Chemical Resolution at Ionic Crystal Surfaces Using Dynamic Atomic Force Microscopy with Metallic Tips

G. Teobaldi,[1] K. Lämmle,[2] T. Trevethan,[3,4] M. Watkins,[5] A. Schwarz,[2,*] R. Wiesendanger,[2] and A. L. Shluger[3,4,†]

[1]*Surface Science Research Centre, Department of Chemistry, University of Liverpool, L69 3BX Liverpool, United Kingdom*
[2]*Institute of Applied Physics, University of Hamburg, Jungiusstraße 11, 20355 Hamburg, Germany*
[3]*Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom*
[4]*WPI-AIMR, Tohoku University, 2-1-1 Katahira, Aoba, Sendai, 980-8577, Japan*
[5]*The London Centre for Nanotechnology, University College London, 17-19 Gordon Street, WC1H 0AH London, United Kingdom*
(Received 3 February 2011; published 25 May 2011)

We demonstrate that well prepared and characterized Cr tips can provide atomic resolution on the bulk NaCl(001) surface with dynamic atomic force microscopy in the noncontact regime at relatively large tip-sample separations. At these conditions, the surface chemical structure can be resolved yet tip-surface instabilities are absent. Our calculations demonstrate that chemical identification is unambiguous, because the interaction is always largest above the anions. This conclusion is generally valid for other polar surfaces, and can thus provide a new practical route for straightforward interpretation of atomically resolved images.

Atomic force microscopy (AFM) operated in ultrahigh vacuum using the dynamical ''noncontact'' mode (NC AFM) is now a well established tool in surface science that is capable of imaging insulating as well as conducting surfaces with true atomic resolution [1,2]. The ability to characterize insulating surfaces and control surface processes down to the atomic scale is extremely important for numerous applications in chemistry, catalysis, nanoscience, and nanotechnology and can be achieved only using AFM. The exact chemical nature and structure of the AFM tip apex as well as the identity of the foremost tip atom are ultimately responsible for the formation of atomic-scale contrast [3], but are notoriously difficult to control. AFM tips are typically fabricated *ex situ* from silicon or metals and hence possess an oxide layer, either due to the manufacturing process itself or by oxidation in air. Even if the oxide layer and air-induced contaminants are removed *in situ* by sputtering or heating, extra material can be transferred between tip and sample due to the small distances usually required to obtain atomic resolution. In fact, such tip changes are frequently observed before atomic resolution is achieved.

On binary and more complex ionic surfaces, the polarity of the tip apex determines whether anions or cations are imaged as protrusions [3]. Therefore, it is impossible to assign image features to particular surface atoms without knowing the tip polarity. As a result, in spite of the many successes of NC AFM, interpretation, stability, and reproducibility of atomically resolved images are still hampered by difficulties in preparing and characterizing the tip apex and by structural instabilities caused by the strong tip-surface interaction [1]. In this Letter we demonstrate that metallic tips can resolve the surface atomic structure on ionic surfaces at tip-sample separations that avoid such

instabilities and enable the unambiguous interpretation of atomic-scale chemical contrast. In addition, we present a simple *in situ* technique to determine whether a tip exhibits metallic behavior or not.

We selected NaCl(001), the prototypical binary ionic surface, as our sample system. To independently identify the sublattice that interacts strongest with the tip, and to estimate the absolute tip-sample distance, Co-salen molecules were deposited onto the substrate. Imaging and spectroscopy data were recorded with atomic resolution in an area with an isolated molecule on the bare substrate. Details of sample preparation and data acquisition can be found in Ref. [4]. All experiments were performed in an ultrahigh vacuum cryostat system with a homebuilt low temperature microscope [5] at about 8 K. The whole Si cantilever, including the tip, was coated *in situ* with nominally 4 nm of Cr, which adheres well to the oxide layer of standard Si tips, to produce a conducting path between tip apex and cantilever stage.

