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Temperature dependence of normal-emission photoelectron diffraction and analogies with extended x-ray-absorption fine structure

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The temperature dependence of normal-emission photoelectron diffraction (NPD) of the prototype adsorbate-substrate system Se–Ni (001) was studied. Two interesting observations emerged. Thermal diffuse scattering yielded a decreasing peak-to-valley contrast ratio in NPD with increasing temperature characterized by an effective temperature $\Theta_{\text{eff}} \sim 135$ K. Also, a new low-temperature form of $p(2\times2)$ selenium structure was observed, with $d_\perp$ estimated to be larger by $\sim(0.06\text{–}0.1)$ Å than the room-temperature form. The new form, which is probably undissociated H_2Se, is apparent through a systematic NPD peak shift reminiscent of extended x-ray-absorption fine structure (EXAFS) spectra. It is noted that NPD, though usually associated with low-energy-electron diffraction, in fact has strong similarities to EXAFS. This is particularly evident in the importance of an extended k-space data set and in the temperature sensitivity.

I. INTRODUCTION

In 1974, Liebsch proposed that surface structural studies on adsorbate-covered clean surfaces similar to low-energy-electron diffraction (LEED) might be advantageously carried out using photoelectrons.[1] The relation of the angle-resolved photoemission (ARP) final state to a LEED state has long been recognized,[2-4] and various theories dependent on LEED formalisms have been developed to treat photoelectron diffraction (PD) data.[4-6] In addition, several experiments have been reported which have generally confirmed Liebsch's initial hypothesis concerning the structural sensitivity of PD.[7-10] Our group has addressed the characterization of normal emission photoelectron diffraction (NPD), in which the photoemission intensity of an adsorbate core level is measured normal to the surface as a function of photon (and thus kinetic) energy.[7] In NPD, an intensity-energy curve similar to a LEED I-V curve is generated which, when compared to theoretical curves, may yield a surface structure. Given its genesis, PD is usually conceptualized by its relation to LEED, and the same general accuracies and limitations are usually perceived to be associated with the two methods.

In this paper, we take the view that while this comparison to LEED is valuable, an equally enlightening comparison of *normal* photoelectron diffraction to extended x-ray absorption fine structure[11,12] (EXAFS) can be drawn. The important point is that the initial step in PD and surface EXAFS—an excitation of an electron localized in an adsorbate core level—is the same, while the details of the final-state scattering in PD are best described by their relation to LEED. The fact that the electron source in PD is localized as in EXAFS implies that it is a phase-coherent process: The phase of the wave leaving the absorbing atom is fixed for each energy. A direct result of this is PD's ability to deal with disordered overlayers not normally accessible with LEED.[7,9] Specializing to NPD we note that, while the NPD intensity-energy curves resemble LEED I-V curves, their calculated behavior actually mimics EXAFS data, with $d_\perp$, the interplanar spacing between the overlayer and the outermost substrate layer being the important structural parameter, rather than the nearest-neighbor distance, R_{NN}. This result, first observed by Li and Tong[13] and emphasized elsewhere,[7,8] is illustrated in Fig. 1. In the top three curves, the calculated selenium 3d normal emission ARP intensity for the $p(2\times2)$ Se–Ni (001) system is plotted for three different values of $d_\perp$. The oscillation frequency is seen to increase monotonically with $d_\perp$ in much the same way as EXAFS oscillation frequencies increase with nearest-neighbor distances. The lower curve in Fig. 1 shows our experimental data. The match to the $d_\perp = 1.55$ Å calculation reported previously[7] is evident. The registry of the selenium layer with the nickel surface was found to be relatively unimportant in determining the calculated result[13]: Nearly the same curve was obtained for different local site geometries, if they were compared at the same $d_\perp$.

