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1979 J. Phys. C: Solid State Phys. 12 4977

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The stability of ionic crystal surfaces

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Received 14 May 1979

Abstract. When there is a dipole moment in the repeat unit perpendicular to the surface in an ionic crystal, lattice sums in the electrostatic energy diverge and the calculated surface energy is infinite. The cause of this divergence is demonstrated and the surfaces of any ionic or partly ionic material are classified into three types. Type 1 is neutral with equal numbers of anions and cations on each plane and type 2 is charged but there is no dipole moment perpendicular to the surface because of the symmetrical stacking sequence. Both these surfaces should have modest surface energies and may be stable with only limited relaxations of the ions in the surface region. The type 3 surface is charged and has a dipole moment in the repeat unit perpendicular to the surface. This surface can only be stabilised by substantial reconstruction. These conclusions are important for the analysis of the surface structure of ionic crystals.

1. Introduction

The surfaces of ionic crystals determine many important properties such as mechanical strength, sintering and shape. This fact has led to studies of the structure by LEED and ion scattering (Mark *et al* 1975, Duke 1978, Laramore and Switendick 1973, Kinniburgh 1975, 1976, Kinniburgh and Walker 1977, Netzer and Prutton 1975, Ellis and Taylor 1978, Taylor and Ellis 1978), and to theoretical calculations of both the structure and thermodynamic properties (e.g. Benson *et al* 1963, Benson and Yun 1967, Benson and Claxton 1968, Welton-Cook and Prutton 1977, Tasker 1979a, b).

The stability of a surface is determined by the surface energy, E_s , which can be defined as (Stoneham 1976)

$$E_s = (\text{Cohesive energy of finite crystal}) - (\text{Number of atoms}) \\ \times (\text{Cohesive energy per atom in infinite crystal})$$

and is the excess energy associated with the surface. Bertaut (1958) showed that when there is a dipole moment in the unit cell perpendicular to the surface, the surface energy diverges and is infinite. Such surfaces therefore cannot exist and their apparent natural occurrence has been associated with adsorption of foreign atoms or surface roughening (Benson and Yun 1967). However, more recently such surfaces in metal oxides have been prepared and studied by LEED (Taylor and Ellis 1978, Ignatiev *et al* 1977). The aim of this paper is to demonstrate and clarify the divergence that occurs in the surface energy of certain charged surfaces. The divergence has a true physical origin and is not a result of the lattice summation techniques, and it has important consequences for the interpretation of LEED data.

2. General properties

One of the causes of confusion about the stability of charged surfaces arises because many of the methods for summing the Coulomb potential are only conditionally convergent and cannot be applied in these cases. Parry (1975, 1976) has derived a new Madelung sum that is appropriate to the study of surfaces and that includes correctly the dipole terms necessary for a discussion of charged surfaces. The expressions were derived by use of the Ewald method and have also been obtained by Bertaut's approach (Heyes *et al* 1977). These sums have been applied to the static and dynamic properties of ionic crystals (Tasker 1979a, b, Heyes *et al* 1977). The expressions give the electrostatic potential at any place in terms of a potential due to a planar sublattice of charge q at a perpendicular distance of z . A sum over each sublattice on each plane gives the total electrostatic potential. For distances z greater than a few interionic spacings the contribution from a planar sublattice reduces to the particularly simple form

$$V(z) = (2\pi/A) qz \quad (2.1)$$

where A is the area of the unit cell in the plane. This expression is identical to the potential due to an infinite charged plane of charge density

$$\rho = q/A. \quad (2.2)$$

The field due to the charged plane, E , is then given by

$$E = (2\pi/A) q \quad (2.3)$$

and is constant.