To characterize the tip, we recorded $\Delta f(U)$ curves with the bias voltage U applied between cantilever stage and sample holder stage. Such curves can be recorded repeatedly, e.g., after tip changes. Figure 1 displays three different $\Delta f(U)$ curves with Cr-coated tips. A sign of formation of a metallic Cr-terminated tip is smooth parabolic curves without jumps, which look identical independent of the sweeping direction (i.e., no hysteretic behavior); cf. Fig. 1(a). Tips that do not possess a metallic apex exhibit discontinuities in the curves indicative of charge reconfigurations due to tunneling processes between localized states at the tip apex; cf. Fig. 1(b). For such tips, either the Cr coating was not sufficient or the tip-sample interaction led to transfer of Cr to the surface exposing an insulating oxide layer on a Si tip. To exclude tunneling from a

metallic tip into localized states in an insulating sample, we recorded $\Delta f(U)$ curves at rather large tip-sample distances. Figure 1(c) shows another type of $\Delta f(U)$ curves. The apparent hysteresis can be attributed to slow charge relaxation processes implicating a badly conducting tip apex.

Although curves like those shown in Fig. 1(a), in our experience, are an unambiguous sign of a metallic tip, we cannot be absolutely sure that the tip has not picked up single Cl or Na atoms. However, the calculations below demonstrate that this is unlikely for Cr tips without forming a hard contact with the surface. Moreover, using the metal-coated tips for several years we have noticed that they are much more likely to lose rather than pick up material: after tip changes, we usually observe bumps rather than holes on the surface, and contacting the surface leads to tips that are usually shorter (visible by the movement of the z piezo to keep Δf constant) and blunter (a larger negative Δf is required to obtain the same image quality).

Atomic resolution imaging and subsequent 3D force field spectroscopy [6] were performed with a metallic Cr-coated tip [$\Delta f(U)$ curve as in Fig. 1(a)] within the region displayed in Fig. 1(d). Details of the procedure used to extract force curves from the experimental $\Delta f(x, y, z)$ data set can be found in Ref. [4]. Based on the position of the

Co-salen marker molecule, which adsorbs with its central Co atom on top of Cl sites, protrusions in Fig. 1(d) represent the Cl sublattice [7]. The exemplary force curves recorded above a protrusion (Cl) and depression (Na), respectively, are shown in Fig. 2(a). Note that no absolute z scale can be obtained from experimental spectroscopy curves alone. However, the presence of a marker molecule provides an estimate of the lower limit of absolute tip-sample separation. In the presented data set, the distance of closest approach was chosen to obtain the best resolution of the surface ions in the vicinity of the molecule, but without altering the original position of the molecule. Density-functional theory (DFT) calculations [7] have demonstrated that the Co-salen molecule adsorbs in a planar configuration at ≈ 0.38 nm above the surface plane. Calculations presented in [4] demonstrate that the short-range interaction between the Cr tip apex and the Co-salen enters the repulsive regime at a separation about 0.15 nm. Assuming that closer approach would lead to strong deformation or displacement of the molecule, we estimate that the minimum tip-surface separation required to avoid manipulating the molecule is ≈ 0.53 nm.

To understand the origin of the atomic-scale contrast and investigate the mechanism of the interaction of a metallic nanoasperity with an ionic surface, we performed extensive DFT calculations of this system with different tip models. Our simulations, employing a 30 atom cluster model for the Cr tip, demonstrated that the short-range force is stronger over the negative Cl ion [7]. However, in this model the tip is not metallic and its interaction with the surface is overestimated due to an artificial electron transfer from the surface to the tip and an incomplete correction of basis set superposition errors. As at long separations the tip-surface interaction depends very sensitively on the tip
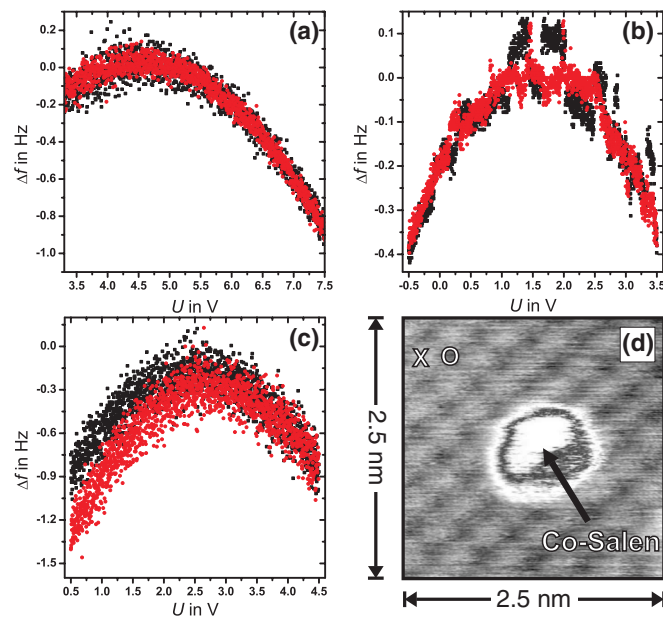

