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S. D. Kevan

June 1980

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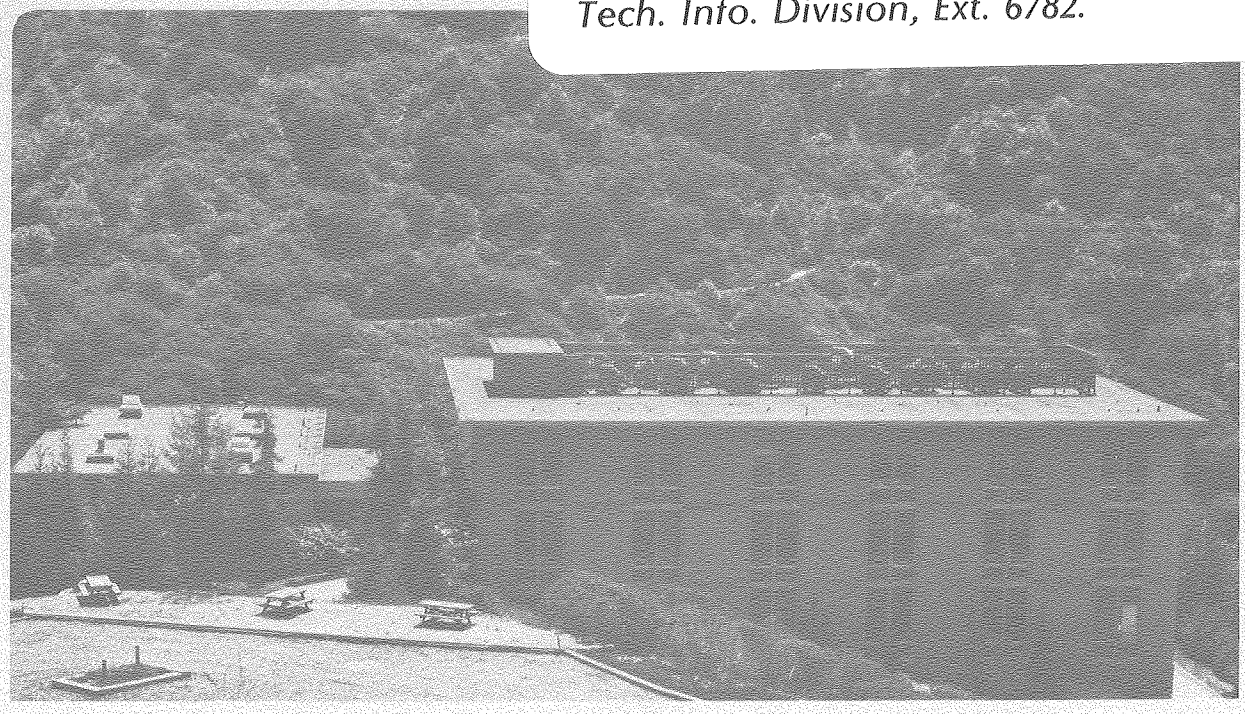

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NORMAL EMISSION PHOTOELECTRON DIFFRACTION STUDIES AT SSRL

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Abstract

A series of experiments designed to characterize the surface structural sensitivity of photoelectron diffraction is described. The technique's relation to LEED and to surface EXAFS is explored, and useful comparisons to the latter are pointed out. The application of normal emission photoelectron diffraction to disordered overlayers is shown to be reasonably straightforward. Data on both two dimensionally and three dimensionally (multiple-site) disordered overlayers are presented. The localized, atom-specific nature of PhD is shown to lend the technique real potential in the study of molecular adsorbate systems.

I. Introduction

Several years ago it was pointed out that diffraction experiments on adsorbate covered clean surfaces similar to low energy electron diffraction (LEED) might be advantageously carried out using photoelectrons.[1] The source of electrons in such a photoelectron diffraction (PhD) experiment would be localized on a particular adsorbate species, and the final state would consist of a component emitted directly toward the detector and of a component first scattered off the substrate before travelling to the detector. If the differential (angle-resolved) photoemission cross-section of an adsorbate core level were to be measured as a function of some final state parameter, oscillations would be expected due to interference between these two components. The details of these interference patterns should be sensitive to the local geometry around the adsorbate species. Since the initial hypothesis, several PhD experiments have been performed with the intention of investigating the technique's surface structural sensitivity, and a good deal of success has been reported.[2-5]

The scattering mechanisms involved in PhD are quite similar to those in LEED. Indeed, the PhD final state is calculated using the algorithms developed in treating LEED data.[2-4,7-9] For this reason, PhD is usually conceptualized by its relation to LEED. On the other hand, an equally valuable comparison to

surface EXAFS can be made. The absorption events in PhD and SEXAFS are the same, and both processes are phase coherent: the phase of the wave incident on the surface is fixed for each energy. These characteristics are in contrast to the situation in LEED, and produce certain desirable characteristics which will be the subject of this paper.

