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Electron tunnelling at surfaces of Mott insulating *d*- and *f*-metal oxides: the *ab-initio* interpretation of STM images

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Abstract. In this communication we describe recent progress in the first-principles theoretical modelling of surface electronic structure and elevated temperature atomically-resolved STM images of surfaces of semiconducting *d*- and *f*-metal oxides. The presence of strong electron correlations in the 3*d* and 5*f* shells of metal ions in NiO, CoO and UO₂ makes conventional computational methods based on the local spin density approximation (LSDA) of density functional theory unsuitable for *ab-initio* calculations of the surface electronic structure of these oxides. By using the LSDA+U approach, which combines LSDA with the Hubbard U term, we explain the origin of the contrast reversal of experimental STM images of the NiO (001) surface. We also show how the symmetry of surface states is responsible for the order of magnitude difference in the contrast of STM images of NiO (001) and CoO (001) surfaces, and we describe how theoretical simulations make it possible to identify the atoms that are seen in STM images of the (111) surface of UO₂.

Introduction

Antiferromagnetic insulating transition metal oxides form a class of compounds whose electronic structure cannot be described using conventional band theory. The origin of the insulating behaviour of those oxides was explained in 1937 by Peierls who pointed out that band theory fails when the inter-site tunneling of electrons is suppressed by the on-site Coulomb repulsion between electrons. The anomalous electronic behaviour of transition metal oxides associated with strong electron correlations in the 3*d* shell, also manifests itself in compounds containing ions of actinide elements. Metal ions in actinide oxides (for example, in UO₂) contain partly filled 5*f*-shells where electrons are localized in the vicinity of atomic cores. The magnitude of the Hubbard parameter *U* describing the strength of electron-electron interaction in the 5*f* shell is comparable with the magnitude of *U* characterizing the 3*d* electrons in transition metal oxides.

So far, experimental and theoretical studies of transition metal and actinide oxides were mainly focused on their *bulk* properties. In our work [1, 2, 3] we investigate the *surface* properties of the 3*d* and 5*f* oxides. This field has recently attracted attention of many research groups worldwide. This stems from the interest in magnetic properties of metal oxides that are being considered as potential components of future media storage devices. Interest in surface properties of uranium oxides is driven by the recent discovery of unusually high catalytic activity of their surfaces. Transition metal oxides are also known to be catalytically active, and there is evidence for the existence of a link between the unusual surface properties displayed by the 3*d* and 5*f* oxides and the role played by strong electron correlations in the formation of surface electronic states in these materials.

1 Electronic structure and tunnelling at oxide surfaces

Evaluating the tunneling current using the Bardeen approximation, we arrive at

$$I(L \rightarrow R) = \frac{2\pi}{\hbar} \sum_{L,R} (n_L - n_R) |M_{LR}|^2 \delta(E_R - E_L), \quad (1)$$

where matrix element M_{LR} is given by

$$M_{LR} = \frac{\hbar^2}{2m} \int_A d^2A \left[\Psi_L(\mathbf{A}, z_A) \frac{\partial}{\partial \mathbf{r}} \Psi_R^*(\mathbf{A}, z_A) - \Psi_R^*(\mathbf{A}, z_A) \frac{\partial}{\partial \mathbf{r}} \Psi_L(\mathbf{A}, z_A) \right]. \quad (2)$$

Integration in (2) is performed over an arbitrary surface A separating the entire space into the left-hand and right-hand side parts, one including the tip and the other including the sample, in such a way that the effective *one-electron* potential vanishes everywhere at this surface. Formula (2) shows that in order to interpret an STM image, it is often *sufficient* to investigate the asymptotic behaviour of the real space distribution of the density of electronic states in the vacuum gap separating the STM tip and the surface.

For many metallic and band insulating surfaces the effective one-electron states can be found using conventional density-functional techniques based on the local density approximation. However, predictions of metallic ground states for CoO and UO₂ and the near metallic ground state for NiO made using LSDA shows that this strategy cannot be followed in an investigation of the electronic structure of 3d and 5f oxide materials. In our work we use the LSDA+U method [4] that has proved to be successful in addressing a number of fundamental issues relevant to the *bulk* properties of UO₂ and NiO [5, 6]. The LSDA+U method combines the LSDA treatment of electron correlations in delocalized *s* and *p* orbitals with the spin-unrestricted Hartree–Fock (UHF) treatment of localized *d* or *f* orbitals. In practical calculations, the UHF correction amounts to the renormalization of the matrix of the LSDA potential [7] (the correction applies only to the spatially localized *d* and *f* orbitals)

$$V_{jl}^\sigma \equiv \frac{\delta E_{LSDA+U}}{\delta \rho_{lj}^\sigma} = \frac{\delta E_{LSDA}}{\delta \rho_{lj}^\sigma} + (\bar{U} - \bar{J}) \left[\frac{1}{2} \delta_{jl} - \rho_{jl}^\sigma \right], \quad (3)$$

where ρ_{jl}^σ is the density matrix of electrons occupying partly filled electronic shells of metal ions (the 5f shell in UO₂ and the 3d shell in NiO and CoO).