Surfaces can be studied by considering the crystal as a stack of planes. Since equations (2.1) and (2.3) do not diminish with increasing distance z the electrostatic sum must be over the whole crystal unless cancellation of these terms occurs. Although the potential (2.1) becomes infinite at infinite distances from the plane, it should be noted that when the crystal is constructed as a neutral block the infinities cancel and the potential becomes constant at large distances. (In fact, it becomes zero in all cases except where there is a dipole moment perpendicular to the surface.) Similarly the field (2.3) cancels to zero outside a neutral crystal block, irrespective of the stacking sequence. We consider the three different possible stacking sequences illustrated in figure 1. In figure 1(a) each plane has overall zero charge since it consists of both anions and cations in stoichiometric ratio. The potential (2.1) cancels on each plane since the contributions of the sublattices are equal and opposite. Additional planes in the surface of the crystal make no contribution to the energy of ions in the bulk of crystal, and the lattice sums required for the Madelung energy at any ion site need include only a few planes either side of that site. Figure 1(b) shows a stacking sequence of charged planes. However, the repeat unit consists of three planes in a symmetrical configuration and hence there is no dipole moment perpendicular to the surface. Each plane contributes a term in the potential of the form of equation (2.1), but a sum over the three-plane repeat unit cancels the potential to zero. Addition of extra neutral repeat units at the surface of the crystal cannot therefore affect the energy of ions in the bulk, and again the Madelung sums for the potential at any ion site are rapidly convergent. Figure 1(c) shows the stacking sequence of alternately charged planes producing a dipole moment perpendicular to the surface. The two-plane repeat unit produces a potential at large distances whose magnitude is given by

$$V = 2\pi|q|a/A \quad (2.4)$$

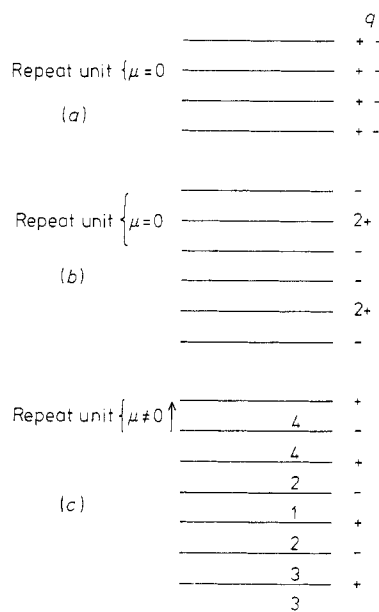


Figure 1. Distribution of charges q on planes for three stacking sequences parallel to surface. (a) type 1 with equal anions and cations on each plane; (b) type 2 with charged planes but no net dipole moment perpendicular to surface; (c) type 3, charged planes and dipole moment normal to surface.

where a is the interplanar spacing. Addition of an extra neutral repeat unit of two planes on the surface of the crystal will affect the energy of ions an infinite distance below the surface. Consequently the Madelung sum cannot be truncated and must include contributions from every plane out to the surface.

We can see that there will be an electric field at any ion site in the crystal. Consider an ion on plane 1 of figure 1(c). The field from the planes labelled 2 cancels by symmetry. This is true in general even if the planes are not regularly spaced as in the figure. For example, along the (111) direction in the zincblende structure the planes have the sequence shown in figure 1(c) but are not evenly spaced. They are grouped in pairs with a larger spacing between the pairs. However, the fields at an ion site due to adjacent planes cancels since the ion is tetrahedrally coordinated. The potential due to a plane does not take the limiting value given by equation (2.1) until the distances are greater. The field at plane 1 of the figure due to the planes 3 is zero since they are a dipole layer, and similarly the remaining planes in the bulk of the crystal do not contribute to the field. The planes labelled 4 also give no field, but we are left with the field due to the surface plane, which is not cancelled in any neutral crystal block.

