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Temporary negative-ion resonances in the NiO(100) high-resolution electron-energy-loss spectrum

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The NiO(100) Fuchs-Kliwer phonon spectrum has been investigated by high-resolution electron-energy-loss spectroscopy (HREELS) at beam energies of 0.8–17 eV and the intensity distribution of the phonons relative to the dielectric properties of the NiO substrate has been considered. Over most of the range, the spectrum is well behaved, with the single-loss phonon energy at ~ 70.5 meV and multiple excitations decreasing according to the predicted Poisson distribution. At 5.0-, 8.5-, and 13.5-eV primary beam energies, however, a substantial resonant enhancement in the phonon cross section is observed. The enhancement is accompanied by a shift from the Poisson intensity distribution to favor higher multiple excitations and an increased scattering away from the specular lobe. The energies correspond to maxima in the nickel oxide unfilled density of states and the resonances are assigned as temporary negative-ion states in which the electrons of the HREELS beam are trapped briefly into these levels.

I. INTRODUCTION

Electrons in a low-energy beam can be trapped into unfilled electronic states upon scattering from a solid surface with a corresponding resonant effect in the electron-energy-loss probability. We show evidence below for the formation of a temporary negative ion (TNI) at the NiO(100) surface using high-resolution electron-energy-loss spectroscopy (HREELS). While negative-ion resonances have been observed for physisorbed molecules at solid surfaces,^{1–3} very few resonances have been reported for the surface itself in the absence of molecular adsorbates.

Electron trapping by gas phase molecules is a common phenomenon and is well understood.⁴ At low pressures, molecular ions can exist for relatively long times (10^{14} – 10^{15} s) due to their electronically and collisionally isolated nature. The long lifetime aids in their detection by electron spectroscopic methods.⁵ Because of the delocalized nature of their electronic states, it was at first assumed that negative-ion lifetimes would be too short to be easily detectable in solid systems. By allowing only weak interaction between the negative-ion state and the substrate band structure, e.g., as is present with physisorbed molecules, it was found that TNI resonances could, indeed, be created in the condensed phase. Demuth, Schmeisser, and Avouris were among the first to detect negative-ion resonances at surfaces, using H_2 , O_2 , N_2 , and CO physisorbed on Ag films.¹ Other systems with reported TNI resonances include O_2 on niobium² and on graphite.³ More recently, TNI phenomena have been observed in chemisorbed systems. For example, TNI formation has been noted for benzene adsorbed on Pd(100),⁶ HCOO^- on Ni(110),⁷ and OH^- on NiO(100).⁸

Another way to increase the lifetime of a potential TNI state in solids is to provide a localized unoccupied state at the substrate itself. This tactic was successfully employed with $\text{UO}_2(111)$, where a TNI resonance could be formed by trapping a low-energy electron into unoccupied $5f$ levels.⁹ Since NiO is a charge-transfer insulator, the availa-

bility of highly localized nickel-derived states^{10,11} may also contribute to the TNI scattering mechanism proposed for OH^- on NiO(100) observed in the HREEL spectrum.⁷ Its midrange band gap of 4.3 eV (Ref. 12) allows NiO to be studied by HREELS with a minimum loss of resolution.¹³ The nickel oxide HREEL spectrum shows intense Fuchs-Kliwer phonons, as is typical of metal oxides in general,¹⁴ due to the strong dipolar coupling of lattice ion displacements with the electron beam. Theory describing the expected behavior of Fuchs-Kliwer phonon intensities as a function of primary electron-beam energy is well developed,¹⁵ and TNI formation can easily be identified by analysis of the phonon spectrum.

We report HREEL spectra for adsorbate-free NiO(100) and analyze the dielectric response of the Fuchs-Kliwer phonons to an electron beam with energies ranging from 0.8–17 eV. Our studies indicate that, while the predicted dielectric response is observed over most of the energy range, deviations occur at energies corresponding to the resonant population of unfilled states. The electrons are temporarily trapped into the unoccupied states, thus increasing their lifetime in the vicinity of the NiO surface and allowing greater interaction with the Fuchs-Kliwer phonon modes.

