Crystallographic dependence of recoiled O⁻-ion fractions from Ni{100}c(2×2)-O and NiO{100} surfaces

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The negative-ion fractions of oxygen directly recoiled from a Ni $\{100\}c(2\times2)$ -O and a NiO $\{100\}$ surface have been measured as a function of the crystal azimuthal angle and the recoiled atom exit trajectory from the surface. The data exhibit a pronounced angular dependence of the ion fractions, i.e., the recoiled O⁻ ion survival probability depends on both its perpendicular velocity and the distance between the recoiled O⁻ and the chemisorbed O atoms and Ni substrate atoms. A theoretical analysis of the data suggests that at steep exit angles, the angular dependence of the ion fraction is dominated by the lateral dependence of the survival probability of a negative-ion state oriented perpendicular to the surface. At grazing exit angles, the angular structure of the negative-ion fraction is due to the lateral dependence of the probability of formation of negative-ion states oriented along the surface. These combined experimental and theoretical results for charge transfer provide a detailed microscopic map of the local electron tunneling rates between an individual atom and the surface.

I. INTRODUCTION

The energies and lifetimes of excited states as well as the electronic charges of atoms and molecules at or near metal surfaces are controlling factors in many dynamical phenomena. For example, electrons or photons can stimulate desorption of surface atoms if electronically excited repulsive states are localized and sufficiently long lived.¹ The angular, velocity, charge, and electronic state distributions of sputtered and scattered particles depend strongly on the lifetimes of the electronic states.^{2,3} The lifetimes of excited states contribute to the broadening of adsorption peaks⁴ in the spectroscopy of adsorbed species. In the conventional interpretation of chargetransfer data between atoms and surfaces, it is assumed that charge transfer occurs at such large atom-surface distances that the surface structure is not a significant perturbation.⁵ Several groups have recently performed experiments on impurity-covered surfaces that have shown that the lateral corrugation of the surface potential must be included for proper interpretation of the data.⁶⁻⁸ Theoretical studies have subsequently verified that both the tunneling rates and energy shifts can be strongly influenced locally by impurities coadsorbed on a surface.

Although of fundamental importance for the understanding of catalytic promotion and poisoning phenomena,¹⁰ surface reactivity, and ion-sputtering and ionscattering processes, relatively little has been learned about the spatial dependence of atom-surface electronic tunneling rates from ion-scattering experiments. The reason for this is that the lateral dependence of chargetransfer probabilities is difficult to measure directly using ion-surface scattering techniques since the width of the ion beam is always much larger than the dimension of a surface unit cell. A direct method of studying the spatial dependence of charge-transfer probabilities at keV energies with atomic-scale resolution is developed herein using the direct recoiling method of the technique of time-of-flight scattering and recoiling spectrometry (TOF-SARS).¹¹

This paper presents a detailed investigation of the negative-ion fraction of oxygen directly recoiled¹² from a Ni $\{100\}c(2\times 2)$ -O and a NiO $\{100\}$ surface. These O⁻ ion fractions have been measured as a function of the crystal azimuthal angle and the recoil atom exit trajectory from the surface. The data show that there is a strong angular dependence of the charge-transfer probabilities between an atom and the surface. A theoretical model involving the complex scaling method¹³ has been used to calculate the energy shifts and broadening of the O⁻ states and the charge exchange probabilities between the atom on its exit trajectory and the surface. These combined experimental and theoretical results for charge transfer provide a detailed microscopic map of the local electron tunneling rates between an individual atom and the surface. This information has direct relevance for the microscopic understanding of the reactivity of surfaces.

II. EXPERIMENT

A. TOF-SARS technique

The TOF-SARS technique has been detailed in several previous publications.^{11,12,14} In short, it consists of bombarding a sample with keV rare-gas ions and detecting the scattered and recoiled particles. The instrumental details employed are as follows. A 4-keV Ar⁺ beam is

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pulsed onto the sample at a 30-kHz rate, with a 30-ns pulse width, and an average current density of 0.1 nA/mm^2 . The scattered and recoiled particles are velocity analyzed through a 152-cm-long time-of-flight drift tube and both the neutral and charged particles are detected with a channel electron multiplier. The signal is amplified, discriminated, and fed to the stop input of a time-to-amplitude converter (the start input being provided by the pulse generator). The signal is then analyzed with a multichannel pulse height analyzer and displayed as particle distribution versus time of flight. The scattered and recoiled intensities are obtained by integrating narrow time windows under the corresponding TOF peaks.

