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Effects of adsorbates on charge exchange in Li⁺ ion scattering from Ni(100)

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Resonant charge transfer during the backscattering of 3.0 keV Li⁺ from hydrogen- and iodine-covered Ni(100) is probed with time-of-flight spectroscopy. Hydrogen adsorption on Ni(100) induces only a small increase of the surface work function and the neutralization probabilities for backscattered Li are not significantly affected. Iodine adsorbs with some net negative charge, so that a dipole directed into the surface is expected. Such a dipole would increase the work function thereby decreasing the neutralization probability. Iodine adsorption decreases the work function of Ni(100), however, and the neutralization probabilities for Li scattered from the iodine sites are always larger than for scattering from nickel sites. These results suggest that the local charge density associated with adsorbed iodine is not uniform. © 2003 American Vacuum Society.

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I. INTRODUCTION

Charge transfer between atomic particles and solid surfaces is of great interest from both fundamental and practical points of view. Charge exchange is important in the sense that it governs the equilibrium between gaseous and solid phases that is central to many surface chemical reactions. It is also important in surface analytical methods that employ ion beams, such as secondary ion mass spectrometry (SIMS) and ion scattering spectroscopy (ISS). Because surface adsorbates can greatly modify charge transfer probabilities,¹ their effects need to be quantified in order to obtain a comprehensive understanding of charge exchange.

Low-energy ion scattering employing alkali ions has been previously used to probe the effects of adsorbates on charge exchange. For alkali ion-surface collisions, the dominant electron exchange mechanism is resonant charge transfer (RCT).² This is because the alkali *ns* valence levels are close in energy to the surface work function of solids. When an alkali is near the surface, its ionization level overlaps the Fermi level, which enables electrons to resonantly tunnel between the ion and the solid. RCT involves only the outer shell electrons, so that the charge exchange probabilities are strongly influenced by the local electronic environment at the surface.

Several groups have studied alkali ion scattering from alkali-adsorbate covered metal surfaces,³⁻¹⁰ and the effects of alkali adsorbates on RCT are relatively well understood. Alkali adsorbates donate charge to the substrate thereby forming dipoles that are oriented away from the surface, which lower the surface work function. The decreased work function causes the neutralization probabilities of the scattered particles to increase. Furthermore, the local electrostatic potential (LEP) near the alkali adsorbates is smaller than the potential away from the adsorbate sites, particularly at low coverage. As a result, neutralization is greatly en-

hanced for particles scattered from the adsorbates sites as compared to those scattered from substrate atoms.

In contrast to the electropositive alkalis adsorbates, however, the amount of information available for ion scattering from electronegative adsorbates is minimal. This article investigates the effects of hydrogen and iodine adsorption on charge exchange during Li⁺ ion scattering from Ni(100). Both of these adsorbate species attract electrons from the substrate, and it has been shown in prior work that they are negatively charged.¹¹⁻¹⁶ The neutralization probabilities of the Li projectiles are only minimally affected by hydrogen adsorption, which is consistent with the small work function change. Although adsorbed iodine is overall negatively charged, the surface work function is actually reduced. These results suggest that the iodine adsorbates are polarized so that the effective local potential is reduced directly above the adsorbate site.

II. EXPERIMENTAL DETAILS

The Ni(100) sample was cleaned *in situ* in the ultrahigh vacuum (UHV) chamber by repeated cycles of 1 keV Ar⁺ bombardment and annealing at about 1000 K. Following this procedure, low-energy electron diffraction (LEED) displayed a sharp 1×1 pattern. The cleanliness of the surfaces was checked with Auger electron spectroscopy (AES), which indicated no evidence of carbon or oxygen impurities. The surface was reacted with atomic hydrogen by backfilling the chamber with H₂ in the presence of a hot tungsten filament located ~5 cm from the surface. The exposures, which are reported in langmuirs (1 L=10⁻⁶ Torr s), are based on the total pressure of H₂. Thus the actual exposures to atomic hydrogen are much smaller than the reported values. Iodine was deposited from a solid-state electrochemical cell based on a AgI pellet,^{17,18} with the sample at room temperature. The cell was operated at temperatures between 140 and 160 °C. After each iodine deposition, the surface composition was checked with AES, which showed no silver or oxygen impurities. The iodine exposures are reported in μA min, i.e.,

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the product of the operating current and exposure time. It is estimated that a $10 \mu\text{A min}$ exposure corresponds approximately to one I_2 molecule impinging on each surface atom. Changes in the surface work function ($\Delta\phi$) upon adsorption were determined by the energy shift of the secondary-electron cutoff measured with an electrostatic analyzer (ESA). The secondary electrons were generated by impinging a 200 eV electron beam onto the sample.