Our group has worked at SSRL using the normal emission photoelectron diffraction (NPD) acquisition mode in which the intensity of an adsorbate core level is measured normal to the surface as a function of photon and kinetic energy. A graphic illustration of the NPD effect is shown in Fig. 1, where EDC's of the p(2x2) Se/Ni(001) system taken at a series of photon energies are displayed in three-dimensional photon energy-binding energy-intensity plot. Intensity oscillations of the Se(3d) level (E_B = 57 eV) as well as the nickel valence band and 3p(E_B = 68 eV) are clearly visible. It will be seen shortly that the Se(3d) oscillations are particularly sensitive to surface structure.

II. Ordered Overlayers

Our efforts were initiated on the Se/Ni(001) system since it has become a well characterized model system in surface science and also since the Se(3d) level is well placed and yields good intensity for our purposes. Tong and Li performed the NPD

calculations[6] on this system shown in Fig. 2 along with our experimental data on the Se(3d) level obtained by taking a cut through the surface in Fig. 1 at E_B = 57 eV. Before making a comparison several features of Tong's calculations are worthy of note. The predicted effect is large and systematic: the oscillation frequency increases monotonically for increasing values of $d_\perp$, the interplanar spacing between the selenium layer and the outermost nickel layer. The oscillations have an appearance similar to those in EXAFS except that the EXAFS structural parameters are nearest neighbor distances rather than $d_\perp$ and that the EXAFS oscillations can be treated with a simple, single scattering theory rather than the more complicated multiple scattering theory required in NPD. It is furthermore found that the lateral registry of the Se layer relative to the nickel substrate is not particularly important in determining the calculated NPD result: $d_\perp$ is the only critical structural parameter. While the experimental peak intensities are not matched by any of the calculated curves, it has been argued elsewhere[2,6] that the match to peak energy positions alone is expected to be determinate. A good fit is found for the $d_\perp = 1.55\text{Å}$ calculation, in good agreement with the accepted value, and indicative of a 4-coordinated adsorption site.

A variety of other ordered chemisorption systems have been studied and, where calculations exist, satisfactory fits have

been obtained. A list of systems studied to date may be found in Table I.

An interesting application and possible test of the technique's sensitivity to $d_\perp$ is shown in Fig. 3 where two NPD curves of the p(2x2) Se/Ni(001) system are shown. In the upper curve, the crystal was cooled to 120K before exposing to H_2Se and the curve was generated without warming the sample. The lower curve was obtained from the same surface after heating to 500K and then cooling back to 120K. One observes a systematic shift to lower photon energy indicating, most likely, that $d_\perp$ has increased by $\sim$.1-.2Å. Presumably, the H_2Se does not dissociate before heating, and while it prefers the 4-coordinated hollow site, the presence of hydrogen forces a slight increase in $d_\perp$. Calculations are in progress to test this hypothesis. These curves exemplify the need to work to higher kinetic energies: peaks at higher energy disperse more rapidly with $d_\perp$ so that more accurate structural determinations are possible. Calculations predict that accuracies typical of EXAFS (.01-.02Å) are possible. The improvement over LEED accuracies would presumably be due to the localized nature of PhD and its phase coherence.

III. Disorder Effects

Another result of PhD's added phase coherence over LEED is

that there is no coherence length restriction in PhD. This is most easily seen by imagining a PhD experiment performed on an isolated adsorbate atom on a surface: there would still be a direct and a substrate back-scattered component of the final state which must add coherently, and a diffraction effect would still be observed. The implication is that two-dimensionally disordered overlayers should still give a PhD effect. Experimental verification of this is seen in Fig. 4, where NPD curves of low coverages of Se/Ni(001) which gave no ordered LEED superstructure are shown. The similarity of the disordered overlayer results to those of the ordered overlayer indicates first that NPD deals effectively with disorder in two dimensions and also that the dominant NPD scattering mechanism is off the substrate. A similar effect has been obtained in the Se/Ni(111) system.