The recoiled O^- ion fractions (Y) were determined by collecting the TOF spectra of neutrals (N) and ions (I)simultaneously using an acceleration lens to temporally separate the N and I particles. A voltage of +4 kV on the acceleration tube provided adequate separation of the recoiled O^- and O^0 . Using different acceleration voltages, it was determined that most of the ions were O⁻; the ion fraction of positive and doubly charged negative oxygen ions was < 1%. Ion fractions were calculated as Y = I/(N+I) with an error of <2%. Since the acceleration tube focuses the ions and not the neutrals, the intensities of the recoiled O^- and O^0 peaks must be calibrated. Calibration was achieved by measuring the total recoiled intensity (N+I) with all elements along the flight path grounded and then (1) by using a high positive voltage on the acceleration tube to accelerate the O^- or (2) by using a high voltage on a deflector plate to deflect the ions; similar results were obtained by either method. Oxygen atoms that are directly recoiled¹² into $\phi = 41^{\circ}$ by 4-keV Ar⁺ have an energy of ≈ 1.86 keV; in this energy range, the detector response to both N and I particles is similar.12

B. Sample preparation

The Ni{100} crystal was prepared by polishing with consecutively finer diamond pastes, with the final polishing using 0.05- μ m alumina. The crystal was adjusted by laser reflection such that the uncertainty in the incident angle α over an azimuthal rotation of 135° was <0.3°. The surface was cleaned in the UHV chamber by repeated cycles of 2-keV Ar⁺ sputtering at ≈ 500 °C followed by annealing at ≈ 600 °C. No contaminants were detectable by either TOF direct recoiling or Auger-electron [using low-energy electron-diffraction spectroscopy (LEED) optics]. A sharp (1×1) LEED pattern was obtained after annealing the clean surface. This pattern was used for an approximate azimuthal alignment of the crystal. An azimuthal alignment of $<\pm1^{\circ}$ was obtained from the azimuthal pattern of 4-keV Ne⁺ scattering.

A sharp $c(2\times 2)$ -O LEED pattern corresponding to chemisorbed oxygen was obtained after roomtemperature exposure to 60-L O₂. The $c(2\times 2)$ -O structure has been thoroughly studied¹⁵ and it is now well accepted that the oxygen atoms are in fourfold-hollow sites and about 0.9 Å above the outermost Ni layer. A LEED pattern characteristic of a NiO surface¹⁶ was obtained after room-temperature exposure to ≈ 1200 -L O₂ and annealing to ≈ 250 °C for 10 min. The $c(2\times 2)$ -O and NiO structures are shown schematically in Fig. 1.

III. THEORY

The probability for charge transfer between an atom and a metal surface depends both on the relative position of the atomic level with respect to the Fermi energy and on the tunneling rates between the atomic state and the surface. A first-principles calculation of the energy shift broadening of atomic states outside and а Ni{100} $c(2\times 2)$ -O surface is impossible with present computational resources. A qualitative description and understanding of the experimental result can, however, be obtained from a simplified model.

The starting point is the results from a recent calculation of the energy shift and broadening of atomic negative-ion states as a function of distance outside a jellium surface.¹³ The calculation employs the complex scaling method.¹⁷ In Fig. 2, the calculated shifts $\epsilon^0(Z)$ and widths $\Gamma^{0}(Z)$ of the $O^{-}(^{2}P)$ state as a function of atom-surface separation (Z) outside a clean metal surface are plotted. The $O^{-}(^{2}P)$ state is of p character and is therefore threefold degenerate. These three states shift downward as the surface is approached. The downshift closely follows the bare surface potential. It can be seen that the m=0 state has slightly lower energy than the $m = \pm 1$ states. This is due to the larger overlap with the attractive surface potential. The two $m = \pm 1$ states oriented along the surface have lifetimes that are about one order of magnitude longer than the m = 0 state. This is primarily due to the order of magnitude greater broadening of the m=0 state as the surface is ap-



FIG. 1. Schematic diagrams of the Ni $\{100\}c(2\times 2)$ -O and NiO $\{100\}$ surfaces showing the principal crystallographic axes.



