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Spin-contrast in non-contact SFM on oxide surfaces: theoretical modelling of NiO(0 0 1) surface

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Abstract

Low-temperature non-contact scanning force microscopy (NC-SFM) is now being used to try and measure the exchange force with metal tips on magnetic oxide surfaces. This demanding test of NC-SFM has yet to prove successful and therefore it is important to use a theoretical model to predict the magnitude and range of the exchange force, and the best way to measure it. In this study, a simple model of a spin-polarized tip has been used to measure the difference in interaction over opposite spin Ni ions in an ab initio simulation of the NiO(0 0 1) surface. The contribution of the exchange force and the role of ion instabilities in the tip–surface interaction are calculated, and used as an example to predict whether spin-contrast over ions should be observable in NC-SFM experiments and how best to achieve this. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Computer simulations; Atomic force microscopy; Construction and use of effective interatomic interactions; Magnetic surfaces; Nickel oxides

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1. Introduction

The non-contact scanning force microscope (NC-SFM) has now demonstrated [1,2] its ability to study a wide variety of surfaces at the atomic scale. Although it is not yet fully established as a reliable surface science technique, there is enough experimental confidence to begin expanding its role beyond topographic surface studies with atomic resolution. In particular, interest in the possibility of directly measuring differences of the exchange interaction with different surface sites has been motivated by the early suggestions from spin-polarized scanning tunneling microscopy (STM) [3], that the magnetic force between tip and sample at small distances (2–5 Å) could be measured. The recent introduction of low-temperature ($T <$ 15 K) NC-SFM [4] and the associated reduction in thermal noise has made this possibility even more feasible, and now several experimental NC-SFM groups are actively pursuing the measurement of atomic scale spin structure with magnetized metallic tips. Due to the well-defined magnetic surface structure and the ease of preparation of an atomically clean surface [5], the idea of measuring the

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exchange interaction on anti-ferromagnetic oxide surfaces, such as NiO, CoO and MnO, looks particularly attractive.

In NC-SFM, a cantilever with a tip at the end oscillates in the plane perpendicular to the surface, so that the tip periodically moves in and out of the short-range interaction region. The tip–surface interaction affects the parameters of these oscillations. In most cases the cantilever is subject to positive feedback such that it oscillates with constant amplitude and a specified frequency change. Topographic contrast in images can be generated by measuring the height of the tip at constant frequency change as a function of its position over the surface. The most spectacular way of experimental demonstration of the exchange effect with NC-SFM would be to measure a difference in contrast above metal atoms. For example, on the NiO(0 0 1) surface, attempts have been made to observe image contrast along parallel rows of Ni ions with anti-parallel spins running along the $\langle 1 1 0\rangle$ surface axis or between different Ni ions along the $\langle 1 0 0\rangle$ axis (see Fig. 1). However, since the surface sublattice seen as bright in images is unknown a priori, this cannot be the only way.

A possibly more promising approach could be to measure force vs. distance curves above different surface sites. This is within the reach of low-temperature NC-SFM [6] but requires very high sensitivity, low signal to noise ratio and good statistics. The latter implies repeating these measurements many times over different sites with the same tip. The best performance in this mode is achieved if the tip does not enter the repulsive part of the interaction and the force at the shortest tip–surface distance satisfies certain criteria formulated, for example, in Refs. [7–9]. However, it should be noted that the tip–surface distance is not known in experiments and therefore it is very difficult to remain in the ideal attractive interaction region. Advancing the tip too close to the surface leads to instability in SFM operation and tip crashes caused by tip–surface adhesion [10]. In some cases [11] resulting adsorption of the surface material on the tip can provide better topographic imaging. However, contamination of the end of a metallic tip by oxide will make the spin-contrast impossible due to strong increase in the distance between spin-polarized atoms in the tip and in the surface. Most experiments are therefore performed simply by advancing the tip very slowly until atomic contrast is achieved and only theoretical modelling can correlate the cantilever frequency change with the shortest tip–surface distance. The exchange force is weaker and much more short range than electrostatic 'chemical' forces responsible for topographic contrast and adhesion. Therefore the right balance between these components of the tip–surface interaction necessary for measuring of spin-contrast is determined by the chemical nature of the tip.