The same argument can be applied to any plane in the crystal and the field due to the surface itself is always present. This field, which takes the form of equation (2.3), is constant and extends an infinite distance into the crystal. This implies that the potential at any ion site never reaches a constant bulk value. A similar argument to that above can show that the self-potential relative to the potential outside the crystal increases with distance into the bulk. The energy of a neutral pair of ions never reaches the usual cohesion energy and the surface energy as defined in equation (1.1) is infinite. This is illustrated by the self-potential calculation for sodium chloride by Parry (1976). The

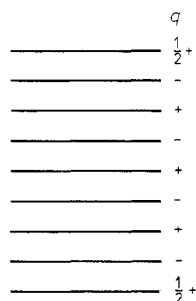


Figure 2. Distribution of charge for a stable crystal block with a type 3 stacking sequence. This can be achieved by vacancies or adatoms on opposite surfaces.

potential and field, equations (2.1) and (2.3), were derived with two-dimensional periodicity on the planes, and so correspond to infinite surfaces. Nevertheless, the conclusions are not significantly modified if the surfaces are finite since the potential and field will only diminish logarithmically with distance and the influence of the surface will be felt over macroscopic distances into the crystal.

Levine and Mark (1966) showed that the charged surfaces of an ionic crystal of general formula MX will be less stable than the uncharged surfaces. Subsequently, the Madelung potentials were calculated at ion sites in finite crystals of binary semiconductors terminated with polar surfaces (Nosker *et al* 1970). This demonstrated the accumulation of potential in the bulk of the crystal and stabilisation was made possible by a uniform surface charge or by reconstruction and facetting. Kummer and Yao (1967) have also demonstrated that the energy of a finite crystal block will be lowered if charge is transferred from the lower to the upper face. This is shown in figure 2; the electrostatic argument given above shows that the electric field at the centre planes is zero and that the surface energy will be finite for any block size. The polar faces of ionic or partly ionic materials cannot, therefore, be stable without substantial reconstruction. The important point, made by Bertaut (1958), is that whenever there is a dipole moment in the repeat unit perpendicular to the surface the lattice sums diverge. In all other cases, for neutral crystals, they are convergent.

The surfaces of any ionic or partly ionic crystal may be classified into three types. Type 1 consists of neutral planes with both anions and cations. Type 2 consists of charged planes arranged symmetrically so that there is no dipole moment perpendicular to the unit cell. Neither of these surfaces affect ions in the bulk of the crystal and they should therefore have modest surface energies. The type 3 surface is charged and there is a perpendicular dipole moment. These surfaces have infinite surface energies (or very large surface energies for finite crystals) and produce a polarising electric field in the bulk. An electrostatic argument therefore indicates that such surfaces cannot exist. The stable surfaces (types 1 and 2) may occur with only small relaxations from the bulk structure whereas the Type 3 surfaces, if they can be prepared, can only occur with substantial reconstruction or with the adsorption of additional charge. In the next section, the types of surface will be illustrated with some simple crystal structures.

3. Crystal structures

The structure of the low-index faces of the rocksalt, fluorite and zincblende crystals will be discussed as examples. The figures used here will show the stacking sequence with the stoichiometry on each plane, but they are not true projections of the structure.

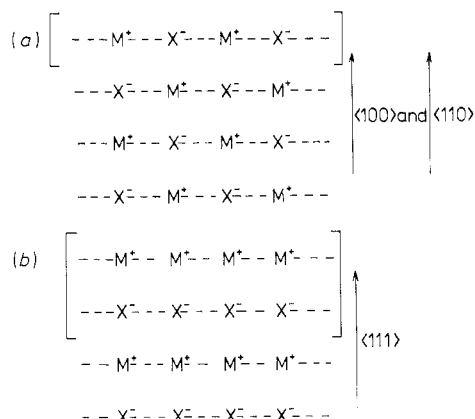


Figure 3. Schematic representation of the stacking sequences in the rocksalt structure, MX: (a) for (100) or (110) surfaces, both type 1; (b) for (111) surface, type 3. Square brackets indicate repeat unit for planar charge density.