2 Electronic states at NiO(100), CoO(100) and UO₂(111) surfaces

Atomically-resolved images of the (100) surface of NiO obtained by Castell *et al* [8] exhibit the reversal of image contrast occurring as a function of the sign of the bias applied to the sample. Image contrast observed at a positive sample bias is significantly higher than the contrast of images observed at a negative sample bias. To explain this effect, in Fig. 1 we plotted the real space distributions of the density of filled and empty surface electronic states of NiO calculated using the LSDA+U approach. These distributions show that, on one hand, at positive applied bias electrons tunnel predominantly into the empty 3d_{3z²-r²} states localized on nickel sites. On the other hand, at negative applied bias the main contribution to the tunneling current comes from the states localized on oxygen sites. Fig. 1 shows that image contrast should be expected to be significantly lower in the latter case than in the

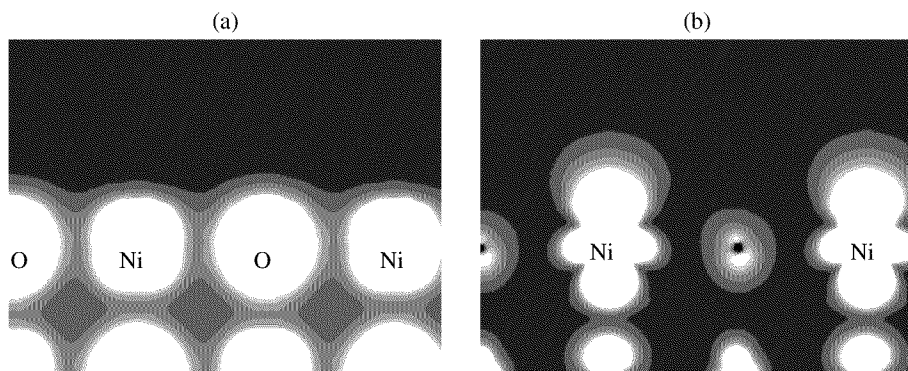


Fig. 1. Valence electron charge density distribution (a) calculated numerically for the NiO(001) antiferromagnetically ordered surface and the distribution of the density of *empty* states (b) calculated for the same surface by integrating over a 1 eV energy interval corresponding to the bottom of the conduction band.

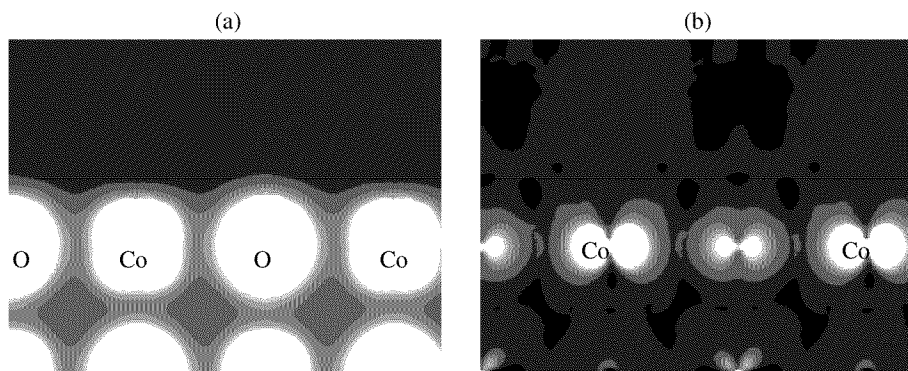


Fig. 2. Charge density distribution (a) and the density of empty electronic states (b) calculated for the antiferromagnetically ordered CoO(001) surface.

former one, in agreement with experimental observations. In experiments [7] conducted on NiO(100) and CoO(100) surfaces we compared the contrast of STM images of the two surfaces obtained under similar experimental conditions. While the atomically resolved images of CoO and NiO looked similar, we observed a significant difference in the atomic corrugation heights. To explain this phenomenon, we have carried out a first-principles investigation of the electronic structure of the CoO(100) surface. The results shown in Fig. 1 and Fig. 2 illustrate the difference in the symmetry of low-lying *d*-states forming the bottom of the conduction band of NiO and CoO. This difference is responsible for the order of magnitude difference in the contrast of experimental STM images observed for the two surfaces [7].

In Ref. [2] we reported the atomically resolved STM images of uranium dioxide UO₂(111). The interpretation of these images is less straightforward since oxygen ions on the (111) surface of the fluoride structure of UO₂ are situated above uranium ions (see Fig. 3). However, the density of states plot shown in Fig. 3 proves that uranium ions still

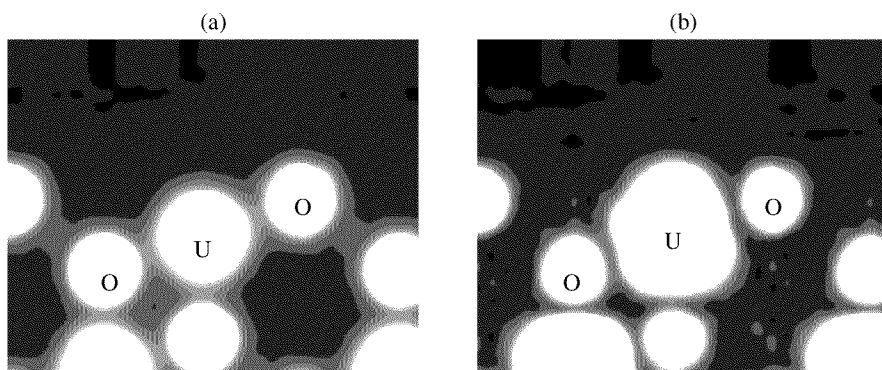


Fig. 3. Charge density distribution (a) and the density of empty electronic states (b) calculated for the antiferromagnetically ordered $\text{UO}_2(111)$ surface.

give the dominant contribution to the tunneling current observed at a positive applied bias. In summary, in this communication we described applications of the LSDA+U method to surfaces of Mott insulating transition metal and actinide oxides and showed how a combination of novel experimental information with the first-principles theoretical modelling gives rise to a new method of investigation of the electronic structure of this unusual class of oxide materials.

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