NPD's sensitivity to $d_\perp$ alone indicates that it might be a valuable tool for studying three dimensionally disordered multiple site adsorption systems. Each site will yield its own characteristic NPD curve and, with sufficiently good statistics, one could in principle resolve two oscillation frequencies. The first experimental evidence for this is shown in Fig. 5, where data for the Se/Ni(111) system are presented. As in Fig. 3, the upper curve was taken of a cold surface after exposing the surface at 120K to H_2Se, while the lower curve is

the result after a 500K anneal. The three major peaks in the lower curve also appear in the upper one, but there also exist extra peaks in the upper curve at positions of valleys in the lower. Presumably, H_2Se is frozen into more than one site when exposing a cold Ni(111) sample. A complete analysis of the effect will be given elsewhere.[10] NPD shows real promise in dealing with the normally troublesome multiple site systems found in surface science. It should be noted that SEXAFS is probably not a good technique for such systems since the nearest neighbor distances are expected to be nearly the same for different sites.

The final disorder effect of interest is thermal disorder. As one heats the sample, the vibrational distribution of $d_\perp$ increases and also the substrate scattering becomes more and more incoherent. One expects the contrast in NPD curves to reduce. Such an effect is observed in Fig. 6, where $(I-I_o)/I_o$ (an EXAFS-like plot with I_o being a smooth atomic background) is plotted over a limited energy range for three sample temperatures. The oscillation amplitude is seen to drop markedly. There is at present no theoretical model with which to treat these data, but work in progress has produced some intriguing results.[10] The localized nature of PhD should produce a good deal of information concerning surface properties from such data.

IV. Molecular System

The localized nature of PhD should be perhaps most useful in studying molecular adsorbate systems. The reason for this is that the electron source is localized on a particular atomic species so that, in effect, a structural determination of that species alone may be undertaken. Results on the CO/Ni(001) system exemplify this effect. Our experimental data on the carbon (1s) level is compared to Tong's calculated results in Fig. 7. The match to peak positions is quite good for $d_{CNi}^{\perp} = 1.8\text{Å}$, corresponding to the accepted one-fold (atop) adsorption site. The effect of varying the CO band length on the carbon (1s) NPP calculation is found to be quite small. The reason for this is that a backscattering event is required to produce structural sensitivity and will be discussed elsewhere.[10] Data on the oxygen (1s) level (available but not yet interpreted) should be quite sensitive to the CO bond length. This atomic specificity effect should simplify surface structural determinations over the usual LEED analyses in which all geometric parameters must be determined simultaneously.

V. Summary

The results of several normal emission photoelectron diffraction experiments have been presented which indicate the major structural sensitivities of the technique. The Se/Ni (001)

systems was the first system studied, and the results were used to show NPD's sensitivity to $d_\perp$ alone. The relation to SEXAFS was pointed out, and the corresponding importance of working at higher kinetic energies was emphasized. In addition, the technique's sensitivity to various forms of disorder was investigated with encouraging results. In particular, the Se/Ni(111) system indicated that applications to multiple site adsorption systems might be reasonably straightforward. Finally, the technique's strength in the study of molecular systems was shown.

Acknowledgements

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10. To be published.

Table I.

Systems Studied to Date by NPD:

c(2x2) Se/Ni(001)

p(2x2) Se/Ni(001)

disordered Se/Ni(001)

c(2x2) Se/Ni(011)

c(2x2) S/Ni(011)

c(2x2) S/Ni(001)

(2x2) Se/Ni(111)

$(\sqrt{3} \times \sqrt{3})$ R30° Se/Ni(111)

disordered Se/Ni(111)

CO/Ni(001)

CO/Ni(111)

O/Ni(001)

Figure Captions

Figure 1. 3-dimensional plot of the NPD effect.

Figure 2. Comparison between experimental and theoretical NPD results on the p(2x2) Se/Ni(001) system.

Figure 3. Comparison of frozen and annealed NPD results for the p(2x2) Se/Ni(001) system.