Empirically, NPD data thus behave similarly to EXAFS data with the important difference that the structural sensitivity is to $d_\perp$ rather than R_{NN}. In the context of investigating this analogy further, we report in this paper new temperature-dependence results on the Se–Ni (001) model system. Taken at face value, these data are of interest in further characterizing the system. Of more general interest, however, is their value in charac-

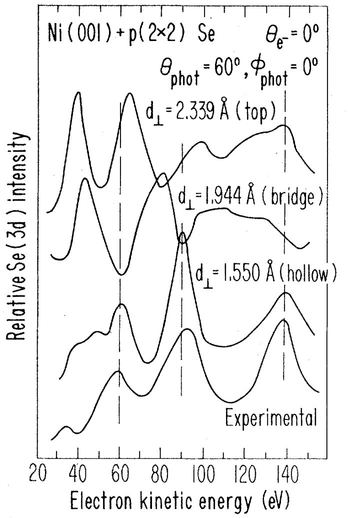

FIG. 1. Top three curves: calculated selenium $3d$ intensity as a function of electron kinetic energy for $p(2\times2)$ Se–Ni (001) at three different values of $d_\perp$ as defined in the text, after Tong and Li. Bottom curve: experimental result.

terizing the NPD phenomenon; in fact, they constitute more evidence for the NPD-EXAFS analogy.

Section II includes some experimental information. Section III presents data that establish two forms of $p(2\times2)$ "Se" on Ni (001) and emphasizes the importance of accumulating an extended k-space data set. In Sec. IV we report a study of the temperature dependence of NPD data. Section V includes a summary and some conclusions.

II. EXPERIMENTAL

Experiments were performed on the 4° branch of Beam Line I at the Stanford Synchrotron Radiation Laboratory. The photoemission spectrometer and our technique for generating NPD data have been described elsewhere.[14] The stored ring current was rather low during these experiments (11–14 mA), but our spectrometer's multichannel detection capability allowed experiments to be performed readily. Complete spectra around the Se $3d$ peak were collected at each photon energy, to permit accurate corrections for background and for energy-dependent resolution.

The nickel crystal, which was oriented to within 1° of the (001) face, had previously been cleaned of bulk impurities so that only minor amounts of argon-ion etching followed by annealing at 600 °C were necessary to produce a clean and ordered surface. Initially, carbon, usually the most tenacious surface impurity, could not be detected using Auger electron spectroscopy, but a small carbon $1s$ peak was visible using photoemission at $h\nu = 360$ eV, a photon energy where the carbon $1s$ level has a reasonably large cross section. It appears that, at least in our apparatus, the C $1s$ sensitivity by photoemission is significantly better than by Auger spectroscopy. We suspect from this experience that minor carbon contamination (<0.05 monolayers) is more prevalent in studies of this surface than the literature tends to imply. A subsequent, more extensive etching-annealing procedure followed by a fairly rapid quenching of the sample was found to produce a contaminant-free surface. Ordered $c(2\times2)$ and $p(2\times2)$ selenium coverages were produced by directing an effusive beam of H_2Se at the clean surface. In the experiments described in Sec. IV, the surface was heated during exposure to ~200 °C, and 20–30 langmuir exposures were sufficient to produce sharp $c(2\times2)$ overlayers. The $p(2\times2)$ coverages of Sec. III required 7–10 langmuirs, but the surface was initially not heated, as explained below. The ambient chamber pressure was 4×10^{-10} Torr, and all surface preparations were observed to be stable for several hours.

III. TWO FORMS OF $p(2\times2)$ Se/Ni(001): THE IMPORTANCE OF AN EXTENDED DATA RANGE

The importance of accumulating EXAFS data as far above the edge as possible is well known and has been emphasized in several places.[15,16] In Fourier-transforming EXAFS data, a contribution to the real space peak widths of $\Delta r \sim \pi/\Delta k$ is introduced by the necessarily finite range of k over which EXAFS oscillations are observable.[17] This broadening at least partially limits the accuracy and resolution of the EXAFS technique. In light of our comments in the introduction, a similar effect should be important in NPD.