Time-of-flight (TOF) spectra were collected with equipment previously described.⁸ The 3.0 keV ${}^7\text{Li}^+$ beam had an energy spread of $<0.2\%$. The beam was deflected across a 1.0 mm^2 aperture to produce 40 ns pulses at a rate of 80 kHz. The beam was incident normal to the surface, and the scattering angle was 168° . The scattered ions and neutrals were detected by a microchannel plate (MCP) array after traveling through an electrically isolated flight tube. The total path length was 1.34 m. "Total Yield" spectra were collected with the flight tube held at ground, while "Neutrals Only" spectra were collected by placing 1500 V on the tube to deflect scattered ions. The entrance to the MCP was held at ground to ensure that ions and neutrals were collected with equal efficiency.

III. RESULTS AND DISCUSSIONS

Typical "Total Yield" and "Neutrals Only" TOF spectra are shown in Fig. 1(a) for 3.0 keV ${}^7\text{Li}^+$ backscattered from clean Ni(100)- 1×1 . The Ni single scattering peak (SSP) represents binary elastic scattering from a single surface atom, while the background arises from Li projectiles that have undergone multiple collisions. The SSPs are reasonably well resolved from the background in both spectra. TOF spectra collected from hydrogen-covered Ni(100) (not shown) are qualitatively similar to those in Fig. 1(a). Note that Li does not backscatter from hydrogen to produce a SSP because of the preferential forward scattering of Li from the lighter H atoms.

Figure 2 shows the surface work function change, $\Delta\phi$, versus H_2 exposure. The work function of clean Ni(100) is 5.22 eV.¹⁹ The work function increases as hydrogen is adsorbed, but the magnitude of the change is relatively small. The increase of the work function suggests that the adsorbed hydrogen particles are negatively charged,¹⁴ which has also been predicted by calculations^{15,16} and shown experimentally.²⁰

The neutral fractions of the singly scattered Li particles were determined by dividing the integrated area of the "Neutrals Only" SSP by that of the "Total Yield" SSP. The areas were calculated following the subtraction of a linear background (typical backgrounds are shown by dashed lines in Fig. 1). Note that the calculated neutral fraction is not very sensitive to the background subtraction procedure because the neutral fractions of the substrate SSP and the multiple scattering background underneath are close to each other.²¹ In fact, the neutral fractions calculated for the Ni SSP by taking the ratio of the neutral to total yields in a ± 20 eV window centered about the Ni SSP maximum without any

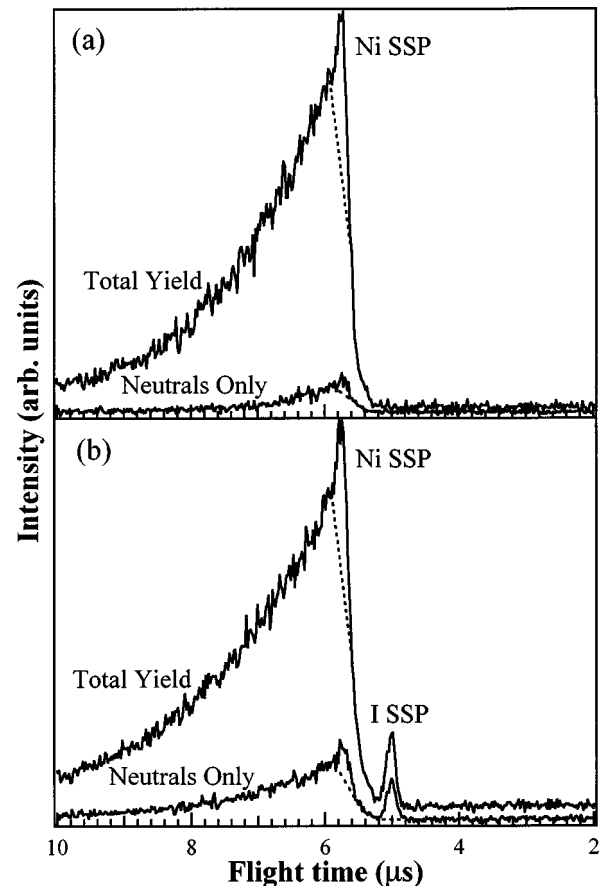


Fig. 1. TOF spectra of the total and neutral yields collected at a 168° scattering angle for normally incident 3.0 keV ${}^7\text{Li}^+$ scattered from (a) clean Ni(100)- 1×1 , and (b) iodine-covered Ni(100).

background subtraction fall within the uncertainty range of the values determined with background subtraction.

