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Charge defects glowing in the dark

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Abstract

We investigate the effects of local charge defects in HREM imaging, using electron densities calculated by density functional methods. As a model of a planar interface with a local charge defect we use the polar MgO (1 1 1)$-\sqrt{3}\times\sqrt{3}R30^\circ$ surface, which has an additional hole per surface unit cell. A complimentary example, the non-polar MgO (1 0 0) surface that has no local charge defect is simulated for comparison. We show that the contrast due to local charge defects is rather high, and suggest that they should be directly observable.

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1. Introduction

There are currently numerous methods for obtaining local structural information using transmission electron microscopy. For example, high-resolution electron microscopy (HREM) and Z-contrast STEM are routinely used to study atomic arrangements at interfaces in materials. Most studies with HREM and Z-contrast have been focused on achieving atomic resolution (1–2 Å) and accurately locating atomic positions. While atomic positions are important, there is much more one would like to know. For instance, if one knew the electron density, in many respects one would not need any further information since, at least in principle, the density fully determines most of the properties including the positions of the nuclei. Electron energy loss spectroscopy has demonstrated that it can be performed with atomic-scale resolution, but this is not a direct measure of the electron density in a material, rather a measure of the local joint-density of states. Electron-diffraction techniques have been recently shown to be successful in determining electron charge density. With convergent beam electron diffraction, bonding charge and charge transfer can be evaluated in bulk materials with the accurate measurement (0.1%) of structure factors [1–13]. Despite experimentally measured surface diffraction intensities having relatively poor accuracy (1–10%), it is also possible to obtain charge transfer information between surface atoms [14,15]. What all of these approaches have in common is the use of electron diffraction to observe charge redistribution in reciprocal space, which only permits the observation of an average result not any local changes. A question then naturally arises: can we ‘‘see’’ charge transfer and local charge defects (i.e. localized charge compensating hole or electron states) directly by imaging in real space, particularly at the atomic level? Charge transfer is very common at interfaces, around vacancy clusters, etc. and direct imaging of these would open up new frontiers for electron microscopy.

In our previous studies, we have shown that charge transfer in a bulk material can lead to a difference of 5–7% in the electron structure factors and that these effects should be detectable in HREM images [16]. In the present work, we will investigate the feasibility of directly imaging local charge defects by HREM. As models of simple planar defects, we will use as two representative cases, a polar surface and a non-polar surface, both simulated in profile mode. The first model is the reconstructed MgO (1 1 1)$-\sqrt{3}\times\sqrt{3}R30^\circ$ surface, denoted as MgO Rt3 for simplicity. The MgO Rt3 surface structure is magnesium

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(Mg) terminated with two Mg vacancies located in the first layer relative to the simple bulk terminated surface [14,15]. Our previous studies indicate that an additional electron hole per surface unit cell is required for charge compensation and that this is primarily localized in the second O layer. The second model used is the non-polar MgO (1 0 0) surface, for which there are only very minimal changes in the electron density at the surface.

The simulations, which we describe, are similar to the imaging configuration that is routinely used for grain boundaries and other defects where local charge defects may be present. We find strong theoretical evidence that one should, in practice, be able to directly observe effects from charge transfer and charge defects in a material by HREM imaging.

2. Numerical method

Multislice image simulations were performed on projected potentials derived from three sets of X-ray structure factors. The first two sets are calculated from neutral atoms, denoted as F^x_{neu}, and bulk ions, F^x_{ion}, from fitted atomic scattering factors using a recent analytical form as a linear combination of five Gaussians:

$$f^x(s) = \sum_{i=1}^{5} a_i \exp(-b_i s^2) + c, \tag{1}$$

where a_i, b_i, and c are tabulated parameters, and s is $\sin(\theta)/\lambda$. The fitting parameters for the neutral atoms (Mg and O) charge density [17] and the self-consistent bulk (MgO) ion charge density [18] are available in the literature.