II. EXPERIMENT

All measurements were carried out at $\leq 4 \times 10^{-8}$ Pa in a 40-L UHV stainless-steel bell jar pumped with a 220 L/s ion pump. The system is equipped with a double-pass cylindrical mirror analyzer (CMA) having Auger and x-ray photoelectron spectroscopic (XPS) capabilities, an ion bombardment gun, and a nonrotatable single-pass 127° sector HREEL spectrometer.¹⁶ The NiO(100) single crystal¹⁷ was cleaned by cycles of argon-ion sputtering, followed by oxygen and vacuum annealing in a procedure previously shown to produce a well-defined surface.¹⁸ A 2-kV Ar^+ beam was used in sputtering to give an ion

current of $10 \mu\text{A}/\text{cm}^2$, as measured at the crystal surface. Oxygen annealing, necessary to replace the oxygen preferentially sputtered from the lattice, was performed at a pressure of 7×10^{-5} Pa and a temperature of 773 K. A final 10-min vacuum anneal was performed at 773 K to drive unincorporated oxygen atoms from the surface. Cleaning cycles were continued until the XPS yielded well-defined peaks characteristic of NiO, HREELS showed an intense Fuchs-Kliwer phonon at -70.5 meV and a well-developed series of multiple excitations in proper intensity distribution, low-energy electron diffraction (LEED) was obtained with well-defined NiO(100) symmetry and low background, and Auger spectra contained no evidence of contamination.

The HREEL spectrometer was operated with a current of 1×10^{-10} A measured at the sample surface. Beam energies were varied from 0.8–17.0 eV. All spectra were taken in the specular mode at a scattering angle of 45° , unless otherwise noted. The spectrometer has an acceptance angle of $\approx 6^\circ$. The resolution obtained on NiO(100) ranged from 12.5 to 16.2 meV (100 – 130 cm^{-1}) due to semiconducting nature of the sample at 300 K, although absolute resolutions of a factor of 2–3 lower are obtainable for conducting substrates.

III. NiO(100) PHONON SPECTRUM

A. Harmonic behavior for nonresonant energies

A typical NiO(100) phonon spectrum, obtained with a primary beam energy of 2.8 eV, is shown in Fig. 1. The

FIG. 1. Typical Fuchs-Kliwer phonon spectrum of NiO(100) with (a) -70.5 -meV single-loss phonon and associated multiple excitations, and (b) spectrum fit by tailing function.

spectrum is comparable to that reported previously for single-crystal NiO (Refs. 13 and 19) and thin nickel oxide films,²⁰ and yields a single-loss phonon at -70.5 meV with additional phonon loss structure at integral multiples to higher loss energies. A phonon gain peak is also detectable at $+70.5$ meV with the loss-to-gain intensity ratio in agreement with that predicted from Boltzmann statistics for the 300-K substrate temperature.²¹ The NiO(100) HREEL spectra exhibit an asymmetry or “tailing” to the higher loss side of the elastic and phonon peaks typical in shape and magnitude of other reported semiconductor HREEL spectra.²² In order to quantify the phonon intensities, the spectra have been fit with an exponential tailing function, as demonstrated for the single-loss phonon peak in Fig. 1(b). The tailing function, which is commonly used in XPS and Auger peak-shape analysis,²³ has been previously described in its present role of fitting HREEL phonon spectra.¹³

The very intense multiple excitations of the -70.5 -meV single-loss phonon are a result of the strong dipolar interaction between the Fuchs-Kliwer phonon mode and the HREEL electron, increasing the probability that the electron will lose energy to the phonon mode on more than one occasion on its approach to and after back-scattering from the NiO(100) surface. Since oppositely charged ion cores are alternately stacked above each other in the NiO rocksalt structure, their vibrationally excited dipole moments add to produce strong electric fields upon low-energy inelastic electron scattering. The field extends for hundreds of angstroms into the vacuum above the surface,¹⁵ and increases the distance over which the electron has a significant probability of interacting with the phonon mode.