FIG. 2. Calculated energy shift (left) and broadening (right) of the $O^{-}(^{2}P)$ state as a function of distance from a jellium surface ($r_{s} = 2.67$). The solid curve refers to the m = 0 state and the dotted curve is the $m = \pm 1$ state. The energy unit is eV and the distance is Z.

proached (see Fig. 2). This face has important consequences for the survival of the negative ion. The survival probability of the $O(m = \pm 1)$ states is very large. If any of these states are formed near the surface, they will survive the outgoing trajectory. The O(m = 0) states is relatively short lived and has a low survival probability along the outgoing trajectory.

The chemisorbed oxygen layer alters the electronic properties of the surface. Chemisorption of a single O atom on metal surfaces has been studied self-consistently using local-density methods.^{9,18} A contour plot of the O-induced electrostatic potential outside a typical metal surface is shown in Fig. 3. At normal distances above the chemisorbed O, the induced one-electron potential ΔV_0^{elst} is positive, reflecting the fact that the O atom is electronegative and induces a weak dipole potential in the surface region. The Friedel oscillations induced along



FIG. 3. Induced electrostatic potential around an oxygen atom chemisorbed in its equilibrium position (Z' = -1 a.u.) on an Al jellium surface ($r_s = 2$). The jellium edge is indicated by the thick vertical line and the oxygen chemisorption position by the "+" sign. The vacuum is to the right. The units are in eV for the potential and Bohr for the distances. The solid contours have the values -0.1, -0.3, -0.5, -1.0, and -2.0 eV. The dashed contours have the values 0.01, 0.1, 0.3, 0.5, and 1.0 eV.

the surface give rise to a damped oscillating potential along the surface.

The inhomogeneity introduced by the O overlayer will induce a lateral corrugation in both the energy shift and broadening of the recoiled O^- level. At present these effects cannot be calculated rigorously. In a previous study of the energy shifts and broadening of hydrogen levels near a single impurity chemisorbed on a metal surface, it was shown that the impurity-induced shifts follow the impurity-induced electrostatic potential.⁹ A qualitative understanding of the experimental results can be obtained by taking this shift into account. To lowest order, the potential induced by the O layer can be estimated using a simple superposition of O-induced potentials,

$$V_0^{\text{elst}}(\mathbf{r}) = \sum \Delta V_0^{\text{elst}}(\mathbf{r} - \mathbf{R}) , \qquad (1)$$

where the sum is over all chemisorbed O atoms. The energy levels of the negative ion will thus be corrugated, i.e.,

$$\boldsymbol{\epsilon}_{m}(\mathbf{R}) = \boldsymbol{\epsilon}_{m}^{0}(\boldsymbol{Z}) + \boldsymbol{V}_{0}^{\text{elst}}(\mathbf{R}) .$$
⁽²⁾

In the present calculation, the use of an Al substrate rather than a Ni{100} surface for the calculation of ΔV_0^{elst} represents a minor approximation that will not significantly influence the results.

At low exit angles the recoiled O atom initially passes very close to neighboring chemisorbed O atoms. In the $\langle 100 \rangle$ direction, the O-O distances during the first two encounters with chemisorbed O atoms are 1.3 and 2.6 a.u., respectively (see Table I). During these close encounters, there is a possibility for transitions between the short-lived m=0 state and the long-lived $m=\pm 1$ states. A numerical evaluation of the matrix element for this transition,

$$V_{0,\pm 1}(\mathbf{R} - \mathbf{R}') = \int d\mathbf{r} \, \psi_0^*(\mathbf{R} - \mathbf{r}) \Delta V_0^{\text{elst}}(\mathbf{r}) \psi_{\pm 1}(\mathbf{R}' - \mathbf{r}) ,$$
(3)

TABLE I. Distance of closest approach between recoiled O⁻ and a Ni atom (R_{Ni}) and a chemisorbed O atom (R_O) along various azimuths δ for two different exit angles, β . Distances are in angstroms.