Figure 2 shows two different NPD data sets accumulated at $T = 120$ K for the $p(2\times2)$ Se–Ni (001) system. The upper curve was accumulated using an unannealed overlayer prepared by exposing to H_2Se at 120 K, while the lower curve was accumulated after an anneal at 450 K. Both surfaces yielded $p(2\times2)$ LEED patterns, though that of the annealed surface was sharper. While the same general structure is observed in the curves, a systematic and monotonically increasing shift of peak positions to lower energy is evident in the upper curve. The amplitude of oscillation is also larger in the lower curve. The data in that curve are in good agreement with our previous data,[7] and are best fitted as before by a calculated curve with $d_\perp = 1.55$ Å, corresponding to the accepted four-coordinated hollow-site adsorption geometry. The most likely explanation for the shifts observed in the upper curve is that $d_\perp$ has *increased* slightly, leading to slightly more rapid oscillations. Since the higher-energy peaks disperse more

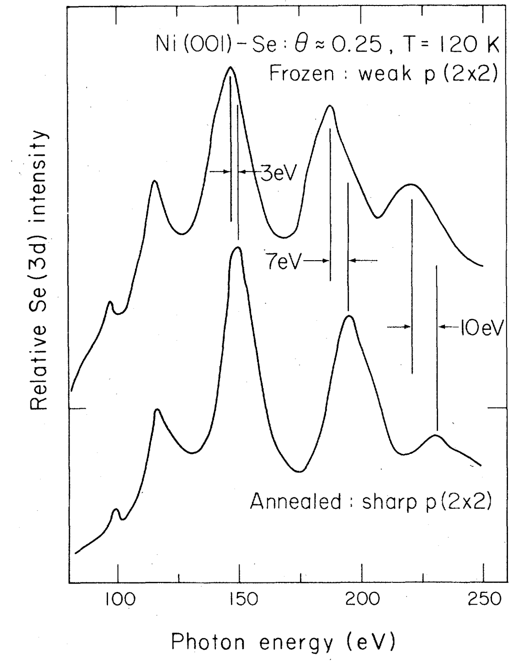

FIG. 2. Comparison of NPD curves for frozen and annealed $p(2\times 2)$ Se–Ni (001). Note the systematic shift of peak energies.

rapidly with $d_\perp$, the higher-energy regions are further out of phase. Indeed, if we had limited our study to $h\nu \leq 160$ eV, the pronounced shift seen in Fig. 2 would have been difficult to discern. The lesson is the same as in EXAFS: An extended data range permits more accurate and higher-resolution NPD studies.

An estimate can be made of the magnitude of the change in $d_\perp$ by two independent methods. The calculations by Tong and Li[13] over a wide range show that the fourth and fifth peaks in Fig. 2 disperse with $d_\perp$ at average rates of ~60 and ~80 eV/Å. Combining this with the shifts indicated in Fig. 2 yields $\Delta d_\perp \approx 0.1$ Å. Another estimate can be made as follows. Assume that the relationships

$$E_p = Ak_p^2,$$

$$d_\perp = B/k_p$$

apply qualitatively to the kinetic energy (E_p) and wave number (k_p) of the peaks in our NPD curves, and to the distance parameter $d_\perp$. It is easy to show that a small shift in $d_\perp$ is given by

$$\Delta d_\perp = -d_\perp(\Delta E_p/2E_p)$$

if E_p is measured from a suitable origin and ΔE_p is the shift in peak energies. This yields $\Delta d_\perp = 0.06$ Å for the upper curve in Fig. 2, in fair agreement with the above estimate of 0.1 Å. Now the observed energy shift ΔE is very easy to resolve in this case, implying that our sensitivity in $d_\perp$ is much better than 0.06–0.1 Å, and certainly substantially better than the ±0.1 Å typical of LEED studies. Indeed, its localized nature and phase coherence should make the ultimate precision (and perhaps accuracy) of NPD as high as that of EXAFS (±0.01 Å).[15,16] Considering the complexity of PD calculations relative to an EXAFS data analysis, however, it is not clear whether such accuracies can be attained in practice.