In the assumption of harmonic lattice oscillations, dielectric theory predicts that the intensities of the multiple-loss phonon spectrum, $s(\omega)$, decrease in a Poisson distribution:²⁴

$$s(\omega) = i(\omega) \otimes \left[\delta(0) + p(\omega) + \frac{p(\omega) \otimes p(\omega)}{2!} + \frac{p(\omega) \otimes p(\omega) \otimes p(\omega)}{3!} + \dots \right]. \quad (1)$$

In Eq. (1), $p(\omega)$ is the single-loss phonon intensity, $i(\omega)$ is the instrument response function, $\delta(0)$ is the elastically scattered, or zero loss, peak, and $\otimes$ represents a mathematical convolution of the $p(\omega)$ phonon excitations. In modeling the electron-phonon interaction, dielectric theory assumes

$$\text{KE}_{\text{electron}} \gg \hbar\omega_{sp}, \quad (2)$$

where KE is the kinetic energy of the electron, and ω_{sp} is the frequency of the Fuchs-Kliwer optical phonons. This condition is satisfied for the greater part of the energy range (3–17 eV) used to acquire the HREEL spectra, although at low energies (≤ 2 eV) a divergence from predicted behavior is seen. Discussion of this effect is given below.

A common method of demonstrating the harmonic nature of the phonon oscillations^{25–27} is to show that the

multiple-phonon excitations follow the predicted Poisson distribution of Eq. (1). By adjusting the intensity of each n -multiple excitation of the Fuchs-Kliwer phonon for the decrease in $n!$, the corrected intensities can be plotted as a function of n to yield a straight line. Figure 2 shows the results of this plot for the NiO(100) HREEL phonon data for a progression of primary beam energies. As expected, linear results are obtained for all energies shown. The slopes become steeper with increase in electron energy due to the shorter residence time in the vicinity of the sample surface for the more energetic electron beams.

B. Dipolar response of NiO(100)

If dipolar scattering mechanism are operative, the probability of creating a surface phonon by inelastic electron scattering will be a known function of the electron momentum component parallel to the sample surface. For a macroscopically thick crystal, the probability is¹⁵

$$\frac{I_{\text{inel}}}{I_0} \propto (k \cos \theta)^{-1} \quad (3)$$

where k is the electron momentum and θ is the angle of the incoming HREEL beam with respect to the surface normal. The probability, expressed as a ratio of the intensity of the phonon single-loss peak, I_{inel} , to that of the elastic peak, I_0 , is therefore inversely proportional to $E_0^{1/2}$, where E_0 is the primary beam energy. For excitations that result from adsorbate-contaminated or otherwise modified thin films, a dependence of E_0^{-1} is obtained instead, due to limitations on the amount of electron momentum transfer that can occur in the thin layer giving rise to the phonon loss peak.¹⁵ The predicted energy dependence provides both a convenient method of distinguishing between intrinsic and extrinsic contributions to the phonon loss intensity, and a measure of the dielectric response of the HREELS scattering. In either thin-film

FIG. 2. Poisson distribution of the NiO(100) phonon spectrum at a series of nonresonant electron-beam energies.

or semi-infinite slab oxides, I_{inel}/I_0 is expected to decrease with beam energy if the dominant contribution to the electron loss scattering is through electron-dipole interactions.

A log plot of I_{inel}/I_0 should be a linear function of the beam energy with a negative slope between $-\frac{1}{2}$ and -1 , depending upon the thickness of the region giving rise to the phonon spectrum. The majority of the "bulk" oxide substrates studied to date display a linear dependence on $\log_e(E_0)$ and a slope that closely approximates the $-\frac{1}{2}$ value of the intrinsic surface.^{26,27} Figure 3 shows the data obtained for NiO(100) as discrete points with a line illustrating the intrinsic $E_0^{-1/2}$ behavior. While a linear "background" closely parallels the expected $E_0^{-1/2}$ slope, it is apparent that the data show large deviations from linearity at 5.0, 8.5, and 13.5 eV. The resonant increase in intensity observed at these energies indicates a departure from the simple electron-phonon dipolar interaction through the opening of new contributions to the scattering mechanism. If the obviously deviant increases in intensity are neglected, linear regression on the remainder of values yields a slope of -0.4 , within error of the $-\frac{1}{2}$ value, for the background intensity decrease.

