Our EXAFS data have given a direct evidence for a local ordering in the highly concentrated $CuBr_2$ aqueous solutions. The elementary unit —a bromine rectangle with a copper at its center—is the same as that of $CuBr_2$ crystals. The distorted-rectangular unit suggests that these units are linked together by their smaller side, and form chains like in the crystal. However, the EXAFS experiments cannot give any indication concerning their lengths, and their eventual stacking. The dynamic or static disorder is a little bit larger than in the crystal. It must be pointed out that this disorder increases continuously when the solution is diluted.

Even in dilute solutions ($c \sim 0.1M$) we have an evidence that half of the Cu^{++} and Br^- ions are not simple hydrated ions but form complex molecules which could be plane square $(CuBr_4)^{--}$ anions or $CuBr_2$ molecules, which is a structural confirmation of the model recently proposed for $NiCl_2$ solutions.[4,5]

The data furthermore give a good example of the power of the EXAFS technique (especially when corroborated with other techniques) in studying the detailed structure of aqueous solutions in all concentration ranges.

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Observation of a Λ_1-Symmetry Surface State on Ni(111)

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An s-p-like intrinsic surface state on Ni(111) has been found which has an energy of $E_i = -0.25$ eV relative to the Fermi energy at $\bar{\Gamma}$ and lies between the L_3 ($E_i \simeq -0.15$ eV) and $L_{2'}$ ($E_i = -0.9$ eV) bulk states. Its momentum dispersion (E vs $\vec{k}_{\parallel}$) and $h\nu$-dependent photoionization cross section have been determined using angle-resolved photoemission with synchrotron radiation. The existence of this state significantly affects spin-polarized photoemission, chemisorption, band-structure, and exchange-splitting interpretations for Ni.

Nickel is one of the most-studied metals because of its interesting electronic, magnetic, and chemisorption properties. However, many properties are not yet unambiguously understood; e.g., its d-band structure (experimental widths are narrower than theoretical), magnetic exchange splitting, nature of spin-polarized photoemission and field emission, etc. For example, an exchange splitting $\delta E_{ex} \simeq 0.3$ eV has been reported[1] which is much smaller than recent theoretical estimates, while several inconsistent papers interpreting spin-polarized photoemission

data claim that (1) the Stoner-Wohlfarth-Slater (SWS) model for bulk Ni does not work,[2] (2) the SWS model for bulk Ni does work,[3] and (3) the SWS model works for Ni(100), but only if (calculated) intrinsic d-like surface states are considered.[4]

We report new angle-resolved photoemission data for Ni(111) obtained with synchrotron radiation which show the existence of a prominent intrinsic surface state of Λ_1 symmetry at the Brillouin-zone center $\overline{\Gamma}$ with an initial energy $E_i = -0.25$ eV. This surface state disperses downwards in energy with increasing parallel momentum $\vec{k}_\parallel$ in all directions and exhibits an $h\nu$-dependent photoionization cross section similar to that we have measured for the s-p-like surface state on Cu(111) at $E_i = -0.4$ eV (at $\overline{\Gamma}$). At low photon energies, $\varphi + 0.25 \lesssim h\nu \lesssim 12$ eV (work function $\varphi \simeq 5.2$ eV), normal emission from this surface state dominates bulk emission. Bulk emission from states near L has also been studied by removing the surface state via chemisorption, and a d-like state L_3 ($E_i \simeq -0.15$ eV) and s-p-like state L_2' ($E_i \simeq -0.9$ eV) have been determined. This ordering of bulk band levels corresponds to a much smaller exchange splitting ($\delta E_{ex} < 0.5$ eV) and lower L_2' energy level than given by recent self-consistent band calculations.[5,6]

Previously, emission from this Ni(111) surface state was incorrectly interpreted as being due to the bulk $L_{3\uparrow}$ state (placed at -0.5 eV).[1] This led to the estimates of the exchange splitting $\delta E_{ex} \simeq 0.3$ eV and of the energy gap $\Delta \simeq 0.5$ eV between E_F and the top of the majority-spin d band in the SWS model.[1] Our estimate is $\Delta \lesssim 0.15$ eV, which is consistent (using a SWS model) with the observed polarity reversal in spin-polarized photoemission near threshold for Ni(111).[2] At photon energies within ~2 eV of threshold, surface-state emission makes a large contribution to the total emission and markedly affects the interpretation of spin-polarized photoemission experiments.