Several factors mitigate against covering such wide data ranges in NPD studies. Analyzer transmission functions generally decrease at higher kinetic energies. Also, in the soft x-ray regime, the usual problems of monochromator flux, resolution, and scattered light become more severe at higher energies. These experimental problems are the primary constraints on our present experimental efforts. They will, however, probably be overcome with the introduction of new synchrotron radiation facilities and monochromator designs. In addition to these practical constraints, there are also some fundamental limitations on the range of useful data, familiar from EXAFS. Temperature effects become more pronounced at higher energies (see Sec. IV), and the scattering cross sections are monotonically decreasing functions of energy.[15-18] Both of these effects reduce the amplitude of oscillation relative to the atomic background. Finally, the atomic photoemission cross section decreases at higher energies. While all of these effects make the quest for extended-data-range-NPD studies appear difficult, in fact these constraints are either surmountable or the same as those in EXAFS. Considering that NPD oscillations are at least a factor of 10 larger than EXAFS oscillations, we feel that higher-energy NPD studies are quite possible.

Our observation of a shift in $d_\perp$ in this system is interesting in its own right. It tends to imply that H_2Se does not dissociate on a cooled Ni (001) surface. If so, there are at least two "chemical" reasons for an increase in $d_\perp$. The first is simply a steric effect: The added bulk of the hydrogens precludes selenium atoms from fitting as far down into the fourfold hollow site. There should also be an electronic effect. Nickel is energetically stabilized by receiving electrons, thus filling its *d* shell. The presence of hydrogen bonded to the selenium atoms will lessen the ability of selenium to donate electrons, producing a weaker and perhaps longer nickel-selenium bond.

IV. THE TEMPERATURE DEPENDENCE OF NPD OSCILLATIONS

In the last section, it was pointed out that thermal disorder is expected to limit the energy range over which useful NPD data may be accumulated.

In order to investigate this point more fully, we have undertaken a detailed study of the temperature dependence of NPD data for the $c(2\times 2)$ Se–Ni (001) system. In the simplest model, one would expect some combination of the temperature sensitivities of LEED and EXAFS to affect NPD data. One expects the usual thermal diffuse scattering of LEED and x-ray diffraction to degrade the NPD final state in much the same way as it destroys the contrast of LEED beams.[18] In addition, the electron source in NPD is itself vibrating, causing a distribution of $d_\perp$'s to contribute to the NPD result. This is analogous to the effect of temperature on EXAFS data, where a distribution of bond lengths causes the amplitude of oscillation to decrease.[15,16] In view of several theories which predict substantially enhanced vibrations of the outermost surface layer relative to those typical of bulk layers,[19-22] this latter effect might be expected to make NPD (and surface-extended x-ray absorption fine-structure) experiments somewhat more sensitive to temperature than LEED.

Most thermal diffuse scattering mechanisms are interpreted in terms of a Debye-Waller factor[17,18]:

$$I \sim \exp[-\langle(\Delta\vec{k}\cdot\Delta\vec{r})^2\rangle]\,,$$

which diminishes the fraction of coherently scattered particles. Assuming a Debye model for vibrational frequencies and amplitudes, and also that the vibrations are isotropic, this equation is reduced to the form familiar from x-ray diffraction studies[17,18]:

$$I \sim \exp\left(-\frac{3|\Delta\vec{k}|^2 T}{m k_B \Theta^2}\right)\,, \qquad (1)$$

with m as the atomic mass, k_B as Boltzmann's constant, T as the absolute temperature, and Θ as the Debye temperature. This functional form is such that thermal effects are most pronounced at high energy and temperature. It has been found empirically that LEED intensities are exponential in temperature, but that Θ is a function of $\Delta\vec{k}$, indicating that the assumptions involved (Debye model) and multiple scattering preclude accurate applications of the simple model.[18] On the other hand, EXAFS data have been shown theoretically[23] and experimentally[24] to follow this simple functional form. It will be interesting to ascertain the extent to which a simple model such as this can treat NPD data.