At the lowest primary beam energies, below approximately 2 eV, the data also diverge from predicted $E^{-1/2}$ behavior. This divergence may partially be due to a breakdown of the dielectric assumption that the beam energy is much greater than the energy of the mode being probed. However, it also contains a large artifactual component due to charging effects felt by the less energetic electron beams. Spectra in this energy range show a significant decrease in resolution and other signs of surface charging. In addition, both elastic peak and phonon intensities are lower than predicted from extrapolation of higher-energy data.

The expected intensity distribution between the elastic and phonon peaks can be calculated absolutely from dipolar theory using the known dielectric constants of nickel oxide. The phonon intensity ratio I_{inel}/I_0 is²⁸

$$\frac{I_{\text{inel}}}{I_0} = \frac{\exp(\hbar\omega_{sp}/kT)}{\exp(\hbar\omega_{sp}/kT) - 1} \frac{\pi e^2}{2\hbar v_{\perp}} \left[\frac{\epsilon_s - 1}{\epsilon_s + 1} - \frac{\epsilon_{\text{hf}} - 1}{\epsilon_{\text{hf}} + 1} \right], \quad (4)$$

FIG. 3. $E_0^{-1/2}$ dependence of phonon/elastic intensity ratio.

FIG. 4. Comparison of calculated phonon/elastic peak intensities with experimental values.

where $v_{\perp}$ is the velocity of the electron normal to the surface, ω_{sp} is the frequency of the Fuchs-Kliwer phonon, and ϵ_s and ϵ_{hf} are the static and high-frequency dielectric constants, respectively.^{14,29,30} Figure 4 compares the experimental data with those calculated from Eq. (4). The plot emphasizes the general agreement of the data with the expected dipolar distribution, when exceptions are made for the 5.0-, 8.5-, and 13.5-eV resonant peaks. Identical sloping behavior is obtained for both the calculated and measured intensities, and it is clear that the dielectric response of the material well describes the "background" intensity of the Fuchs-Kliwer phonons upon which the 5.0-, 8.5-, and 13.5-eV resonant peaks are superimposed.

The experimental data are offset slightly from the calculated response, which could result from our inability to match exactly the tailing observed in the spectra with the simple exponential decay of the empirically derived tailing function. It has been noted,¹⁴ however, that literature values for NiO dielectric constants are perhaps less accurate than desired in analyzing Fuchs-Kliwer phonons, since predicted phonon energies are typically 3–5 % too low when compared with experimental values.

IV. TEMPORARY NEGATIVE-ION EFFECTS IN THE HREEL SPECTRUM

Over most of the energy range of Figs. 3 and 4, the NiO phonon spectrum is well represented by the dielectric description of HREELS electron-phonon interaction. However, at energies in the vicinity of 5.0, 8.5, and 13.5 eV, a significant increase in phonon intensity causes deviations from the expected $E_0^{-1/2}$ dependence. The increase is large enough to be convincingly demonstrated by a visual inspection of the HREEL phonon spectrum, as shown in Fig. 5 for spectra taken at energies above, at, and below the 5-eV major resonant peak. We propose that temporary negative-ion (TNI) resonances occur at these energies and correspond to trapping of the low-

FIG. 5. Spectra taken at beam energies of (a) 11.9, (b) 5.2, and (c) 3.5 eV. The resonant behavior is exhibited by spectrum b.

energy electrons into unoccupied valence-band states, as discussed below. Because the time that the electron spends in the near-surface region is extended by the trapping, the probability that it will interact with a surface phonon mode is proportionately increased.

The three spectra of Fig. 5 were taken under identical spectrometer settings with relative intensity scales as indicated. As can be seen, the spectrum taken in the range of the 5-eV resonance yields an anomalously high intensity for the phonon and its multiple excitations relative to the total scattered electron intensity, but a poorer total elastic plus inelastic HREELS intensity relative to the other spectra in the series. A quantitative measure of this effect is given in Fig. 6, which plots the total integrated

FIG. 6. Dependence of the elastic peak intensity on beam energy.

FIG. 7. Deviation from Poisson behavior at the resonant beam energy.