For our measurements, we have used a new two-dimensional (2D) display-type electron spectrometer that directly displays the angular intensity distribution of photoelectrons within a selected energy pass band ΔE for a cone of emission angles of 86° full width (1.8 sr). This spectrometer permits angle-integrated and angle-resolved photoelectron spectroscopy. LEED (low-energy-electron diffraction), and Auger spectroscopy (AES) to be done on the same sample. An angle-resolved detector permits any escape direction
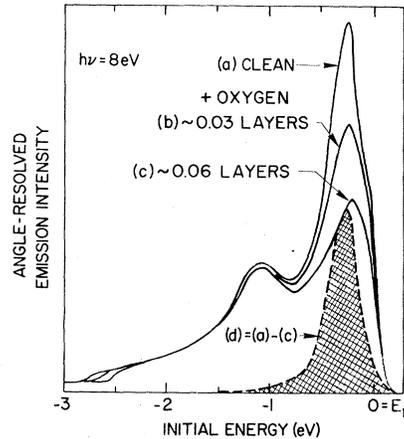
FIG. 1. Angle-resolved energy distributions for emission normal to the surface ($\delta\theta = 4°$) for clean and O_2-exposed Ni(111). The difference curve d shows the surface-state emission.

to be selected with a variable angular acceptance $1.5° < \delta\theta < 35°$. Overall energy resolution (photons plus electrons) with monochromated synchrotron radiation from the 240-MeV storage ring at the University of Wisconsin was 100–130 meV for these measurements. The angular acceptance was $\delta\theta = 4°$ ($\delta\theta = 2°$ gave similar results). Count rates under these conditions were greater than 10^4/sec for the Ni d bands with $6 \lesssim h\nu \lesssim 15$ eV. Ni(111) samples were prepared by Ar-ion etching and annealing in the usual manner, oriented with LEED, and checked for cleanliness by AES in the 2D spectrometer.

In Fig. 1, we present angle-resolved energy distribution curves (AREDC's) with electron emission normal to the surface for (a) clean Ni(111), (b) Ni(111) exposed to 0.5 L (1 L = 10^{-6} Torr sec) of O_2, (c) Ni(111) exposed to 1.0 L of O_2(i.e., $\lesssim 1$ monolayer), as well as the change in emission [difference spectrum (d)] to 1 L of O_2 exposure. For Fig. 1, mixed s-p polarization and a photon energy of $h\nu = 8$ eV were used. The dominant peak at -0.25 eV (~0.3 eV full width at half-maximum) is due to an intrinsic surface state which is highly sensitive to adsorbates (oxygen, CO, etc). For example, less than half a monolayer of adsorbed oxygen causes 50% of the surface-state emission to disappear (curve b) and submonolayer amounts of residual gas (probably CO) shift its energy downwards. Further evidence for a surface state is that the binding energy of this state for normal emission exhibits no dispersion with changes in photon energy, while bulk transitions disperse with photon energy
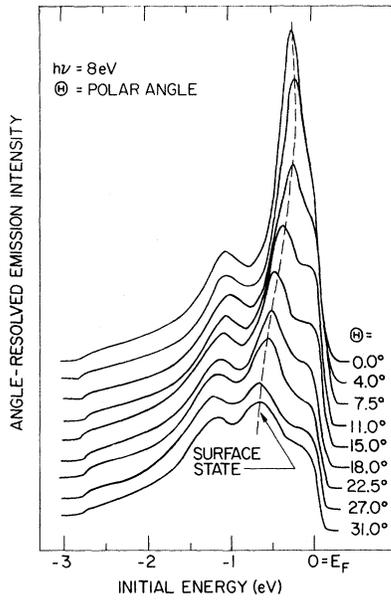
FIG. 2. Angle-resolved energy distributions as a function of emission direction θ in the $\{11\bar{2}\}$ plane showing surface-state dispersion. The relative intensities have been normalized to the lowest peak (Λ_1 band).

FIG. 3. (a) Dispersion of the surface state with parallel momentum $\vec{k}_\parallel$ in the $\langle 1\bar{1}0 \rangle$ direction ($k_{BZ}^{\langle 1\bar{1}0 \rangle} = 1.68$ Å^{-1} = zone boundary). (b) Dispersion of the surface state and two bulk bands near L with excitation energy. The $k_\perp$ momentum scale has been derived from the conduction band of Ref. 7, which was shifted down by 0.5 eV to make the conduction-band minimum L_1 coincide with our experimental value ($L_1 \simeq 6.1$ eV).