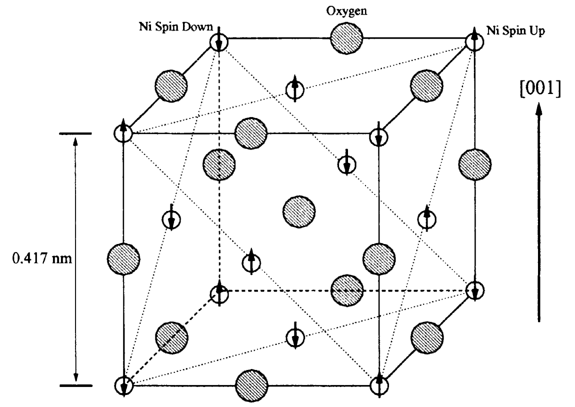

Fig. 1. Structure of NiO, showing the AF_2 anti-ferromagnetic spin structure with adjacent (1 1 1) planes of similar spin Ni ions.

In this study we focus on the NiO(0 0 1) as an example magnetic oxide surface, since it represents the most popular experimental choice and its magnetic properties have been widely studied previously. The aim of the theoretical modelling presented in this paper is to study the possibility of achieving stable differential contrast between different Ni sites for different chemical types of tips. For this purpose we first resort to a very simple tip model and calculate force vs. distance curves over different surface sites for two types of tips using the ab initio Hartree–Fock method and the CRYSTAL98 code described in Section 2. The results presented in Section 3 suggest that in the limit of a rigid surface, a measurable contrast due to different exchange interactions over alternative Ni sites could be achieved at tip–surface ranges common for NC-SFM measurements on insulators. Next we consider whether the interaction with different metallic tips at short distances can cause adhesion of oxide ions to the tip. These calculations are performed with more complex metallic tips. They involve complete relaxation of surface ions in an atomistic pair-potential technique and are presented in Section 4. Finally, we discuss the results and limitations of our model in Section 5.

2. Theoretical model

In a purely ionic picture of NiO the Ni^{2+} ions have a partially filled d shell in a $3d^8$ ground-state configuration, but strong on-site coulomb repulsion makes it an insulator [12], with a band gap of 4.3 eV [13]. It crystallizes in the rock-salt structure (as MgO) with a lattice constant of 0.417 nm and a high-spin anti-ferromagnetic spin structure at low-temperatures (see Fig. 1). Its Néel temperature (T_N) is 523 K and it undergoes a magnetic phase transition above this point. The magnetic properties of NiO are well known and various techniques have established the anti-ferromagnetic AF_2 structure as the most stable with each Ni ion having two unpaired electrons. The AF_2 structure is shown in Fig. 1, with adjacent (1 1 1) sheets of similar spin Ni ions. As yet, no difference in contrast over opposite spin Ni ions has been observed in NC-SFM [14] with metal tips. This directly motivates a theoretical study to investigate whether it should be feasible to measure the difference in the exchange force over this benchmark magnetic oxide surface in an experiment and also to establish the general criteria for successful imaging. Several previous theoretical studies have focused on calculating the magnitude of the exchange force over simpler, metallic magnetic surfaces, such as Fe [15], Cr and Ni [16], and it is therefore difficult to compare them directly with imaging of oxide surfaces.

Since the interactions of interest for atomic scale exchange force imaging are quantum mechanical in nature, a full ab initio treatment of the NiO surface and the tip is required. All calculations on NiO were performed using the periodic unrestricted Hartree–Fock (UHF) method as implemented in the CRYSTAL98 code [17]. This method has been successfully used previously to study the NiO surface [18,19]. All calculations were performed on the (0 0 1) NiO surface (see Fig. 1). The surface is represented by a periodic three layer slab, with a (2×1) surface unit cell, giving a total of 12 atoms in the unit cell. Since the (0 0 1) surface of NiO demonstrates no rumpling and very little relaxation [20,21], the perfect bulk termination with the experimental lattice constant of 0.417 nm has been used. We have found that 10 k-points converged the total energy to within 0.01 eV and used them in all further calculations. The Gaussian basis sets for Ni and O were taken from previous studies on NiO [18]. Test calculations on the surface alone confirmed the anti-ferromagnetic spin structure to be more stable than the ferromagnetic by 17 meV/Ni, which is in good agreement with previous UHF studies [19].