3.1. The rocksalt structure

This is common for binary ionic crystals, MX, including most of the alkali halides and many metal oxides (e.g. MgO, NiO). Figure 3 shows the stacking sequence in the low-index (100), (110) and (111) directions. The (100) and (110) surfaces are both represented by figure 3(a) since the stoichiometry on these planes is the same. The actual structure of the plane is, of course, different. These surfaces are both neutral and type 1 by the designation of the previous section. We therefore expect them to have low surface energies and, indeed, the (100) face is the natural cleavage plane in this structure. The (110) face has a higher surface energy but LiF has been cleaved along this plane (Hobbs 1975). Figure 3(b) shows the (111) face. This is a type 3 surface and electrostatic arguments deny its existence. Studies using LEED of a CoO (111) surface have been reported (Ignatiev *et al* 1977) and these have been interpreted in terms of the bulk structure with a terminating anion plane (Van Hove and Echenique 1979). However, this surface must be stabilised by a more complex defect structure or by the thinness of the oxide layer (Van Hove, private communication) and the interpretation has been criticised by Prutton and Welton-Cook (1979).

3.2. Fluorite structure

Ionic crystals of the type MX_2 can crystallise with the fluorite structure. These include the alkaline-earth halides and oxides such as UO_2 and ThO_2 . There are also some anti-fluorite-structure crystals, e.g. Na_2O , in which the anion and cation sublattices are reversed. Figure 4 shows the low-index stacking sequences which demonstrate all the general types. In figure 4(a) we show the (100) surface that has the 'forbidden' type 3 structure. Only one example of a fluorite (100) surface has been reported and that is for UO_2 (Taylor and Ellis 1978). The structure from this LEED study is not clear but there is evidence for multiple unit cells indicating some restructuring. It is difficult to see how local relaxations can neutralise the surface charge. A complex defect structure, such as can occur in UO_2 , may be present. It is interesting to note that the only occurrences of these type 3 surfaces in the fluorite and rocksalt crystals are in metal oxides. In both

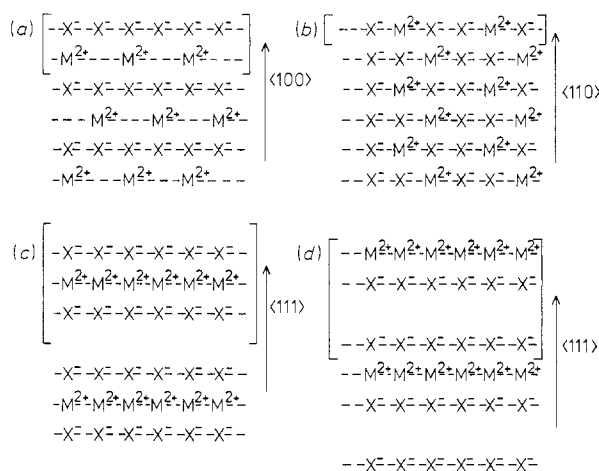


Figure 4. Schematic representation of the stacking sequences in the fluorite structure, MX_2 : (a) for (100) surface, type 3; (b) (110) surface, type 1; (c) (111) surface with terminating anion plane, type 2; (d) (111) surface with terminating cation plane, type 3. Square brackets indicate repeat unit for planar charge density.

cases the cation can exist in different charge states, possibly enabling a surface charge or defect structure to occur. The stability of the anion, O^{2-} , at the surface of these crystals must also be questioned since it is stabilised only by the Madelung potential. Figure 4(b) shows the (110) surface which is a neutral type 1 surface. This will have a small surface energy although calculations show that this is higher than for the (111) face (Tasker 1979b). The (111) face with anion termination is shown in figure 4(c). Here the planes are charged but there is no dipole moment perpendicular to the surface, which is thus of type 2. This surface is the natural cleavage plane in the fluorite structure and we can see that separation of two adjacent anion planes is likely to be energetically favourable. Finally, figure 4(d) also shows the stacking sequence in the (111) direction but here the terminating plane consists of cations. This then becomes a type 3 surface and has an infinite surface energy. (111) cleavage must expose a cation face in the fluorite structure or an anion face in the antiferroite structure.