(equivalently, with momentum perpendicular to the surface, $k_\perp$).

AREDC's are presented in Fig. 2 which show that the surface state disperses downwards with increasing parallel momentum $\vec{k}_\parallel$ ($|\vec{k}_\parallel| \propto E^{1/2} \sin\theta$, where θ is the polar angle of emission). Since the surface-state emission intensity is strongly damped off normal, transitions from the bulk Ni bands near E_F become more visible (e.g., at -0.2 eV for $\Theta = 27°$). These bulk states disperse with $\vec{k}_\parallel$ less than the surface state, and remain when the intrinsic surface state is removed by an adsorbate. For example, a bulk state at -0.2 eV is seen in Fig. 1 (curve c) which is nearly degenerate with the surface state. In Fig. 3, we summarize the energy dispersion of the surface state as well as of two bulk states near L. We observe two bulk transitions which start at initial energies of -0.15 and -0.9 eV below E_F, respectively, near threshold and move to lower initial energies with increasing photon energy. The upper state was studied with the surface state removed by 0.06 monolayers of oxygen (also hydrogen or CO); the lower state was determined from clean Ni(111) spectra. The final energy E above E_F is related to the wave vector $k_\perp$ in a simple way for normal emission from the $\langle 111 \rangle$ surface: According to band-structure calculations, there

is a single parabolic conduction band in the $\Gamma - L$ direction which starts near the vacuum level at the L point and moves monotonically towards higher energy as $k_\perp$ moves from L to Γ. The $k_\perp$ scale in Fig. 3 is based on this band.[7]

For an assignment of initial-state symmetries in Fig. 3(b), we use polarization selection rules as described by Hermanson[8] which we have found to be valid for Cu(111). The only surface (and bulk) state which can be seen in normal emission for Ni(111) must have either Λ_1 or Λ_3 symmetry, which are excited with the electric field vector $\vec{E}$ polarized parallel and perpendicular to the surface, respectively.[8] The Λ_3 band is enhanced by s-polarized light ($\vec{E} \parallel$ surface), whereas the Λ_1 band and the surface state are enhanced by p-polarized light ($\vec{E}$ close to sample normal). Thus, the surface state must have Λ_1 symmetry. Moreover, the surface state lies in a Λ_1-symmetry gap above the top of the observed Λ_1 bulk band.

Band calculations show that the top of the Λ_3 and Λ_1 bulk bands of interest have L_3 and L_2' symmetries, respectively. The L_3 level lies below L_2' in Cu whereas we observe the opposite for Ni. As a result, the bulk bands joining L_2' disperse upward with increasing $\vec{k}_{\parallel}$ (toward W, K, etc.) in Cu but disperse downward for our Ni band topology. The latter is idential, e.g., to that of the minority bands in Callaway and Wang.[9] Since the Cu(111) surface-state dispersion tracks this bulk band, one expects the same behavior for Ni(111), as we in fact observe.

The existence of a surface state in the Λ_1-symmetry gap above L_2' is common to the $\langle 111 \rangle$ surfaces of the noble metals Cu, Ag, and Au.[10,11] To characterize the Ni(111) surface state further, we have measured the angle-resolved $h\nu$-dependent photoionization cross section for the surface state relative to the bulk emission cross section for Ni(111) and Cu(111) under the same conditions. The ratios of surface-state to bulk photoemission intensity are shown in Fig. 4. For Ni(111), there is emission from the Λ_3 band that overlaps the surface emission; therefore, we have used difference spectra such as curves c and d in Fig. 1 to determine the surface and bulk d-band emission intensities. As seen in Fig. 4, the relative cross sections for the Cu and Ni surface states are very similar, both decreasing very rapidly with increasing photon energy. This behavior is similar to the behavior of bulk s-p- vs d-state cross sections.[12] A recent ab $initio$ calculation[13] for Pd(111) gives a Λ_1 surface state which is analogous to the Ni(111) surface state and has predominantly s-p_z character.