In most NC-SFM experiments attempting to detect the exchange force, the silicon NC-SFM tip is coated by a magnetic metallic layer, usually iron, which is prepared so that the end of the tip is ferromagnetic. The magnetic field inside the layer should be strong enough to keep the spin orientation of the atoms closest to the surface constant and not allow it to change due to the interaction with the surface ions. Note that this differs from magnetic force microscopy (MFM), where the whole tip is usually magnetic and the field probes the magnetic domains of the surface. Here we are interested in the interaction of a spin-polarized atom at the tip apex with spin-polarized atoms in the surface.

In the first part of our study we calculate the difference in the exchange interaction between the tip and different surface sites. As the exchange interaction is very short-range, it is reasonable to approximate the whole tip by the last spin-polarized apex atom closest to the surface. To demonstrate how different types of chemical interaction could affect the measurement of the exchange force, we used a chemically active (with respect to the NiO surface) spin-polarized Na atom, and an inert spin-polarized H atom as tip models. The Gaussian basis set for H is from Ref. [22] and the Na set is from [23]. In this initial part of the study, surface relaxation due to the proximity of the tip has been neglected; surface relaxation is dominated by the electrostatic interaction of the tip with the surface, and the tip's potential is not well represented by a single atom. In order to realistically model possible atomic displacements while scanning, a much larger tip and surface unit cell is required, and this is impossible to calculate in ab initio with current computer resources. Hence, initially we focus on establishing the distance range at which the exchange force can be measured, before applying a less expensive simulation technique with a more realistic tip to study the role of atomic displacements.

3. Exchange force

In an attempt to directly calculate the difference in the interaction between different Ni sites due to the exchange force, potential energy curves were calculated as a function of tip–surface separation over spin up and spin down Ni ions. These energy curves were then fitted and differentiated to get the force as a function of distance. Fig. 2 shows the force on a spin up sodium probe, with one unpaired electron, as a function of distance from a spin up Ni ion, a spin down Ni ion and an oxygen ion in the NiO surface. The effect of exchange can be seen directly between 2.5 and 4.2 Å, where there is a clear difference in the force over the spin up Ni and the spin down Ni ions. The maximum difference, at 2.8 Å, is about 0.17 eV/Å, but it is still about 0.05 eV/Å at 4.0 Å. The force over the oxygen ion is less than over both types of Ni ion. The adsorption energy of the Na over the Ni ions is about −2.00 eV and over the oxygen ion is −1.40 eV. The difference in adsorption energy is due to the difference in surface potential probed by the Na ion over the two sites and the charge transfer between the Na atom and the surface. The ionization energy of Na (5.1 eV) is fairly close to the position of the top of the NiO valence band, so as it approaches the surface it transfers charge to the oxygens: at 2.5 Å about 0.25*e* has been transferred to the surface. Above the nickel site, the effectively positive Na probe is repelled by the positive Ni^{2+} ion, but is also strongly attracted to the four neighbouring O^{2-} ions (see Fig. 1). Above the oxygen site, the Na is attracted to the negative O^{2-} ion but is repelled by the four neighbouring Ni^{2+} ions, making it energetically less favourable than the Ni as an adsorption site. It is this net interaction of the Na probe with the surface potential which gives the Ni as the favoured adsorption site. Adsorption on the metal site is consistent with experimental studies of alkali metal adsorption on oxide surfaces [24].