FIG. 1 (color online). Three types of exemplary $\Delta f(U)$ curves obtained with metal-coated tips. Gray (red) and black dots correspond to opposite voltage sweeping directions. The actual conductivity of the tip apex can be evaluated as follows: (a) metallic tip apex, (b) insulating tip apex with localized states, (c) badly conducting tip. (d) Atomically resolved NaCl(001) imaged together with a single Co-salen marker molecule using a metallic Cr-coated tip. Protrusions correspond to Cl sites. The X and O marks indicate the location of the experimental spectroscopy curves shown in Fig. 2.
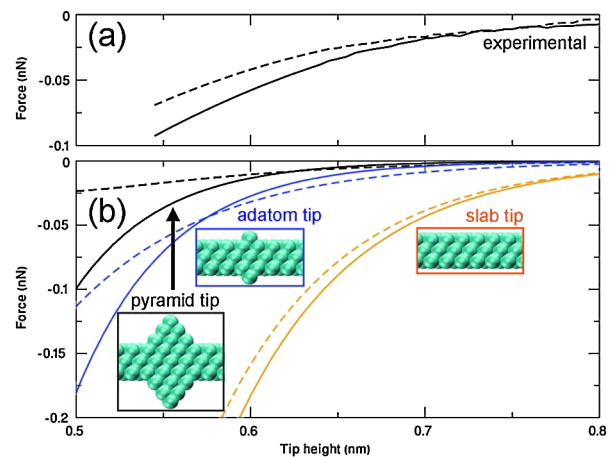

FIG. 2 (color online). (a) Short-range experimental force curves above Cl (solid line) and Na (dashed line) ions, where the tip height at closest approach has been set to match the difference in forces of the pyramid tip model. (b) Simulated force curves for each of the three tip models (see insets) above Cl and Na ions.

and surface electronic structures, it is important to reproduce the metallic nature of the tip in our calculations. We therefore report here only the results obtained with the plane augmented wave VASP code [8] and the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [9]. The NaCl(001) surface was represented by a periodic 5×5 slab of atoms, 3 atomic layers deep with the bottom layer atoms fixed in the bulk positions and the remaining atoms allowed to relax. The tip base was represented by a 5×7 slab of the Cr(110) surface, 3 atomic layers deep, with the central layer of atoms frozen in the bulk positions and with all other atoms free to relax. This Cr slab is slightly stretched or compressed to match the periodicity of the NaCl slab (2.019×2.019 nm^2). This does not significantly affect the electronic structure, and only changes the work function of the Cr slab by ≈ 0.05 eV.

We consider three different tip models based on the Cr slab [see insets of Fig. 2(b)]: (i) the slab alone (slab tip), (ii) the slab with a single protruding adatom (adatom tip), and (iii) the slab with a three layer pyramidal protrusion terminating with a single atom (pyramid tip). Both protrusions are replicated on both sides of the Cr slab, and symmetrically relaxed. For all tips we observe the formation of a surface dipole due to the Smoluchowski effect [10] caused by the incomplete screening of the positive ion cores by conduction electrons, because the spatial variation of the charge density is limited by the Fermi wavelength. The calculated dipole moments for the adsorbed atom (1.23 D/step atom) and the pyramid tip (1.98 D/step atom; see Ref. [4] for details) broadly agree with the results of previous studies on extended steps at metal surfaces ($0.16 - 1$ D/step atom [11,12]) and increase with decreasing the coordination of surface atoms [13]. We note that this fundamental property of metal surfaces is difficult to describe within continuum approximations to the tip polarization [14], and remained unaccounted for in some recent models of Kelvin probe microscopy [15].