The third set of structure factors (F^x_{scf}) was calculated by full-potential density functional theory (DFT) implemented in the WIEN2K program [19,20]. The MgO Rt3 surface structure was modeled by a slab of 13 layers (35 atoms), separated by a vacuum slab of 14 Å in length. The unit cell contains 17 Mg atoms and 18 O atoms at fully relaxed positions using a GGA potential [21]. In a similar fashion, the MgO (1 0 0) non-polar surface was modeled by a slab of 12 layers, separated by a vacuum of 21 Å in length, which was also fully relaxed using WIEN2K. In both cases, the DFT equilibrium lattice parameters for MgO were used which are about 1% larger; this is a typical value and should have almost no effect on any of the conclusions.

The X-ray structure factors in all three cases were directly converted to electron structure factors using the Mott–Bethe formula. To be consistent, F^e_{neu}, F^e_{ion}, and F^e_{scf} refer to the electron structure factors generated from F^x_{neu}, F^x_{ion}, and F^x_{scf}, respectively. The electron structure factors were then projected along the directions of interest (here [1 1 0]) into slices of thickness less than 2.0 Å along the beam direction by

$$V_{\text{p}}(x,y) = \frac{1}{\Omega}\sum_{h,k} F^{\text{e}}(h,k,0)\exp(-2\pi \text{i}(hx+ky)), \tag{2}$$

where $F^{\text{e}}(h,k,0)$ is the projected structure factor. Then the unit cell is cut into thinner sub-slices with a thickness less than 2 Å. Each slice has the same projected potential $V_{\text{p}}(x, y)/n$, where n is the number of slices for one unit cell. Although we recognize that this method ignores conventional high-angle higher-order Laue zone effects, they should in principle be negligible under normal imaging conditions. A slightly more severe approximation is neglect of the higher-order Laue Zone contribution to the 1 × 1 reflections (nominally 1/3(422) spots) for the MgO Rt3 (e.g. Ref. [22]), although these are relatively weak intensities. A constant temperature factor of 0.25 Å^2 for all atoms was used in the simulations, and applied as a simple multiplier in reciprocal space.

For a rigorous investigation of the experimental feasibility of detecting charge defects, two different sets of microscope parameters were used in order to evaluate defocus effects on the image contrast of the charge defects. One is for a conventional H9000 microscope with $C_{\text{s}} = 0.9$ mm, accelerating voltage = 300 kV, beam convergence = 0.68 mrad, and defocus spread = 80 Å, and the other for an aberration-corrected Jeol 2200FS microscope [23] with $C_{\text{s}} = 0.05$ mm, accelerating voltage = 200 kV, beam convergence = 0.1 mrad, and defocus spread = 20 Å.

3. Results

It is well known that a linear Fourier transform relates the structure factors to the charge densities in a material; as a result, different structure factors should represent different charge densities and electrostatic potentials. In most routine HREM image simulations, neutral atom structure factors are used, which ignores the charge redistribution in the material. Another set of structure factors that are routinely used come from self-consistent field (scf) calculations decomposed from the charge density of the crystal. Throughout this paper, we will reference the simulated images as I(src), according to the original structure factor source data (src) used to generate the images, i.e. neu, ion, or scf. The two structures we used are shown in Figs. 1(a) and 2(a). In our simulations, image difference maps were used to understand and quantify the local changes, as shown in Figs. 1(c), (d), 2(c) and (d). The standard deviation (σ) of an image was used as a quantitative measure of the contrast. For the MgO Rt3 structure, the primary changes observed in the atomic positions and charge density occur in the top two or three surface layers, since those near the center of the slab describe the bulk material very well. In our simulation, we have designated the three top layers of the slab as surface layers and the remaining layers as bulk for both MgO Rt3 and MgO (1 0 0) structures. Typical HREM profile images of the MgO Rt3 and the MgO (1 0 0) structures are shown in Figs. 1(b) and 2(b), respectively.

3.1. Image simulation from neutral and ion structure factors

The contrast difference was calculated from the profile images, which are simulated, by neutral atom and ion structure factors at various defocus values (Supplementary