δ	Ni $\{100\}c(2\times 2)$ -O				
	β=29°		$\beta = 11^{\circ}$		
	<i>R</i> _{Ni}	Ro	<i>R</i> _{Ni}	$R_{\rm O}$	
〈100〉	1.64	1.71	1.22	0.67	
〈210〉	2.70	3.82	1.64	1.50	
〈110〉	3.53	2.41	3.12	0.95	
〈320〉	3.86	6.15	2.02	2.42	
〈310〉	5.02	5.40	3.68	2.12	

δ	NiO{100}				
	$\beta = 29^{\circ}$		$\beta = 11^{\circ}$		
	R _{Ni}	Ro	<i>R</i> _{Ni}	R _o	
〈100〉	1.00	1.99	0.39	0.78	
(210)	2.23	4.46	0.88	1.76	
(110)		1.41		0.56	
〈320〉	3.59	7.18	1.41	2.82	
(310)		3.15		1.24	

verifies that such transitions can occur with a finite probability. The present theoretical approach is, however, not adequate for more than a qualitative description of these events. The probabilities for m=0 and ± 1 transitions during a near collision between two O atoms are parameterized as

$$C_{ij}(\mathbf{R}) = C_{ij}^{0} \exp[-(\rho_{O-O}/\xi)^2] \exp[-(Z/\eta)^2], \quad (4)$$

where ρ_{O-O} is the lateral distance between a chemisorbed O and the recoiled atom. The parameters were chosen to simulate the experimental data at the exit angle of $\beta = 11^{\circ}$. In this procedure $C_{0\pm 1}^{0} = 0.005$, $\xi = 1.0$, and $\eta = 2$.

Charge transfer along the trajectory of a recoiled O atom is calculated using the coupled equations,¹⁹

$$\frac{d}{dt}n_{-1} = \Gamma_{-1} \left[-(1-f_{-1})n_{-1} + 2f_{-1} \left[1 - \sum_{m=-1}^{1} n_m \right] \right] + \sum_i C_{-1j}(n_{-1} - n_i) ,$$

$$\frac{d}{dt}n_0 = \Gamma_0 \left[-(1-f_0)n_0 + 2f_0 \left[1 - \sum_{m=-1}^{1} n_m \right] \right] + \sum_i C_{0j}(n_0 - n_i) ,$$

$$\frac{d}{dt}n_1 = \Gamma_1 \left[-(1-f_1)n_1 + 2f_1 \left[1 - \sum_{m=-1}^{1} n_m \right] \right] + \sum_i C_{1j}(n_{-1} - n_i) ,$$
(5)

where $f_m = f_{FD}[\epsilon_m(t)]$.

These coupled equations can be integrated along the different trajectories. The initial charge state of the oxygen is assumed to be $n_{-1}=0$, $n_0=1$, and $n_1=0$. Calculation assuming that the O starts as a neutral atom gives very similar results since the m=0 state would be populated immediately and the relatively low fraction of $(m = \pm 1)$ states would only contribute to a structureless background in the angular distribution of recoiled ions. This point is illustrated in Fig. 4(a), where the shift and instantaneous population of the different O levels is plotted along the $\langle 210 \rangle$ azimuth. It can be seen that the O⁻ state is formed almost immediately. Since the tunneling rate into the m = 0 state is larger than the tunneling rate into the $m = \pm 1$ states, it is predominantly the former state which is formed. After a distance of ≈ 8 a.u., the energy of the O states shifts above the Fermi level and the m=0 ions partially neutralize. The $m=\pm 1$ states are long lived and survive the exit trajectory through the surface.