For each of the three tip models, the apex atom (or, in the case of the slab tip, an atom in the surface layer) is placed directly above either a Na or a Cl ion at various initial tip heights. The tip height is defined [4] as the distance between the topmost Na (Cl) ion and the apex atom of the initially relaxed tip (note there is a rumpling in the surface with Cl ions protruding 0.011 nm). The positions of all free atoms in the system are then fully relaxed. The tip-surface interaction induces an additional polarization of the tip and the surface. To compensate for the artificial interaction of the periodically repeated dipoles, we applied corrections as implemented in VASP [8].

The total energies as a function of tip position are shown in Ref. [4]. For tip-surface distances smaller than 0.6 nm, the short-range chemical interaction above the Cl ion is more attractive than above the Na ion (we note that it is two times weaker than for the cluster tip model). A marked

energy change at a height of about 0.4 nm is due to the jump of the surface Cl ion by about 0.15 nm towards the tip apex. The displaced Cl ion remains charged, and as the tip is retracted away from the surface, it returns back into the surface plane. These results are consistent with our experimental observation that the tip contamination by surface ions is unlikely on a careful approach.

For each tip model and lateral position, the total energy as a function of the tip height was fitted to a Morse function, which was differentiated to obtain the force as a function of the tip height; cf. Fig. 2(b). The tip-surface force decreases with increasing the tip sharpness, since the blunter the tip, the more Cr atoms are closer to the surface for a given tip height, which is defined by the lowest atom. It is also apparent that the sharper the tip, the larger the difference between the forces on the tip above a Cl ion and a Na ion. For the flat slab tip, there is no significant difference between the two lateral configurations, which is to be expected. The other two tip models, in spite of some quantitative differences in the behavior of the force-distance curves, demonstrate reasonable agreement with the experiment in the relevant distance range of 0.5–0.6 nm. Because of their idealized structure, none of the tips gives perfect quantitative agreement with the experiment in the whole distance range; however, there is a good agreement with the measured *difference* between the forces above Cl and Na ions at the closest approach, which is 0.032 nN. For the adatom tip, this difference would correspond to a tip height of 0.53 nm whereas for the pyramid tip to a tip height of 0.55 nm. These results are consistent with the independent estimate of the distance of closest approach on the basis of the adsorption height of the Co-salen molecule and the tip height at which the tip-molecule interaction is likely to induce manipulation (≈ 0.53 nm).

At closer tip-surface separations of ≈ 0.3 nm, the calculations show a significant charge transfer to the tip, which is more pronounced when the tip is above a Cl ion [4]. This chemical interaction due to a hybridization of the Cl $3p$ and Cr $3d$ electronic states decays rapidly as the tip moves away from the surface. Above ≈ 0.4 nm, there is negligible charge transfer and the tip-surface interaction and the image contrast are primarily due to the electrostatic interaction of the *dipole moment* of the tip apex with the surface ions. The orientation of the tip dipole (its positive pole is pointing to the surface) favors the interaction with the negative surface Cl ion and is enhanced by the additional polarization of the tip and the surface caused by the interaction, in agreement with Ref. [11].

To gain further insight into this mechanism of interaction, we analyzed the electrostatic profiles across both the slab and tip models, and the total electronic charge density difference between the profiles for the tip optimized above the NaCl slab and at infinite distance from the slab [4]. Charge redistribution in the tip due to the proximity to the

slab is induced mainly by electronic reorganization. The charge density difference ($\Delta\rho$ [4]) across the pyramid tip positioned at 0.5 nm above the Cl and Na atoms in the surface is shown in Ref. [4]. This redistribution is more pronounced above the Cl ion than the Na ion and increases if the tip gets closer to the surface. The larger induced dipole above the Cl ion is due to the larger polarizability of the Cl ion as well as the surface rumpling.

To summarize, the electrostatic interaction between the permanent dipole in the Cr tip apex dominates the short-range component of the tip-sample interactions above 0.4 nm and is strong enough to allow for atomic resolution. Since the electric dipole points towards the surface with its positive pole, this kind of interaction is more attractive above anions (Cl) than above cations (Na). Using Co-salen as a marker molecule to independently identify the sublattice, which is represented by protrusions, and to estimate an absolute z scale for our experimental spectroscopy data, we could show that chemical resolution can indeed be achieved at a tip-surface distance of ≈ 0.55 nm. Hence, Cr-coated metallic tips enable both atomic resolution at relatively large distances, where tip-sample instabilities are still absent, and unambiguous atom identification. Previous studies demonstrate that on ionic surfaces atomic resolution with a pure Si tip is expected for separations below 0.4 nm with the largest attraction above anions [16]. Using force spectroscopy above different ionic sites to *in situ* characterize the tip apex atom in combination with atomistic modeling of different types of tips requires distances of about 0.3 nm [17,18].

