

SURFACE SCIENCE LETTERS

ON LAYER SPACING RELAXATIONS AT SURFACES OF IONIC CRYSTALS

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There has been considerable interest in the geometric structure of the clean surface of ionic crystals [1-9], including its effects on surface vibrational modes [4]. For the non-polar (100) face of MgO and NiO (both NaCl-type materials), Low Energy Electron Diffraction (LEED) results [5-8] indicate that the bulk structure is maintained with surface atom displacements perpendicular to the surface of $0 \pm 5\%$ of the interlayer spacing (there is no observable difference between the two ions of opposite charge within this uncertainty of 5%). For the polar (111) face of CoO (also a NaCl-type material; an O rather than a Co termination seems favoured in this case) a displacement of the surface atoms towards the substrate by $15 \pm 5\%$ of the interlayer spacing is observed [9] by LEED. Model calculations based on minimizing the total potential energy of a slab [4] indicates for MgO(100) a relatively large inward displacement of 7.8% (averaged over the displacements of ions of opposite signs); however, the theory appears to be unreliable in this respect at the present time [4].

The clear difference observed by LEED in the contractions on different faces of ionic crystals has prompted us to investigate whether it can be explained by a simple electrostatic argument. Suppose one finds that the net electrostatic force acting on a surface atom due to all other atoms of the surface (and the underlying bulk) is particularly stronger for the (111) face than for the (100) face; then one can expect relaxations in the direction of that force which are larger for the (111) face than for the (100) face, assuming for both faces roughly equal compressibilities of the surface interlayer spacings perpendicular to the surface.

The verification of our electrostatic argument is elementary. One sums the components perpendicular to the surface of the forces acting on a test surface ion:

$$F_{\perp} = - \sum_j \frac{e_1 e_j}{r_j^2} \frac{x_j}{r_j},$$

where j runs over atoms other than the test atom at the surface, e_1 and e_j are the ionic charges of the test atom and the other atoms, respectively, r_j is the distance between atoms and x_j its component perpendicular to the surface ($x_j \geq 0$). (By symmetry, on both the (100) and (111) faces of NaCl-type materials, the net force will be perpendicular to the surface.) We make no difference between the positive and negative ions (other than the signs of their charges: $|e_1| = |e_j|$) and so obtain the same relaxations for either type of ion. As a consequence forces acting on a surface atom and originating in atoms of the same surface layer do not contribute to the net force.

The sum over the three-dimensional crystal is easily carried out numerically, but due care to the order of the summations is necessary in order to ensure proper convergence. This is done by grouping the ions in neutral sets. On the (100) face, in each layer parallel to the surface, ions on the four sides of a square (with centre below the test surface ion) are grouped together, only leaving the central ion unbalanced. On the (111) face we sum over pairs of oppositely-charged neighbouring ions, the pairs being grouped in chains extending from the surface into the solid; the chains are grouped on the sides of cylinders with triangular cross-sections, which grow radially away from the central chain extending under the test surface ion.

The result of the calculation is that the net force acting on an ion of the (111) face is about 4.5 times that on the (100) face (for constant lattice parameter and ionic charges); we may *qualitatively* conclude that on the (111) face a contraction several times larger than on the (100) face might be expected. Given the similar lattice parameter of MgO ($a = 4.211 \text{ \AA}$), NiO ($a = 4.168 \text{ \AA}$) and CoO ($a = 4.26 \text{ \AA}$), this result is consistent with the LEED results indicating $15 \pm 5\%$ contraction on CoO(111) and $0 \pm 5\%$ contraction on MgO(100) and NiO(100), even if differences in ionic charges and elastic constants are allowed for.

Contractions of surface layer spacings are also observed on some metal surfaces, especially those that are not close-packed [10]. Here also electrostatic effects may be at play, although they are relatively more complex: according to Finnis and Heine [11], who examined Al(110), electronic charge redistributions occur especially at non-close-packed metal surfaces, creating a net inward force on the surface nuclei.

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