HREEL spectral intensity versus beam energy. At the TNI enhancement energies, the spectral intensity drops considerably in magnitude, indicating that TNI formation at least partially randomizes the scattering away from the dielectric lobe. Note that the phonon intensity maxima of Fig. 3 are now expected to be minima in Fig. 6, as intensity is removed from the elastic beam by increased probability of scattering into a phonon loss mode. As before, primary beam energies of ≤ 2 eV yield abnormally low intensities due to charging and other experimental artifacts.

The TNI resonance also distorts the multiple-loss phonon intensities from the Poisson distribution observed for the nonresonant beam energies, demonstrated earlier in Fig. 2. Figure 7 compares the phonon intensities at the 5-eV resonance with those of the 3.5-eV nonresonant spectrum. The multiple excitations are considerably more intense at the resonant energies, and deviations from the Poisson distribution increase with increasing number of phonons excited. This effect can also be seen qualitatively in Fig. 5.

The HREELS electron analyzer is of fixed orientation relative to the electron-beam monochromator in the present experimental configuration. However, by tilting the sample, it is possible to gain some information on the HREEL spectral intensity away from the dipolar lobe which dominates the specular spectrum.¹⁵ In Fig. 8, the sample was tilted by $\pm 7^\circ$ from the surface normal and the ratio of the single-loss phonon to elastic peak intensity, I_{inel}/I_0 , is shown as a function of beam energy. Data are plotted in the vicinity of the 5-eV resonance for each of the tilted geometries along with the specular data for comparison. All three plots show similar enhancements at the resonant energy. The results of Fig. 8 effectively

FIG. 8. Effect of sample rotation on phonon intensity distribution. (a) $+7^\circ$, (b) 0° , (c) -7° from specular.

eliminate the possibility that the increase in intensities at 5.0, 8.5, and 13.5 eV are due to Bragg peaks in the specular diffraction beam. Bragg " I - V " maxima should be tightly peaked around the specular direction and should therefore disappear upon tilt of the sample.³¹

It can, furthermore, be shown that the TNI resonance energies do not result from errant LEED beams crossing the path of the HREEL spectrometer slit in "emergent" or "grazing incidence" diffraction phenomena.³² Primary beam energies sufficient for diffraction beams to emerge from the surface and backscatter into the spectrometer can be calculated by simple addition of reciprocal-lattice vectors to the electron momentum component parallel to the surface plane.³¹ Specular scattering of the incident electron beam occurred in a plane nominally defined by the $\langle 001 \rangle$ surface normal and the $\langle 100 \rangle$ surface vector. However, LEED measurements indicated that the sample was rotated by 14° clockwise in the azimuthal plane from the nominal geometry. Electron energies for emergent (0,1), (1,1), and (2,0) diffractions are listed in Table I for the experimental

TABLE I. Emergence energy conditions for Bragg diffraction. E in eV.

Beam	$\Phi = 0^\circ$	$\Phi = 14^\circ$
$(\bar{1}0)$	5.9	6.1
$(\bar{1}\bar{1})$	18.3	14.4
$(\bar{1}1)$	18.3	25.4
$(\bar{2}0)$	23.5	24.5

scattering geometry. Neither absolute energies nor relative energy spacings of these grazing emergent beams correspond to the observed HREELS TNI features. Thus diffraction-based explanations for the observed resonances can effectively be ruled out.

V. TEMPORARY NEGATIVE-ION STATE ASSIGNMENTS

NiO(100) HREEL spectra taken with variable electron-beam energies yield the unexpected result of increased electron-phonon interactions at resonant beam energies of 5.0, 8.5, and 13.5 eV. At these energies, the spectrum displays substantially increased Fuchs-Kliwer phonon intensities and a partial randomization of the scattered electron beam out of the specularly diffracted "dipolar" lobe. There is also a shift in phonon intensity distribution away from the predicted Poisson distribution and toward higher intensities for multiple excitations. Bragg scattering is definitely not involved in the phenomenon, as is seen by varying the scattering angle and by comparison with calculated emergent diffraction beam energies. An alternate explanation is that the electron beam is temporarily trapped into unoccupied states in the NiO(100) band structure, forming negative-ion states with sufficient lifetime to be detected by HREELS.