The neutral fraction data is plotted in Fig. 3 as a function of H-induced work function change. It is found that the neutralization probability of Li scattered from the Ni sites is not significantly influenced by H adsorption. For Li^+ ion scatter-

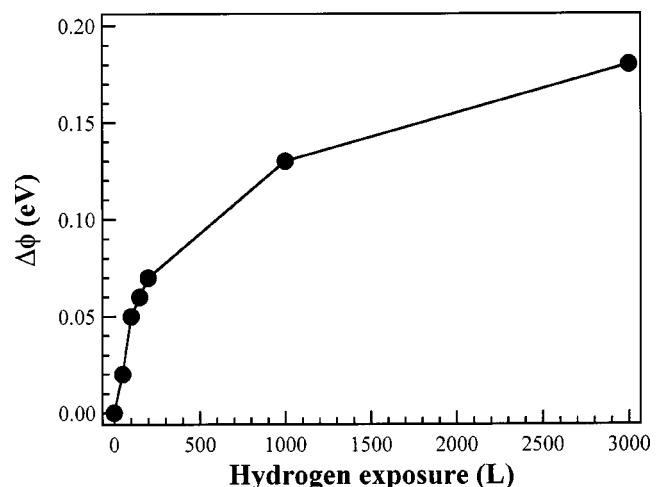


Fig. 2. Work function changes ($\Delta\phi$) of Ni(100) with respect to hydrogen exposure.

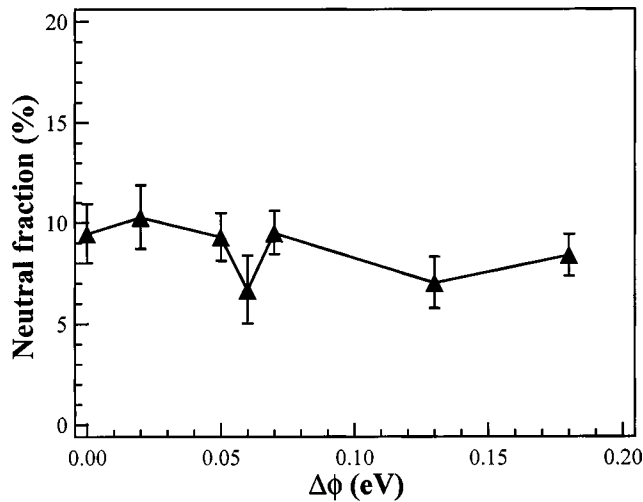


FIG. 3. Neutral fraction of Li singly scattered from Ni(100) as a function of hydrogen-induced work function change.

ing from metal surfaces, an increase of the work function is generally expected to lead to a decrease of the neutral fraction. Since the actual H-induced work function change is small, however, the related effect appears to be smaller than or equivalent to the experimental uncertainty in the neutral fraction measurement itself.

Note that the relationship between the H-coverage dependence of the neutral fraction and the surface work function on Ni(100) is in contrast to H-adsorption on Si surfaces.²² Clean Si has surface dangling-bond states close in energy to the Li ionization level. These surface states are the main source of electrons for charge transfer in scattering from Si. Hydrogen adsorption terminates these unsaturated surface dangling bonds and eliminates the associated surface electronic states. As a result, the neutral fraction of the scattered Li ions decreases considerably upon hydrogenation of Si surfaces.

The ability of neutral fraction measurements to distinguish between sites with differing LEP was previously demonstrated in ${}^7\text{Li}^+$ scattering from Al(100)^{7,8} and Ni(100)²¹ in the presence of alkali adsorbates. There is a clear difference in the neutral fractions collected from adsorbate and substrate sites, especially at low alkali coverage. Unlike alkali atoms, hydrogen is slightly negatively charged, so it is expected that the LEP change induced by hydrogen adsorption would be opposite from that induced by alkali adsorption. Because of the absence of a hydrogen SSP in the backscattering TOF spectra, however, neutral fractions for scattering from hydrogen sites cannot be obtained. More massive adsorbates, on the other hand, can be used to reveal the local electronic environment around a negatively charged adsorbate.