In Fig. 4(b), the energy shift and instantaneous population of the O⁻(m=0) state are plotted along the $\langle 100 \rangle$ and $\langle 210 \rangle$ azimuths for an exit angle of $\beta=29^{\circ}$. Along the $\langle 210 \rangle$ trajectory, the O-O distance is long, therefore the distance between the exit trajectory and a chemisorbed O neighbor is long (Table I). As a result, the effects of the chemisorbed O atoms are relatively minor. For the trajectory along the $\langle 100 \rangle$ direction, the situation is different. Already, after a distance of 7 a.u., the recoiled O will pass above a chemisorbed O atom. The O-induced upshift of the negative-ion state of the recoiled atom enhances the neutralization rate resulting in a lower negative-ion yield for this trajectory.

In Fig. 4(c), the energy shift and instantaneous population of the recoiled atom is plotted along different azimuths for a low exit angle β . The instantaneous population varies relatively smoothly along the $\langle 210 \rangle$ azimuth. In the $\langle 100 \rangle$ direction, there is considerable structure in the population of the m=0 and ± 1 states. After a distance of ≈ 6 a.u., the recoiled O atoms are very close to their nearest O neighbor. At this point there is a finite probability for m=0 to $m=\pm 1$ conversion; it can be seen from the figure how the $m = \pm 1$ population increases at this distance. After a distance of 12 a.u., the recoiled O atom is again relatively close to a chemisorbed O atom. The conversion probability into the long-lived $m = \pm 1$ state is smaller here since the O-O distances are larger. The $m = \pm 1$ states created during the initial part of the trajectory survive the escape trajectory through the surface.

The detailed agreement between the calculated negative-ion fraction and the experimental data can be further improved by the introduction of a more realistic but phenomenological description of the shift and broadening of the negative-ion levels near the surface. In this approach, the change in the exchange-correlation po-



FIG. 4. Energy shifts (upper figures) and instantaneous populations (lower figures) of the different O⁻ levels as a function of distance traveled along the surface. The distance is measured from the initial position of the O atom on the surface. (a) Distance along the $\langle 210 \rangle$ azimuth with exit angle $\beta=29^{\circ}$. The solid line refers to the m=0 state and the dotted line refers to the $m=\pm 1$ state. (b) Distance along two different azimuths, $\langle 100 \rangle$ (solid line) and $\langle 210 \rangle$ (dashed line), with $\beta=29^{\circ}$ for the O⁻ (m=0) level. (c) Distance along two different azimuths, $\langle 100 \rangle$ and $\langle 210 \rangle$, with $\beta=11^{\circ}$. The solid line refers to the m=0 state along $\langle 100 \rangle$, and the dashed line refers to the m=0 state along $\langle 210 \rangle$.

tential induced by the oxygen layer will be taken into account. The shifts of the negative-ion levels are evaluated using first-order perturbation theory,

$$\epsilon_{m}(\mathbf{R}) = \epsilon_{m}^{0}(Z) + \int d^{3}r \,\psi_{m}^{*}(\mathbf{R} - \mathbf{r}) [V_{0}^{\text{est}}(\mathbf{r}) + V_{0}^{\text{exc}}(\mathbf{r})]\psi_{m}(\mathbf{R} - \mathbf{r}) .$$
(6)

The oxygen-induced change in the exchange-correlation potential is estimated using a linear superposition of the potential induced during chemisorption of a single oxygen atom on a metal surface,

$$V_0^{\text{exc}}(\mathbf{r}) = \sum \Delta V_0^{\text{exc}} \quad . \tag{7}$$

 ΔV_0^{exc} can be evaluated straightforwardly in the localdensity approximation,

$$\Delta V_0^{\text{exc}}(\mathbf{r}) = \mu^{\text{xc}}[n^0(z) + \Delta n_0(\mathbf{r})] - \mu^{\text{xc}}[n^0(z)] . \qquad (8)$$