Temporary negative ions increase the residence time of the electron near the surface, thus increasing the effective cross section of the electron-phonon interaction. This phenomenon has been demonstrated by the increase in phonon intensity at the resonant beam energies, as shown in Figs. 3 and 4. TNI trapping also explains the decrease in reflectivity of the total HREEL spectral intensity at the resonant energies in Fig. 6. Once trapped, the electron at least partially loses the preferred specular directionality of the HREELS dipole scattering mechanism, depending upon the length of time it is held in the TNI state.

The observation of a TNI resonance at the NiO surface is, in part, made possible by the localized nature of its conduction band;^{10,11} TNI resonances on conductive surfaces have only been reported to date for weakly interacting adsorbate states¹⁻⁷ due to the short lifetime expected for delocalized, conductive systems. Partial metallization of the NiO(100) surface, by preferential sputtering with Ar⁺ (Ref. 33) or slow surface reduction under H₂,¹⁸ significantly decreases the resonant phonon enhancement described above. The effect of either method of defect production has profound changes in the nature of the NiO(100) surface and in the Fuchs-Kliwer phonon spectrum, complicating sputtered/reduced NiO TNI HREELS analysis. Interpretation of the defect-laden NiO(100) HREEL phonon spectrum is the topic of an additional publication.³³

The NiO valence-band structure has been studied extensively by both experimental^{11,12,34} and theoretical^{10,35-38} methods. Bremsstrahlung isochromat spectroscopy (BIS) has determined that the NiO unoccupied density of states (DOS) possesses a large maximum at 4

eV followed by a series of three smaller maxima of comparable size at 9.5, 13.5, and 18 eV, with energies reported relative to the Fermi level.^{12,39} Cluster³⁵ and band-structure^{10,37,38} calculations assign these states to nickel-derived $3d^9$, $3d^8 4s$, $3d^8 4p$, and $3d^{10} \underline{L}$ states, respectively. The symbol $\underline{L}$ indicates an oxygen $2p$ hole, resulting from charge transfer from oxygen to the nickel upon compound formation.

While an accurate work function for the NiO(100) sample is not available from our measurements, an average of 4.4 eV taken from literature values^{34,40,41} can be used to estimate the TNI energies relative to a Fermi-level reference. Adding the work function to our values gives 9.4, 12.9, and 17.9 eV relative to E_f . Comparing these values to the BIS results shows a clear correspondence to the unfilled DOS maxima of $3d^8 4s$ (9.5 eV), $3d^8 4p$ (13.5 eV), and $3d^{10} \underline{L}$ (18 eV). The $3d^9$ maximum in the unoccupied DOS represents a bound state at -0.4 eV relative to the vacuum level (4 eV less the 4.4-eV work function) and cannot be formed by resonant trapping of electrons with positive kinetic energies. Thus the TNI resonance features accurately reproduce the known structure of the nickel oxide unfilled density of states.

Values for BIS were obtained on charge-balanced NiO, whereas the states accessed in TNI resonance measurements are proposed to produce a negative "NiO¹⁻" ion. Also considering the uncertainty in the work function of the NiO substrate and the difficulty in accurately determining Fermi levels of the NiO(100) surface, the TNI resonances are thus quite close in energy and are assigned to a temporary trapping of the scattering electron into these unoccupied states.

VI. CONCLUSIONS

In this paper, we show that electrons can be trapped into unoccupied NiO DOS to create temporary negative ions that are detectable by HREELS. The TNI states, at 5.0, 8.5, and 13.5 eV, produce resonance enhancement of the NiO(100) Fuchs-Kliwer phonon spectrum, due to an increased opportunity for interaction between the scattering electron and the Fuchs-Kliwer surface phonon mode. The resonances due to trapping into nickel-derived states in the unoccupied DOS are identified by comparison with photoelectron spectroscopy and cluster calculations. Except for the resonant increases in spectral intensity at the TNI energies, the NiO(100) Fuchs-Kliwer phonon spectrum otherwise follows dipolar scattering behavior.

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