In this vein, we studied the neutralization probability for Li^+ backscattered from iodine adsorbed on Ni(100). Typical TOF spectra are shown in Fig. 1(b). In all the spectra collected, the Ni SSPs and I SSPs are well separated so that the neutral fractions can be independently monitored for single scattering from the different sites. Note that background sub-

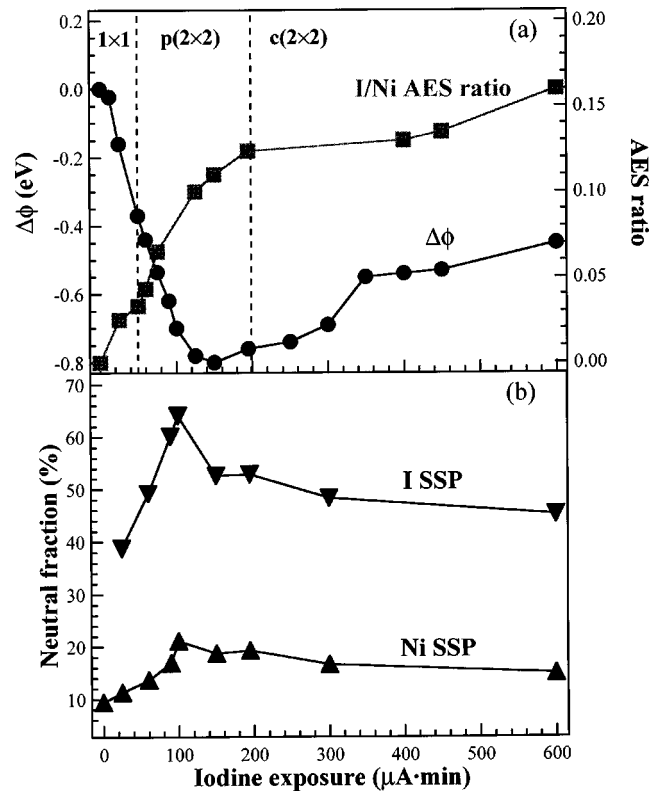


FIG. 4. (a) Iodine-induced work function change ($\Delta\phi$) of Ni(100) and the ratio of the I(MNN)/Ni(LMM) AES peaks as functions of iodine exposure. (b) Neutral fractions of the iodine and nickel SSPs as functions of iodine exposure.

traction was straightforward for the I SSPs because of their simple shape and the absence of any significant multiple scattering signal underneath the peaks.

Figure 4(a) shows the I-induced work function change and the ratio of the AES I(MNN)/Ni(LMM) peaks as functions of iodine exposure on Ni(100). The AES data show that the iodine coverage increases rapidly for exposures below 200 $\mu\text{A min}$, but the increase slows for higher exposures. The work function decreases with increasing iodine exposure up to $\sim 150 \mu\text{A min}$, after which it begins to increase slightly. Nevertheless, the work function change is always negative with respect to clean Ni(100), regardless of the iodine coverage. This is unexpected considering that the iodine adsorbate is negatively charged.¹¹⁻¹³ Such an anomalous change in the work function has also been found, however, for halogen adsorption on other transition-metal surfaces, such as W (Refs. 23 and 24) and Ta (Ref. 25). The origin of this phenomenon is still unclear, especially on the atomic scale.

LEED suggests that the behavior of the work function in different exposure regimes is surface-structure related. When the iodine exposure is below 50 $\mu\text{A min}$, no significant change in the substrate (1×1) LEED pattern is observed. At an iodine exposure of about 100 $\mu\text{A min}$, a sharp $p(2\times 2)$ pattern is obtained. As the iodine exposure is increased to 250 $\mu\text{A min}$, the $p(2\times 2)$ pattern has clearly transformed into a $c(2\times 2)$ pattern. Associated with changes in the ad-

sorbate coverage, the iodine adatoms may occupy different surface sites, which leads to the different LEED patterns and the detailed shape of the work function curve, as seen in Fig. 4. Note that early studies by Jones and Woodruff^{26,27} also reported a $c(2 \times 2)$ structure for I/Ni(100), but a $p(2 \times 2)$ phase was not observed. In their experiments, iodine exposure was achieved by introducing pure I₂ gas into the chamber, however, which may have resulted in larger coverages than were realized here.