Since the Smoluchowski effect is universally observed on corrugated metal surfaces [19], an electric dipole will always be present at a metallic tip apex. For common metallic or metal-coated tips (e.g., tungsten [20]), it will point with its positive pole into the vacuum region, i.e., towards the sample surface [11]. In most cases anions are more polarizable than cations and protrude out of the surface plane due to surface rumpling [21]. Both effects will enhance the attractive interaction of anions with the tip. Therefore we suggest, more generally, that on ionic surfaces atomic resolution imaging with metallic tips should be feasible at relatively large distances, where tip-sample instabilities are absent, and that the largest interaction is always expected with the anion sublattice. Thus, for metallic tips qualitative interpretation of contrast patterns on ionic surfaces can be made independently of the tip material and apex structure based only on the positions and charges of surface ions. Successful implementation of this approach will facilitate atomic-scale research on more complex technologically relevant polar surfaces utilized, e.g., in catalysis.

* aschwarz@physnet.uni-hamburg.de
† a.shluger@ucl.ac.uk
 [1] C. Barth, A. S. Foster, C. R. Henry, and A. L. Shluger, Adv. Mater. **23**, 477 (2011).
 [2] F. J. Giessibl, Rev. Mod. Phys. **75**, 949 (2003).
 [3] W. A. Hofer, A. S. Foster, and A. L. Shluger, Rev. Mod. Phys. **75**, 1287 (2003).
 [4] See supplemental material at http://link.aps.org/supplemental/10.1103/PhysRevLett.106.216102 for details regarding experimental and theoretical aspects.
 [5] M. Liebmann, A. Schwarz, S. M. Langkat, and R. Wiesendanger, Rev. Sci. Instrum. **81**, 053902 (2010).
 [6] H. Hölscher, S. M. Langkat, A. Schwarz, and R. Wiesendanger, Appl. Phys. Lett. **81**, 4428 (2002).
 [7] K. Lämmle, T. Trevethan, A. Schwarz, M. Watkins, A. L. Shluger, and R. Wiesendanger, Nano Lett. **10**, 2965 (2010).
 [8] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).
 [9] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[10] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[11] J. Y. Park, G. M. Sacha, M. Enachescu, D. F. Ogletree, R. A. Ribeiro, P. C. Canfield, C. J. Jenks, P. A. Thiel, J. J. Saenz, and M. Salmeron, Phys. Rev. Lett. **95**, 136802 (2005).
[12] J. F. Jia, K. Inoue, Y. Hasegawa, W. S. Yang, and T. Sakurai, Phys. Rev. B **58**, 1193 (1998).
[13] K. Besocke, B. Krahl-Urban, and H. Wagner, Surf. Sci. **68**, 39 (1977).
[14] L. Nony, A. S. Foster, F. Bocquet, and C. Loppacher, Phys. Rev. Lett. **103**, 036802 (2009).
[15] F. Bocquet, L. Nony, C. Loppacher, and T. Glatzel, Phys. Rev. B **78**, 035410 (2008).
[16] A. S. Foster, A. Y. Gal, J. D. Gale, Y. J. Lee, R. M. Nieminen, and A. L. Shluger, Phys. Rev. Lett. **92**, 036101 (2004).
[17] R. Hoffmann, L. N. Kantorovich, A. Baratoff, H. J. Hug, and H. J. Güntherodt, Phys. Rev. Lett. **92**, 146103 (2004).
[18] R. Hoffmann, D. Weiner, A. Schirmeisen, and A. S. Foster, Phys. Rev. B **80**, 115426 (2009).
[19] H. Ibach, *Physics of Surfaces and Interfaces* (Spinger-Verlag, Berlin, 2006).
[20] Y. Naitoh, Y. Kinoshita, Y. J. Li, M. Kageshima, and Y. Sugawara, Nanotechnology **20**, 264011 (2009).
[21] P. W. Tasker, J. Phys. (Paris), Colloq. **41**, C6-488 (1980).