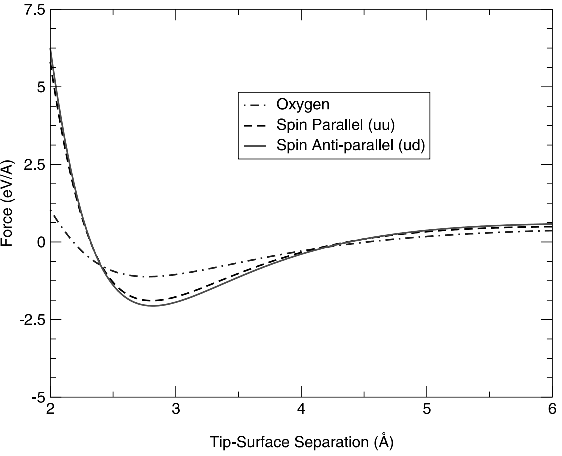

Fig. 2. Force as a function of tip–surface separation for a spin up Na probe over spin up Ni, spin down Ni and oxygen ions in the NiO surface.

In Fig. 3, the same calculation is repeated, but now with a spin up hydrogen atom, with one unpaired electron, as a probe. The large ionization energy of H (13.6 eV) means that there is very little charge transfer between the probe and surface. The hydrogen atom is much more inert to the NiO surface than the Na atom [25]. This can be seen by the lack of a minimum in the force curves, even over the oxygen ion. Again, there is a clear difference in force over the spin up and spin down Ni ions, but it is weighted a little closer to the surface than for the Na probe. At 2.5 Å the difference in force is about 0.17 eV/Å, which is the same magnitude as for the Na probe at 2.8 Å. It increases steadily from that point and is about 1.0 eV/Å at 2.0 Å.

To understand how these results would translate into frequency changes of the cantilever oscillations in a real NC-SFM experiment, the model

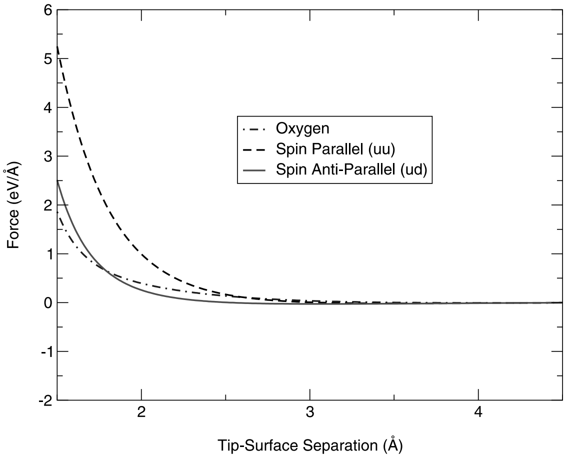

Fig. 3. Force as a function of tip–surface separation for a spin up H probe over spin up Ni, spin down Ni and oxygen ions in the NiO surface.

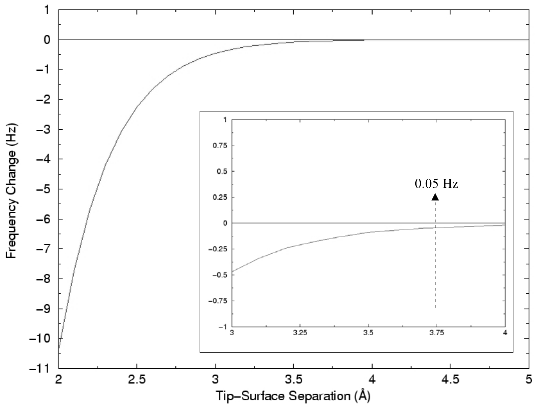

Fig. 4. Plot of the frequency change due to the difference in force over spin up and spin down Ni ions probed with a hydrogen atom. The inset shows a blow-up of the main curve with the point at which the frequency change is 0.05 Hz labelled.

of cantilever oscillations described in Ref. [10] is applied. The interaction of a real macroscopic tip with the bulk sample would result in large 'background' forces, such as the van der Waals force and possibly electrostatic forces. However, these forces are not site dependent on the atomic level. Therefore the cantilever oscillations are just simulated in the calculated force field due to the difference in the interaction between the H probe and opposite spin Ni ions in the NiO surface. Since the exchange force was very similar in both the H and Na probe, the H probe was chosen for this part as it is more inert to the NiO surface and gives a minimum for exchange force detection. The differential frequency change curve was produced with a cantilever amplitude of 6.7 nm, eigenfrequency of 201 kHz, and a spring constant of 37 N/m, as in experiments on NiO [26].

