at 0.5 eV above the valence band and thus exhibits a larger shift than that for surface atoms of the perfect (111) surface.

In contrast to the flat (111) surface, stepped surfaces exhibit a considerable atomic relaxation. The largest displacements of ions on steps are about 0.1 Å. The general tendency in step relaxation is such that the ions situated on the step edge are moved outward making the step "sharper". This is opposite to what is observed for the steps on (100) surfaces of the ionic crystals with rock salt structure where the relaxation makes the steps "smoother".

It follows from a simple geometrical consideration that the steps of the same type on the (111) surface may have a crossing angle of only 60°, while steps of different types may cross only at a 120° angle. Since type I steps are energetically more favourable we expect that the steps on the cleaved surface will have a crossing angle of 60° rather than 120°. This correlates with the sharp crossing angles (less than 60°) between the steps on the cleaved CaF_2 (111) surfaces observed by scanning force microscopy [3]. However, the comparison with experiments is not straightforward, because so far atomic resolution in imaging has not been achieved yet, and it is not clear whether the edges of the observed steps are straight on an atomic scale.

4. CaF_2 surface oxidation

The CaO crystal has the rock salt structure with a lattice constant only 10% smaller than that of CaF_2. This allows the epitaxial growth of a thin CaO film on top of CaF_2 (111) with an interface structure shown in Fig. 2. This structure was suggested in Ref. [13] where results from X-ray photoelectron diffraction experiments are also shown suggesting the existence of such an oxide film.

For technical reasons, in our calculations we

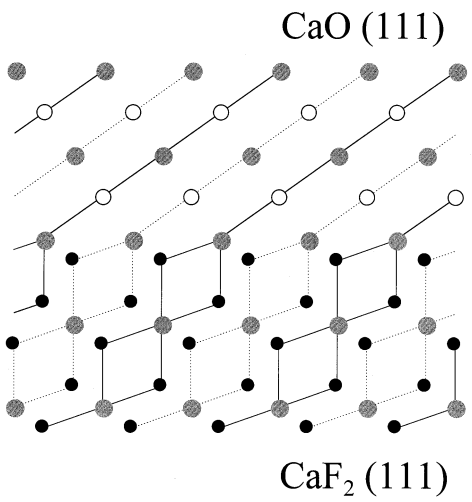

Fig. 2. Cross-section of the $CaF_2(111)/CaO(111)$ interface in the (110) plane perpendicular to the (111) interface plane as suggested in Ref. [12]. Notations are same as in Fig. 1. Open circles denote oxygen ions.

added another CaF_2 layer on top of CaO to stabilize the open CaO(111) surface. While optimizing the geometry of this sandwich-like slab we kept the lattice constant of CaF_2 unchanged. Therefore, the CaO layer was stretched in lateral direction and consequently compressed in the direction perpendicular to the interface. We found no interface states split from the normal F(2p) and O(2p) valence band states in the band structure of the slab. The total density of states is essentially the superposition of the CaF_2 and CaO densities of states. The O(2p) band was found 2.7 eV above the top of the F(2p) band. The shape of the O(2p) band slightly differs from that in bulk CaO due to the lattice distortions in the layer. The position of the oxygen band is in agreement with measurements on an oxidized surface [6].

5. Conclusions

Some atomic and electronic properties of the $CaF_2(111)$ surface have been obtained using an ab-initio method. The calculated position of the oxygen feature in the density of states with respect to the F(2p) band is in agreement with UPS experimental data. A complete understanding of this bandgap photoemission observed in a much wider energy range for the air cleaved surfaces needs more calculations of the electronic structure of the defective surfaces and especially considering other surface stoichiometries like surface hydroxide.

The assumption that the microscopic step edges at $CaF_2(111)$ surfaces are aligned along [110] crystallographic directions and the calculated large difference in formation energies of type I and type II steps leads to the conclusion that the crossing angle between steps should preferentially be 60°. The direct experimental information about the structure of atomic scale steps and step formation energy is not available so far. However, the observed sharp crossing angles between macroscopic steps and fracture patterns of triangular shape supports this hypothesis.

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