In this expression, $n^{0}(z)$ is the unperturbed charge density of the jellium surface, Δn_{0} is the oxygen-induced charge density on the surface, and μ^{xc} is the exchangecorrelation potential.¹⁸ Since the oxygen atom is chemisorbed in a negative state, the induced exchangecorrelation potential will be strongly negative in its vicinity. This negative potential locally reduces the surface barrier. The tunneling rates between the recoiling oxygen and the surface will therefore be enhanced above a chemisorbed oxygen atom. This effect can qualitatively be taken into account by the introduction of a lateral corrugation of the widths Γ ,

$$\Gamma_{m}(\mathbf{R}) = \Gamma_{m}^{0}(z) \left| 1 + A \sum_{\mathbf{R}_{0}} \exp(-B\rho_{0-0}) \right| .$$
 (9)

The best fit of the experimental data is obtained using A=2 and B=1.

The theoretical approach to the description of the charge-transfer processes in this experiment is by necessity phenomenological. Due to the complexity of the problem, no first-principles calculations of the energy shift and broadening of atomic levels outside realistic metal surfaces have yet been performed. The comparison between the experimental and theoretical results will therefore focus on general features rather than details. As will be shown in the next section, the present level of theory is sufficient for reasonable agreement between theory and experiment. The development of an improved theoretical method for calculation of energy shifts and broadenings of atomic and molecular levels near corrugated surfaces is in progress.

IV. RESULTS AND DISCUSSION

A. Time-of-flight spectra

An example of a typical TOF spectrum obtained from 4-keV Ar⁺ impinging on a Ni{100} $c(2\times 2)$ -O surface with +4 keV on the acceleration tube is shown in Fig. 5. Peaks due to scattered Ar [Ar(S)] and directly recoiled O⁰ [O⁰(R)] and O⁻ [O⁻(R)] are observed. These TOF



FIG. 5. Time-of-flight spectrum for 4-keV Ar⁺ impinging on Ni{110} $c(2\times 2)$ -O. The three peaks labeled Ar(S), O(R), and O⁻(R) correspond to scattered Ar, directly recoiled O⁰, and directly recoiled and accelerated O⁻, respectively. The experimental conditions are recoiling angle $\phi = 41^{\circ}$, beam incident angle from surface $\alpha = 18^{\circ}$, and crystal azimuthal angle $\delta = 0^{\circ}$ along the $\langle 110 \rangle$ direction.

peaks are identified by application¹⁴ of the classical binary elastic collision model. Ar(S) corresponds to quasisingle scattering of Ar from Ni, i.e., the projectile experiences one large angle deflection (small impact parameter p collision) which may be preceded or followed by minor deflections. O⁰ and O⁻ correspond to oxygen atoms that are directly recoiled from a quasisingle collision of an impinging Ar^+ , i.e., small-angle deflections may precede and follow the primary close collision. The positions of the Ar(S) and O⁰(R) peaks are independent



FIG. 6. Recoiling intensity of neutrals plus ions (N+I) versus azimuthal angle δ at incident angles of $\alpha = 12^{\circ}$ and 30°.



FIG. 7. Recoiling O⁻ ion-fraction plot for the Ni{100} $c(2\times 2)$ -O surface using 4-keV Ar⁺ ions and $\phi = 41^{\circ}$. The O⁻ ion fractions are plotted as a function of exit β and azimuthal δ angles.

of the incident α and azimuthal δ orientations of the sample and very close to the TOF predicted by the binary collision model, indicating that the major contributions to these peaks are from single collision events. The position of the O⁻(R) peak corresponds to the TOF of O⁻ ions accelerated through 4 keV from the energy acquired in the binary collision. The broadening of the Ar(S) peak on the long TOF side is due to multiple scattering. As described in Sec. II A, the intensity of O⁻(R) is



higher than that of $O^0(R)$ due to focusing of the ions and must be corrected according to the calibration in order to obtain ion fractions.