We have accumulated NPD curves for the $c(2\times 2)$ Se–Ni (001) system at various temperatures above and below room temperature. Three data sets are shown in Fig. 3 for $T = 300$, 500, and 700 K. Only the region between 130 eV $\leq h\nu \leq$ 210 eV photon energy was accumulated in most of our curves, to speed data acquisition. This is the energy region where one partial wave[25] dominates the atomic excitation step and also where the atomic background is smooth.[26] These points will be important later. The effect of increased temperature is apparent in Fig. 2: The amplitude of oscillation decreases significantly at higher temperatures.

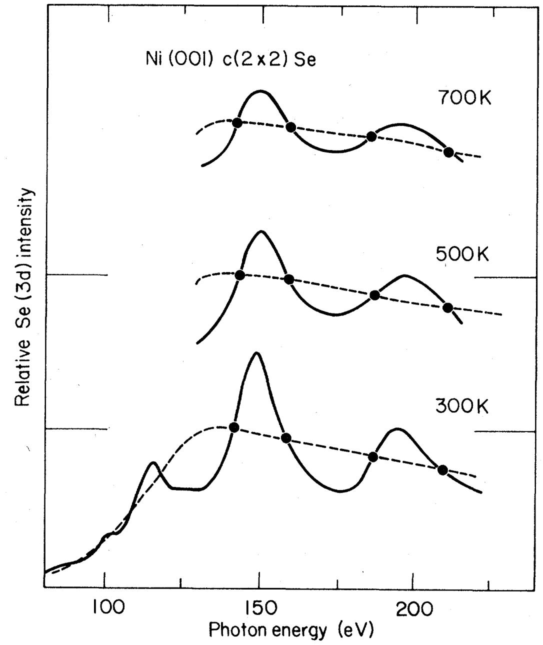

FIG. 3. NPD results taken at three temperatures for the $p(2\times 2)$ Se–Ni (001) system. Dashed lines indicate an approximate atomic background as explained in the text.

To treat the data, we wish first to isolate the scattering contribution by producing an EXAFS-like plot of $(I - I_0)/I_0$, where I_0 is a smooth atomic background. Liebsch showed[1] that such a separation is not rigorously meaningful in general for initial states other than s levels, due to interference between the two outgoing partial-wave components of the final state. Such a separation, however, is a good approximation for a $3d$ level in this particular energy range, where the $d\rightarrow f$ channel dominates.[25,26] In practice, the separation is still not completely straightforward. Fortunately, the general results we will derive are not particularly sensitive to the exact technique one chooses to use, provided the curves are treated consistently. All of our curves, when superimposed and scaled, intersect to within 1–2 eV of photon energies $h\nu = 142$, 159, 186, and 210 eV. Hence, we assumed that scattering effects are negligible at these energies and determined I_0 as a smooth curve through those points which also smoothly joins the high- and low-energy data at selected temperatures. The resulting plots of I_0, shown as dashed curves in Fig. 3, actually resemble one another

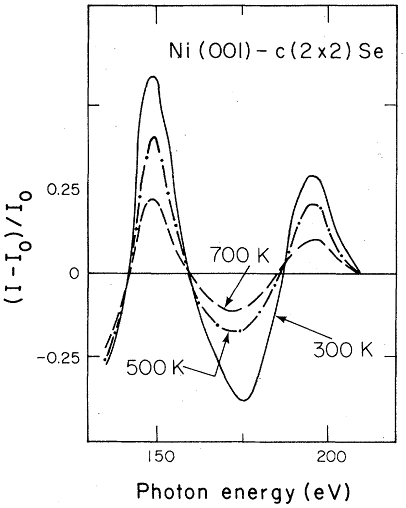

FIG. 4. Plots of $(I-I_0)/I_0$ for the three temperatures in Fig. 3. Curves are smoothed versions of the real data.

closely, providing a good self-consistency check. Plots of $(I-I_0)/I_0$ are shown in Fig. 4 for these three temperatures, and a pronounced temperature effect is again observed.