The neutral fractions of the I and Ni SSPs are shown in Fig. 4(b) as a function of I₂ exposure. As iodine is initially adsorbed, the I and Ni SSP neutral fractions both increase, reaching maximum values following an exposure of about 100 μ A min. The neutral fractions then begin to decrease and become nearly constant following larger iodine exposures. It is noteworthy that the shape of the work function curves are roughly “mirrored” in the neutral fraction curves. This is consistent with the prediction of the RCT model that the neutral fraction should change in the opposite direction as the work function.²

A striking feature of Fig. 4(b), however, is that the I SSP neutral fractions are considerably larger than those of the Ni SSP over the entire iodine coverage range. Based on a simple consideration of the surface charge distribution, the negatively charged iodine atom, along with its image charge in the substrate, should create a dipole that points inward. Because of the dipole, the potential should be higher in the vicinity of the adsorbate as compared to a bare metal site. But the large neutral fractions of the I SSP suggest, however, that the LEP is actually lower at iodine sites.

Although it may appear straightforward to explain the large neutral fraction by considering only the increased electron density at the iodine site, this does not determine the RCT neutralization probability. The occupied iodine states lie at about 5.5 eV below the Fermi level,²⁸ so that resonant electron transfer to the Li ionization level is rather unlikely. In fact, in all cases of charge transfer to alkalis, the electrons originate from the metal valence band. It is actually the position of the Fermi level, i.e., the local potential, at the halogen site that makes the dramatic difference in the neutralization rate, rather than the total electron density.

In order to account for the experimental results within a coherent framework, it is apparent that the simple dipole model must be modified. Based on density-functional-theory calculations, Wu and Klepeis²⁹ proposed a three-dipole-layer model for halogen adsorption on transition-metal surfaces that is able to match previous experimental observations without invoking complex adsorbate phases. The model is based on the notion that the charge distribution of the adatom has internal structure because the halogen atom is polarizable. Their results showed that the halogen-induced charge redistribution could be modeled by the sum of three dipole layers. The uppermost dipole layer results from the polarization of the halogen adatom by the field of the metallic surface and points outwards. The second is due to the electronic charge transfer from the metal to the adsorbate. The third arises from the effect of Smoluchowski smoothing in the

near-surface region of the metal. The overall work function change is thus determined by the competition between the negative contributions of the first and third dipoles and the positive contribution of the second dipole.

This three-dipole-layer model is adopted here to explain our results for charge transfer in ⁷Li⁺ ion scattering from iodine-adsorbed Ni. Recall that the ⁷Li⁺ ion collides with the surface directly on top and the scattered particle exits nearly perpendicularly, i.e., the scattered particle “feels” the potential directly above the target atom. Since the polarized iodine atom has an attractive potential at its very top, the LEP at that point is lower than it is above a Ni surface atom. The attractive potential lowers the atomic energy level of the projectile, thereby increasing the neutralization probability. The differences between the iodine and nickel sites thus lie in the fact that a free electron is more easily transferred to the projectile when it is above an iodine atom than when it is above a substrate atom due to the reduced potential. As a result, the I SSP neutral fractions are larger than those of the Ni SSP. Note that the neutral fraction for Li projectiles scattered from iodine adsorbates on Fe(100) decreases for grazing exit trajectories.³⁰ This is because the repulsive potential induced by the electronegative iodine and its image charge, i.e., the second dipole, becomes more prevalent when the charge transfer occurs away from the center of the iodine atom.

Our results show that the effects of iodine adsorbates on ion-surface charge transfer are twofold. First, iodine adsorption induces inhomogeneity in the LEP, i.e., a difference in the effective local work function between the I and Ni sites. This effect is reflected in the very different neutralization probabilities of Li projectile scattered from I or Ni. Second, the LEP at a specific surface sites changes with respect to the iodine coverage. On average, these changes appear as the macroscopic work function change. This average effect is reflected in the small changes of each individual neutral fraction curve with iodine coverage, as seen in Fig. 4, which “mirror” the shape of the work function curve.

IV. CONCLUSIONS

The neutralization probabilities of 3.0 keV Li⁺ ions scattered from the hydrogen- and iodine-covered Ni(100) surface were measured with TOF spectroscopy. Hydrogen adsorption on Ni(100) induces only a small increase of surface work function, hence the neutral fraction for the backscattered Li particles does not change significantly. In contrast, iodine adsorption decreases the work function of Ni(100). Although the fine structure in the iodine-coverage dependence of the neutral fractions can be directly related to work function changes, unexpected high neutralization probabilities are found for Li scattered directly from iodine sites. The lower electrostatic potential above the iodine adsorbates is explained by a large polarization effect within the iodine itself. Our results show that the effect of negatively charged adsorbates on charge exchange in alkali ion scattering reflects the differences in LEP above particular scattering sites. Similar results for Li scattering from halogen adsorbates are also

found with iodine- and bromine-covered Fe(100) and Fe(110) surfaces, which will be discussed in detail in upcoming publications.³⁰

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