B. Oxygen recoiling intensities

The oxygen (N+I) recoil intensity as a function of azimuthal angle δ at two different incident angles $\alpha = 12^{\circ}$ and 30° is shown in Fig. 6. For $\alpha = 12^{\circ}$, the exit angle between the recoil trajectory and the surface is $\beta = 29^{\circ}$, therefore the observed features are due exclusively to shadowing of the primary ion along the incoming trajectory.¹¹ Three minima are observed along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 210 \rangle$, and two maxima are observed along $\langle 310 \rangle$ and $\langle 320 \rangle$. The minima are due to shadowing of O atoms by other O atoms since $\alpha = 12^{\circ}$ is smaller than the critical incident angle¹¹ α_c for O recoiled along those azimuths. The maxima occur along azimuths where interatomic spacings are relatively large and $\alpha_c < 12^{\circ}$. For $\alpha = 30^{\circ}$ or $\beta = 11^{\circ}$, the same intensity pattern is observed; however, in this case it is due exclusively to blocking¹¹



FIG. 8. Calculated negative ion fraction as a function of exit β and azimuthal δ angles for the Ni{100} $c(2 \times 2)$ -O surface. The ion velocity and orientation of the crystal are the same as in Fig. 7. (a) Calculated using $\Gamma_m^0(z)$ and $\xi_m(\mathbf{R})$ according in Eq. (2). (b) Calculated using energy shifts and broadenings according to the approximations of Eqs. (6) and (9).

FIG. 9. Experimental and calculated recoiled O⁻ ion fractions vs azimuthal angle δ for four different exit angles β for Ni{100} $c(2\times 2)$ -O. (a) Experimental. (b) Calculated using $\Gamma_m^0(z)$ and $\xi_m(\mathbf{R})$ according Eq. (2). (c) Calculated using energy shifts and broadenings according to the approximations of Eqs. (6) and (9).

along the outgoing trajectory. The azimuthal alignments of these recoil intensities indicted that the O atoms are being recoiled from the outermost surface layer.

C. O⁻ ion fractions for the $c(2 \times 2)$ -O surface

The O^- ion fractions Y were collected as a function of the Ar^+ beam incident angle to the surface α and the crystal azimuthal angle δ . The angle between the recoiling trajectory and the surface is $\beta = 41^{\circ} - \alpha$. The results are plotted in Fig. 7 as a three-dimensional surface in (β, δ) space. The theoretical ion fractions, calculated using the methods described in Sec. III, are shown in Fig. 8. Approximately 3 h of collection time was required to obtain the data in Fig. 7 with good statistics. In order to avoid ion-beam-induced effects on the surface structure, the sample was reannealed and redosed with O₂ after ion doses of 10^{13} ions/cm², i.e., $\approx 10^{-2}$ ions/surface atom. The Y values follow the general trend of increasing as the ion velocity perpendicular to the surface increases, varying from 2–10 % at low β up to 13–18 % at high β . The observed features indicate maxima and minima along



FIG. 10. Experimental and calculated recoiled O⁻ ion fractions vs exit angle β for Ni{100} $c(2\times 2)$ -O along three azimuths δ . (a) Experimental. (b) Calculated using $\Gamma_m^0(z)$ and $\xi_m(\mathbf{R})$ according to Eq. (2). (c) Calculated using energy shifts and broadenings according to the approximation of Eqs. (6) and (9).

various principal azimuths that are symmetrical about the $\langle 100 \rangle$ direction. Note that at the extreme β values used, i.e., $\beta = 11^{\circ}$ and 29°, the maxima and minima along the various azimuths are exactly reversed. This is best observed from the individual δ scans of Fig. 9 at different β values. At low β , the maxima are along the $\langle 100 \rangle$, $\langle 210 \rangle$, and $\langle 110 \rangle$ azimuths while the minima are along the $\langle 310 \rangle$ and $\langle 320 \rangle$ azimuths; these are reversed at high β .