3.3. The zincblende structure

This occurs in many compound semiconductors including ZnS, GaAs etc. Although these materials are only partly ionic, the electrostatic interaction can determine their surface behaviour (Mark *et al* 1975). Figure 5 shows the low-index surfaces. Both the (100) and (111) surface (figures 5(a) and (c)) are of type 3 and forbidden. The (110) is neutral and of type 1. Experiments confirm this, since all the zincblende compounds cleave along the (110) faces. The polar (100) and (111) surfaces have been prepared by ion bombardment and other techniques but they always show substantial reconstruction with multiple unit cells on the surface (Mark *et al* 1975). In contrast, the (110) surface usually has the simple (1×1) primitive surface cell structure. Although electrostatic forces seem to determine surface stability in these compounds, the covalent nature of the bonding may allow surface reconstruction and redistribution of surface charge to occur more readily than in mainly ionic materials.

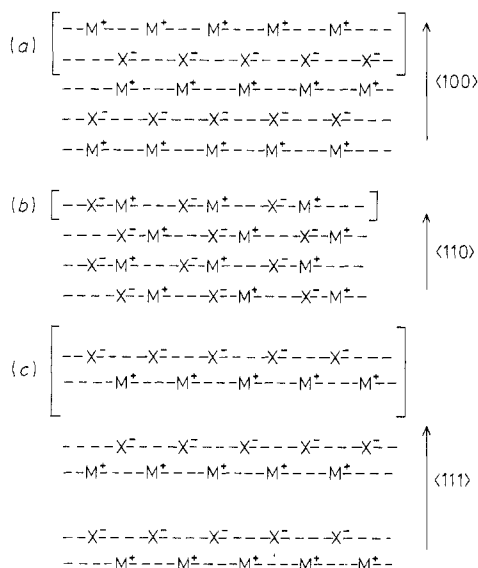


Figure 5. Schematic representation of stacking sequence in the zincblende structure, MX: (a) (100) surface, type 3; (b) (110) surface, type 1; (c) (111) surface, type 3. Square brackets indicate repeat unit for planar charge density.

4. Conclusions

The surfaces of any ionic or partly ionic crystal can be classed into one of three types: type 1, neutral surfaces with stoichiometric proportions of anions and cations in each plane; type 2, charged surfaces, with no dipole moment in the repeat unit perpendicular to the surface; and type 3, charged surfaces that have a dipole moment in the repeat unit perpendicular to the surface. These surfaces have an infinite surface energy and an electric field due to the charged surface is present throughout the crystal. They therefore cannot exist as a simple termination of the bulk structure and this has important consequences for the interpretation of measurements of surface structure. The number of possible surfaces that can be present for any crystal structure is therefore restricted and, in general, these type 3 surfaces are not observed in ionic crystals. The only ionic materials for which these surfaces have been prepared are CoO and UO₂ and both these substances can support a complex defect structure. The compound semiconductors can also be prepared with polar surfaces but they always show restructuring. This may be particularly likely because of the covalent nature of the bonding. Type 2 surfaces (e.g. (111) in the fluorite crystals) only have a zero dipole moment if the crystal terminates with the appropriate plane, and this will determine the surface plane.

The analysis of LEED experiments requires the assumption of a surface structure which is used to obtain a fit to the data. The simple electrostatic argument limits the possible structures. Although type 1 and type 2 surfaces may resemble a simple termination of the bulk structure, the surface plane for the type 2 surface is determined by stacking sequence. Type 3 polar surfaces must be reconstructed and analysis in terms of the perfect structure will not be adequate except, possibly, for microcrystallites and very thin layers.

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