Fig. 4 effectively shows the magnitude of frequency change as a function of tip–surface separation that must be measured to see a difference over Ni ions in an NC-SFM image. The most advanced low-temperature NC-SFM [4], scanning at about 13 K, can measure frequency changes down to 0.05 Hz (an order of magnitude better than room-temperature NC-SFM). This value has been marked on Fig. 4 and it occurs at 3.75 Å. Assuming that a hydrogen atom is a good model of a magnetic tip, the theoretical study of NiO predicts that the difference in contrast over spin up and spin down can be seen with a low-temperature NC-SFM when the lowest point of the tip oscillations is less than 3.75 Å from the surface.

4. Ion instabilities

The most significant assumption in the calculations in the previous section is that relaxation of surface ions due to interaction with the tip can be neglected. As one can see in Fig. 4, the contribution to the image contrast due to the difference in the exchange interaction increases rapidly as the tip–surface distance decreases. The displacements of the tip and surface ions at tip–surface distances shorter than about 4.5 Å can be significant [10, 27,28]. At even shorter distances they may lead to instability of these ions and, in some cases, to their adsorption on the tip (surface). These instabilities cause large changes, or jumps, in the tip–surface force and prevent stable imaging. Therefore it is important to find out whether, in an experiment, force jumps may occur before the tip gets close enough to the surface to measure the exchange force difference.

To investigate the effect of surface relaxation, the interaction of different metal tips with the MgO surface is used as a model system. As a cubic oxide, with very small surface relaxations and little rumpling, MgO represents a good model of the oxide surfaces considered in imaging of the exchange force. However, the main advantage is that much more is known about the adsorption of metal clusters on MgO than on any other oxide surfaces [5]. It is impractical to model every possible metal tip interacting with every possible oxide surface, but by using adsorption data the tip–MgO interaction potentials can be modified to represent the particular 'metal tip'–'oxide surface' pair of interest.

The tip–surface interaction is treated using an efficient static atomistic simulation technique and the SCIFI code [29]. This atomistic technique is the only possible option for calculating the large unit cell sizes needed to adequately model surface displacements. Since the focus of this study is on ion relaxation, only the forces which influence this effect have been considered i.e. microscopic and image forces, whereas the exchange force due to spin interaction can be neglected completely.

To represent the MgO surface, a 5 × 5 × 2 (in terms of eight atom unit cells) MgO cluster was used. To model the metal tip at the microscopic and macroscopic scale, a four atom metal pyramid with its apex towards the surface was placed at 0.25 nm below a conducting sphere [29] representing the macroscopic silicon tip (see Fig. 5). The pyramid apex is a good model of a metallic tip apex, since it is known to be the lowest energy configuration of Fe_4 [30,31] and several other metal clusters. The top layer of the cluster modelling the surface is allowed to relax with respect to the microscopic and image forces. The positions of the atoms in the pyramid were frozen throughout the study.

The interatomic potentials for the MgO surface are taken from Ref. [32]. The initial potentials for the metal tip and its interaction with the surface are taken from HF calculations for the interaction of palladium with the MgO surface [33]. To model tips made from metals other than Pd, the potential between the metal ions of the tip and the oxygen ions in the surface is altered directly to reproduce the adsorption potentials for the specific metal ion on oxygen sites in the oxide surface. The adsorption energies, equilibrium positions and source of information are given in Table 1. For this study, calculations have been performed with Pd, Cu, Na and a generic metal, called M^*. Pd represents a metal atom which is very weakly adsorbing, although this interaction is still much stronger than the H probe, which has an adsorption energy of only −0.04 eV. Cu has been shown to adsorb weakly on oxygen sites in the MgO surface [34], but demonstrates a stronger interaction than Pd. Cu is also a spin-polarized atom and is therefore of possible interest as a candidate for detecting the exchange force. A Na tip has been included to represent a more strongly interacting tip, although in principle Na prefers to adsorb on Ni in NiO, its interaction with oxygen is still of interest for the purpose of surface relaxation. M^* represents a

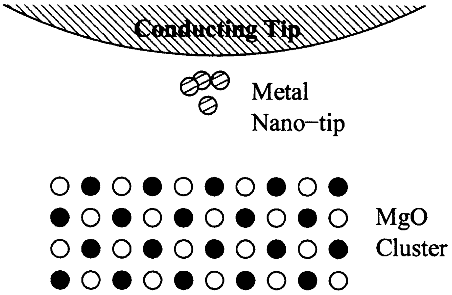

Fig. 5. Schematic diagram of the tip–surface set-up used to model surface oxygen instabilities. The metal tip is represented by a four atom pyramidal nano-tip and a fully polarizable conducting macroscopic tip [29].