In Fig. 5, we show the dependence of $\ln[(I-I_0)/I_0]$ on temperature for the two photon energies corresponding to the two peaks in Fig. 3. Aside from substantial random scatter, an approximately linear plot is obtained. The functional form of Eq. (1) is therefore obeyed, although the Debye model *per se* is inappropriate. It is instructive to replace Θ in Eq. (1) by an effective temperature Θ_{eff}, then use it to fit the data. If effective temperatures are derived from the slopes of linear least-squares fits to the data at the two peak energies, the results are $\Theta_{\text{eff}} = 135$ and 133 K for photon energies of 149 and 192 eV, respectively. A consistent, but probably less accurate, value of $\Theta_{\text{eff}} = 125$ K was derived from the amplitude of the *minimum* at $h\nu = 174$ eV.

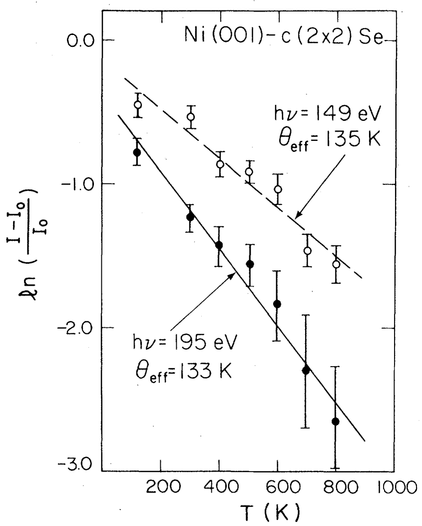

FIG. 5. Plots of $\ln[(I-I_0)/I_0]$ vs absolute temperature for 149- and 192-eV photon energy.

These results deserve several comments. First, the linearity of the plots suggest that some simple model might explain the temperature dependence. Of course, logarithmic plots are not very sensitive to details of the functional form of the temperature variation of NPD amplitude, and to infer that a Debye-Waller factor explains our data would be premature. Second, the effective temperatures are rather low compared to typical bulk Debye temperatures of nickel. This is consistent with, but does not prove, enhanced surface vibrational motion. It does prove the importance of not underestimating thermal diffuse scattering in NPD. Finally, and perhaps most important, the effective temperatures for the two peak photon energies are, within statistical errors, identical. Further work is needed to determine over what energy range this final conclusion is valid, but it lends further credence to the concept of an effective temperature Θ_{eff} describing thermal diffuse scattering in NPD.

V. SUMMARY AND CONCLUSIONS

We have reported temperature-dependent NPD studies. Several empirical similarities between NPD and EXAFS were noted. The two techniques are complementary in their structural sensitivities, yielding $d_\perp$ and R_{NN}, respectively. A combined surface EXAFS-NPD experiment would be of interest. It is remarkable that EXAFS an angle- and energy-integrated technique, and NPD, an angle- and energy-resolved technique, should possess such qualitative similarities. The characteristic shift of NPD peaks with $d_\perp$ has always indicated to us that some theoretical framework might be applicable which is simpler than the LEED formulations currently in use in treating NPD data. If the temperature-dependent NPD data we have presented are typical, they provide further evidence that such a simple model exists. The immediate conclusion from this work is that NPD efforts will benefit from extended data ranges acquired from cooled surfaces. We are also led to suggest a search for a simpler theoretical framework in which NPD data may be interpreted.

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