In summary, our assignment of bulk bands

differ markedly from recent band calculations,[5,6,9] with L_3 and L_2' inverted in order and with L_2' being much lower than calculated. Our value for L_3 is compatible with an exchange splitting δE_{ex} < 0.5 eV and, if we associate L_3 with the majority band ($\Delta \lesssim 0.15$ eV), its proximity to E_F is compatible with both the observed sign change in spin-polarized photoemission[2] just above threshold[3] and the Stoner continuum gap $\Delta \simeq 0.075$ eV. Namely, the transition to positive spin polarization takes place at about 2Δ above threshold because of the high density of majority spins near L_3.[3] The Λ_1 surface state affects photoemission (especially spin-polarized), field-emission, chemisorption, and ion-neutralization properties of Ni(111). For example, the large surface-state photoemission near threshold (see Fig. 4) is essentially nonmagnetic (based on calculated s-p bands) and affects the magnitude of the spin polarization. Tunneling from the tail of the surface state at E_F explains the low spin polarization in field emission from Ni(111) ($< 3\%$)[14] in the absence of sp bulk bands at E_F. Strong s- and p-electron adsorbate bonding interactions (relative to d-electron effects) have been reported[15] for Ni(111); these are likely due in part to the intrinsic Ni(111) surface state reported here.

FIG. 4. The ratio of surface to bulk emission intensity (normal emission) for the Ni(111) and Cu(111) surface states. P-polarized radiation is incident 60° from normal.

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Single–Rayleigh-Phonon Interaction in the Scattering of He from LiF(001)

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Energy analysis has been performed on 63-meV He atoms scattered from 135°K LiF(001) along the $\langle 010 \rangle$ direction. The results suggest that single Rayleigh phonons dominate the interaction near specular scattering. Points on the dispersion curve are determined uniquely and suggest a limiting speed of sound of $(4.2 \pm 0.5) \times 10^5$ cm/sec.

Since the early work of Cabrera, Calle, and Manson[1] on inelastic scattering of atoms by crystal surfaces it has been hoped that atomic-beam scattering could provide useful information about surface-phonon spectra. It appears at this time that an ideal coupling of such experiments with a rigorous theory may only be accomplished in the limit of single-phonon processes. Experiments to data have only reported scattered angular intensity distributions. The most interesting cases have shown intensity maxima and/or minima in the inelastic scattering about specular or diffraction peaks for LiF(001),[2,3] Ag(111),[4] and Au(111).[5] Several types of analysis exist for these structures[2,2,6-10] using various approximations. For example, one type of important simplification is to assume a flat surface, conserving tangential momentum, or at another limit, to assume only Rayleigh phonons are involved so that the phonon only transfers tangential momentum. We have felt that appropriate approximations will only be substantiated when both energy and angular distributions can be made in a regime where single-phonon interactions are dominant. Under these conditions the ideal beam scattering experiment can uniquely determine the frequency (ω) and surface tangential momentum vector ($\vec{Q}$) of the phonon involved. In this Letter we report the first such experiment. We feel the data indicate an interaction dominated by a single–Rayleigh-phonon process. We first review the kinematics involved for our type of experiment.

For a single-phonon process, associated with the specular peak, which scatter in the plane of the incident beam and the surface normal, i.e.,

the phonon travels in plane, the conservation laws can be written

$$k_s \sin\theta_s = k_i \sin\theta_i + \binom{G}{L} Q, \tag{1a}$$

$$k_s^{\ 2} = k_i^{\ 2} + \binom{A}{C} \frac{2m\omega}{\hbar}, \tag{1b}$$

where θ is measured from the surface normal and ω and Q are taken as positive scalar quantities. The symbols $G = +1$ and $L = -1$ represent gain or loss of parallel momentum, since the phonon can travel in either direction, and $A = +1$ and $C = -1$ represent annihilation and creation of the phonon, respectively. Equations (1a) and (1b) can be combined to eliminate k_s and give a simple relationship $\omega = \omega(Q, k_i, \theta_i, \theta_s, m)$. Therefore, with a specified incident particle (k_i, θ_i, m), at each in-plane scattered angle, θ_s, there are four unique curves of $\omega = \omega(Q)$ along which the solution for a particular phonon interaction must lie if it is to satisfy the conservation Eqs. (1a) and (1b). Figure 1 shows a plot of such solutions for a sub-specular scattering. The case (C, G) yields no positive ω solution so that these processes are not permitted for the specified conditions. The possible scattering solutions are now given by the intersection of these curves with the dispersion curves for a particular crystal surface of interest. For illustrative purposes, a hypothetical set is shown as dashed curves in Fig. 1. We have used the nomenclature and qualitative features of the calculations of Allen, Alldredge, and De-Wette[11] for a model which should represent LiF reasonably well; these are not computed curves for LiF, however.