Table 1
Comparison of adsorption energies, E_{ad}, equilibrium positions, r_{eq}, and references for adsorption of metal ions over oxygen in an oxide surface

Metal	E_{ad} (eV)	r_{eq} (Å)	Reference
Pd	−0.48	2.4	[33]
Cu	−0.90	2.1	[34]
Na	−1.40	2.0	This study
M^*	−4.00	2.4	N/A

Pd and Cu are over an MgO surface. The values for Na are taken from the adsorption on NiO from the calculations above and M^* represents a generic metal which has a strong adsorption to the surface.

metal ion which is strongly adsorbing on oxygen sites in the surface.

For most of the metal tips used in experiment, the strongest interaction will be with the oxygen ions in the surface [5]. Therefore in this section we will focus on the tip interaction with the MgO surface above oxygen ions only. However, we should note that our conclusions will hold for other surface sites characterized by similar adsorption energies. Fig. 6 shows how the force on different metal tips varies as a function of tip–surface separation over an oxygen ion in the MgO surface. For the Pd tip the force increases very smoothly as the tip–surface separation decreases, to a maximum of 1.19 eV/Å at 2.8 Å. At this distance the oxygen ion displaces by only 0.05 Å. Beyond this point the tip starts to feel a repulsive force from the surface. The force behaviour for the Cu tip is very similar to that of the Pd tip, but as expected the interaction is slightly stronger. The force increases smoothly to a maximum of 1.89 eV/Å at 2.6 Å and at this distance the oxygen ion displaces by only 0.11 Å. Again beyond this point the tip begins to be repelled by the surface. For these relatively inert tips the displacements of the surface ions are not significant and the difference in displacements between sites with different spin orientation should be very small. The Na tip repeats this smooth behaviour with an increase in overall force to a maximum of 2.49 eV/Å at 2.6 Å and a displacement of oxygen by 0.20 Å.

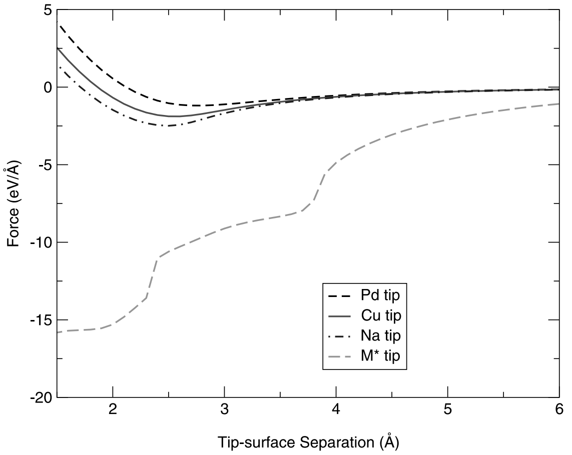

Fig. 6. Force on the tip as a function of tip–surface separation for different metal tips over an oxygen ion in the MgO surface. Tip–surface separation is measured with respect to the equilibrium position of the oxygen ion without interaction with the tip.

The force curve for the strongly interacting M* tip is very different to the previous tips. Although initially the curve is smooth, the force is already much larger than for the other tips. At 3.8 Å there is an abrupt jump in the force, from 5.6 to 7.3 eV/Å. This is caused by displacement of the oxygen ion by 0.8 Å towards the tip. The displacement remains fairly constant until, at a tip–surface separation of 3.4 Å, the tip and oxygen ion are only separated by 2.6 Å. After this point the force curve is smooth until at 2.4 Å there is another jump. Here the tip is so close to the surface that oxygen ions other than the one directly under the tip start to jump. However, the ion jump at 3.8 Å is of more relevance to this discussion, since it indicates the closest tip–surface separation for NC-SFM scanning with a metal tip of M* character.