These results can be understood from the discussion of Sec. III. When an O⁻ passes above a chemisorbed O atom, the affinity levels shift upwards. This effect reduces the survival probability of the negative-ion state as shown in Fig. 4(b). O⁻ recoiled above rows with short O spacings will therefore neutralize more rapidly than above rows with long spacings due to the short distance between the recoiling trajectory and chemisorbed O atom. This effect causes a reduction in Y for O atoms moving along O-rich rows at steep exit angles, in agreement with the experimental observations. The effect is relatively weak in the $\langle 210 \rangle$ direction, but can clearly be seen along the $\langle 100 \rangle$ and $\langle 110 \rangle$ azimuths. At small exit angles, the recoiled O atoms initially pass very close to neighboring chemisorbed O atoms. During these close encounters, there is a possibility for transitions between



FIG. 11. Experimental and calculated recoiling O⁻ ionfraction plot for the NiO{100} surface using 4-keV Ar⁺ ions and $\phi = 41^{\circ}$. The O⁻ ion fractions are plotted as a function of exit β and azimuthal δ angles. The calculated values were obtained from the parameterizations of the energy shifts and broadenings according to Eqs. (6) and (9).

the short-lived m=0 state and the more long-lived $m=\pm 1$ states. As was shown in Fig. 4(c), the $m=\pm 1$ states thus formed have a high survival probability. The angular dependence of Y at grazing exit is therefore opposite to the situation at steeper exits. At grazing exit, a high Y value is expected for trajectories along rows with short O spacings.

Features along the incident-beam direction are best observed by the individual β scans of Fig. 10. Two distinct mimima are observed along $\langle 100 \rangle$ at $\beta = 14^{\circ}$ and 20°, a single broad minimum is observed along $\langle 210 \rangle$ at $\beta = 12^{\circ}$, and two shallow minima are observed along $\langle 110 \rangle$ at $\beta = 15^{\circ}$ and 22°. The detailed agreement between the theoretical and experimental curves is not as good as for the azimuthal plots. Qualitatively, the theoretical curves show features similar to the experimental data. The increase in negative-ion yields at positions where the recoiled oxygen atom passes above chemisorbed oxygen atoms at small exit angles can clearly be seen.

D. O^- ion fractions for the NiO{100} surface

The experimental and calculated O⁻ ion fractions from the NiO{100} surface are shown as three-dimensional plots in Fig. 11, and individual δ scans are shown in Fig. 12. Unlike the case of the $c(2\times 2)$ -O surface above, where the maxima and minima in Y were reversed at extreme β values, the maxima and mimima observed in Y for NiO remain at the same δ positions for all β values.



FIG. 12. Experimental and calculated recoiled O⁻ ion fractions vs azimuthal angle δ and exit angle β for NiO{100} at two different exit angles β . (a) Experimental. (b) Calculated according to Eqs. (6) and (9).



FIG. 13. Experimental and calculated recoiled O⁻ ion fractions vs exit angle β for NiO{100} at two different azimuthal angles δ . (a) Experimental. (b) Calculated according to Eqs. (6) and (9).

The individual β scans are also changed from the previous case, as shown in Fig. 13.

The theoretical description of an O atom interacting with a NiO surface cannot be based on the arguments presented for an O atom interacting with the $c(2\times2)$ surface. The oxide surface is ionic rather than metallic. The O-O distances are too small to permit the effects of the oxygen layer to be estimated using the linear superposition approximations of Eqs. (1) and (7). A calculation of the recoiled ion fraction using energy levels and widths parameterized according to Eqs. (6) and (9) was performed (Fig. 11). Considering the approximations made, it is rather surprising that the general features of the plot agree so well with the experimental plot.

The dependence of the ion fractions on the lateral position of the recoiling trajectory and the vertical distance of the trajectory above the surface indicate that the chargetransfer mechanism between an oxygen atom and the surface is sensitive to atomic structure.

V. CONCLUSIONS

This paper has reported on the direct observation of a lateral dependence of the charge-transfer probabilities between an atom and a corrugated surface. The qualitative features of the experiment can be understood from simple general arguments. The experimental data clearly demonstrate the need for an improved understanding of how atomic energy levels shift and broaden near realistic metal surfaces. These types of measurements, combined with theoretical modeling, can provide a detailed microscopic map of the local reactivity of the surface. This information can be of crucial importance for the understanding of various impurity-induced promotion and poisoning phenomena in catalysis and electron-density maps from scanning tunneling microscopy (STM).

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