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Atomic geometry of steps on metal-oxide single crystals

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Abstract

The concepts of coordinative unsaturation and excess surface charge are used to predict which atomic geometries are likely to be most stable along step edges on metal-oxide single crystals. The specific case of steps on $Fe_3O_4(1\,1\,1)$ is considered in detail, and two step structures are identified as having the lowest coordinative unsaturation and excess charge/step unit cell. This approach to step stability should be applicable to other crystal structures having both ionic and covalent components to their interatomic bonding.

Keywords: Stepped single crystal surfaces; Iron oxide

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1. Introduction

The atomic geometry of steps on single crystals is very important in crystal growth, chemisorption, catalysis, etc. While elements and simple compound crystal structures often have only one atomic arrangement for a given step orientation (particularly for single-atom step heights), the situation can become quite complicated for more complex crystal structures and for multi-atom step heights. An important class of compounds for which very little is known about step structure is metal oxides [1], many of which have complicated crystal structures such as perovskite, corundum and spinel. Scanning probe microscopy (SPM) has not been able to image the detailed structures of atoms along step edges. The best approach would be to calculate the energies of step geometries using ab initio techniques, but because of the very low symmetry at steps, that is a very challenging task, and no metal-oxide step structures have been calculated.

This paper is an attempt to determine what step geometries on metal oxides are most likely to have the lowest surface energy. The atomic bonding in metal oxides has both covalent and ionic character, so both charge neutrality in the ionic limit, and coordinative unsaturation associated with

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covalent bonding, are considered. The approach is applied to magnetite, Fe_3O_4, which possesses most of the complexities that occur in metal-oxide crystal structures. While it is not a substitute for state-of-the-art calculations of step structures, this approach is intended as a guide to which structures should be considered theoretically and in interpreting experimental data [2].

2. Stability of terraces

2.1. Covalent bonding

A great deal of work, both experimental and theoretical, has been devoted to the structures of semiconductor surfaces where atomic bonding is predominantly covalent. The most stable surface structures are those that minimize the number of dangling bonds at the surface; i.e., minimize coordinative unsaturation. It is straightforward to count the dangling bonds on an unrelaxed surface, although the actual surface may relax and rehybridize its covalent bonds in order to minimize its surface energy. A good discussion of this approach is given in Ref. [3]. For the metal oxides considered here, we will assume that a smaller density of dangling bonds implies a more stable surface [4]; the absolute number of dangling bonds is not significant.

2.2. Ionic bonding

For highly ionic compounds, surfaces can be of several types, depending on the charge neutrality of surface planes and the nature of the normal dipole moment at the surface; Refs. [5,6] discuss the properties of ionic surfaces in detail. For surfaces such as rocksalt (1 0 0), every atomic plane parallel to the surface has zero net charge (i.e., is charge neutral), and the surface dipole moment does not depend on the macroscopic size of the crystal; such surfaces are generally quite stable, do not reconstruct, and exhibit minimal relaxation [1]. At the other extreme is the unrelaxed rocksalt (1 1 1) surface, which has alternating planes of positive and negative charge and thus a normal dipole moment whose magnitude increases linearly with the thickness of the crystal; such surfaces are unstable and will relax, reconstruct or facet in order to minimize the dipole moment and eliminate excess surface charge.

Finnis [7], building on pervious work by Gibbs [8] and Cahn [9], has developed an approach to determining the "excess" of a quantity (e.g., atom type or charge) on terraces of ionic materials. His approach utilizes a "tapered termination" below the surface in order to evaluate excesses in a way that is independent of how many atomic planes of the crystal are considered and independent of any reconstruction and non-stoichiometry in the region of the surface. He applied that method to Fe_3O_4(1 1 1) and estimated the relative stability of three possible surface terminations. Here we extend his approach to steps, also using Fe_3O_4(1 1 1) as the model surface. However, as with Finnis' work on terraces, the approach is equally applicable to other surfaces and to other crystal structures as well.

2.3. Fe_3O_4(1 1 1) structure

Fe_3O_4 (magnetite) exhibits almost all of the complexities that can occur in metal-oxide crystal structures. Its atomic bonding contains both covalent and ionic components. Its crystal structure—inverse spinel—is relatively complicated, with 14 atoms in the primitive FCC unit cell. The Fe cations occupy sites coordinated both tetrahedrally and octahedrally with oxygen ions; in the most commonly used ionic model [10], the tetrahedral Fe ions all have a formal valence of +3, but the octahedral Fe ions are half +3 and half +2. If all ions actually had their formal charge, no planar termination of the bulk structure results in charge neutral surfaces for any of the low index terraces. It is thus a good material on which to test step stability criteria. Ref. [10] describes the structure of Fe_3O_4 in detail. A side view of the crystal structure of Fe_3O_4, with the (1 1 1) plane horizontal and into the page, is shown in Fig. 1(a). Normal to the [1 1 1] direction, the crystal structure consists of (nearly) close-packed planes of oxygen ions, separated by two alternating types of iron ion planes. One plane consists of all octahedrally coordinated Fe ions (3 for every 4 O ions in a plane), centered