5. Discussion

This study demonstrated that in principle it should be possible to measure the difference in interaction of a tip covered by spin-polarized atoms over spin up and spin down Ni ions in the NiO surface using NC-SFM. Using a spin-polarized hydrogen atom, the theoretical model predicts that the difference in force would produce a measurable frequency change at tip–surface separations of less than 3.75 Å. Since H was very inert to the NiO surface, this distance should be considered as the pure exchange force limit for a monatomic tip. For more chemically reactive tips, the real limiting factor in the measurement is the point at which ion instabilities begin. For example, the strongly interacting M* tip induced a jump of the oxygen ion at a tip–surface separation of 3.8 Å. This is before the exchange force limit and tips with this strength of interaction could not image the difference in force over opposite spin Ni ions. We should note that the calculated tip–surface distances discussed above serve just as indicators as there is no reliable way of measuring them experimentally. They are, however, within the range of distances for which a semi-quantitative agreement between the predicted and experimental images has been achieved before [11,35]. Therefore we believe that the adsorption energies shown in Table 1 could serve as useful criteria for choosing the tip material and analyzing the experimental images.

Our results imply that a successful experimental attempt to detect the exchange force must use a tip that is only weakly chemically interacting with the magnetic oxide surface. At present most experimental set-ups favour iron coated tips for detecting the exchange force, but there is evidence that there is a strong interaction between Fe and oxygen in oxide surfaces [5], such as alumina [36]. Experiments demonstrate that Fe transfers charge to the surface to form the Fe^{2+} and is then adsorbed on oxygen sites. This implies that ion jumps may prevent imaging of the exchange force with an iron tip. This study suggests that a more inert material similar to copper would allow tip advancement closer to the surface without instabilities, greatly increasing the ease of measuring the exchange force. The weakness of interaction also serves to reduce contrast in images due to microscopic forces, making it easier to see any differences in contrast due to the exchange force.

The extreme sensitivity of the low-temperature NC-SFM means that it can atomically resolve the surface via microscopic forces at distances much farther than normal NC-SFM. The atomic contrast in frequency change predicted by modelling of the CaF_2 surface [11] was still about 0.2 Hz at 5.0 Å, so a low-temperature NC-SFM could potentially measure atomic contrast at tip–surface separations much greater than this. This is too far for the difference in exchange force over spin up and spin down Ni ions to be measured, and in real low-temperature NC-SFM experiments atomic resolution of the difference in microscopic force over O and Ni ions will be achieved before it is possible to measure the difference in exchange force over Ni ions. Successful imaging of the exchange force will require first achieving atomic resolution on the surface of NiO, at distances where opposite spin Ni ions appear identical in images. Then the frequency change should be gradually increased to reduce further the shortest tip–surface separation until the exchange force can be measured. This procedure is extremely difficult, but has already been achieved with room-temperature NC-SFM techniques on the CaF_2 surface [35].

Another problem for imaging of the exchange force, is that it is not obvious which sub-lattice in the NiO surface will be imaged as bright and therefore it is impossible to identify the atom under the tip. Although most metal tips should interact more strongly with the oxygen ions, the study of Na showed that this is not always the case. In light of this, experimentally it would be better to produce frequency change vs. distance curves directly over the whole surface unit cell, so-called force spectroscopy [6]. This would be much more thorough way of analyzing the difference in force, rather than trying to tell if certain atoms are 'brighter' in an image. The resultant force map can be easily compared directly with theory to interpret the image and see if the exchange force plays a role.

In summary, we have demonstrated that the magnitude of the difference in exchange force over opposite spin Ni ions in the NiO surface could be sufficient to produce a measurable change in cantilever oscillation frequency in a low-temperature NC-SFM experiment. The probability of the surface ion instabilities preventing stable imaging and causing tip contamination is directly determined by the strength of chemical interaction between tip and surface. Therefore greatest success should be achieved with tips coated in metals that are weakly interacting with magnetic surface.

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