Figure 4. Results for low coverage disordered selenium overlayers on Ni(001) compared to c(2x2) results.

Figure 5. Comparison of frozen and annealed NPD results for (2x2) Se/Ni(111) system.

Figure 6. $(I-I_0)/I_0$ for the c(2x2) Se/Ni(001) system at three different temperatures.

Figure 7. NPD experimental and theoretical results for the Carbon (1s) level in CO/Ni(001).

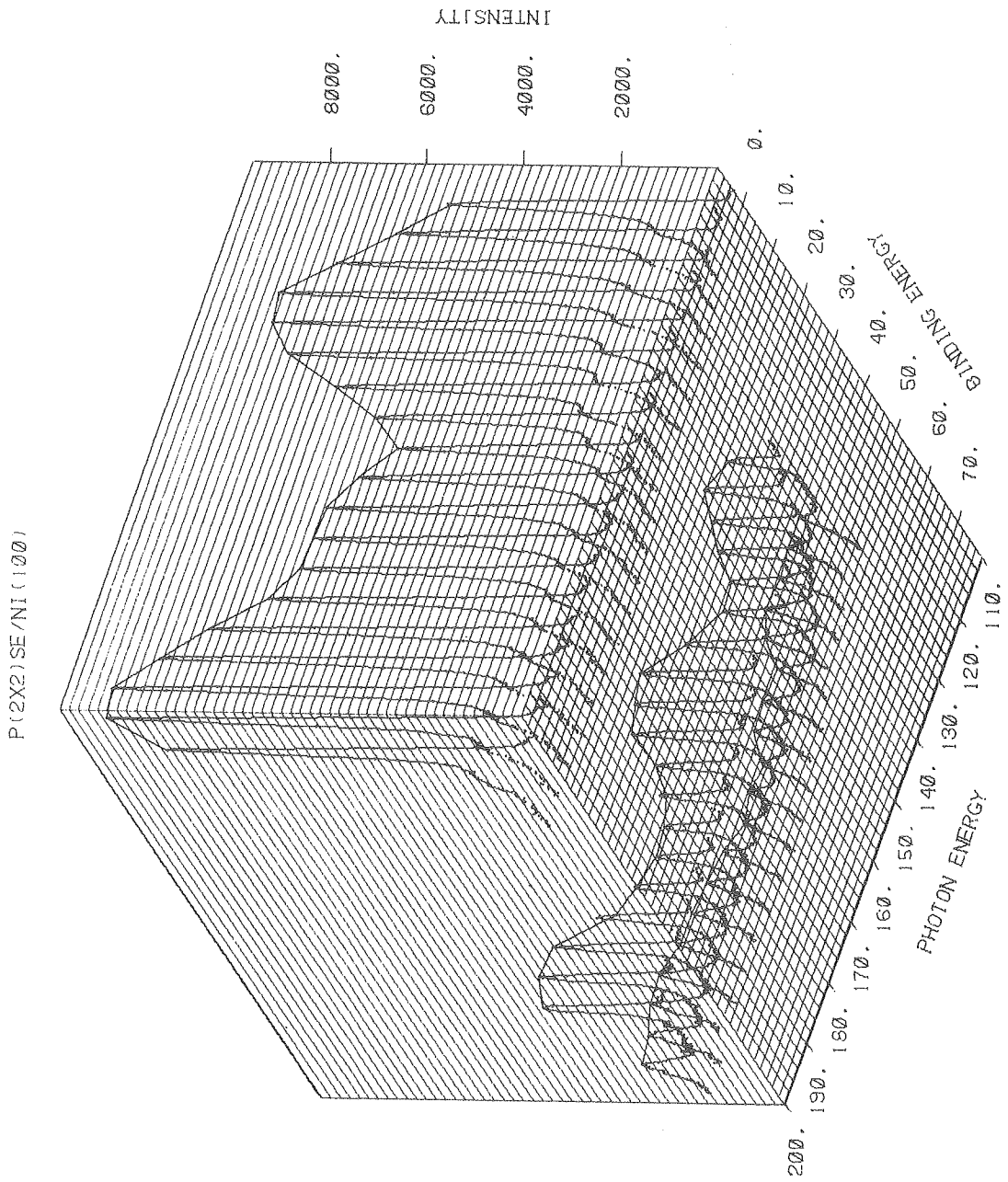

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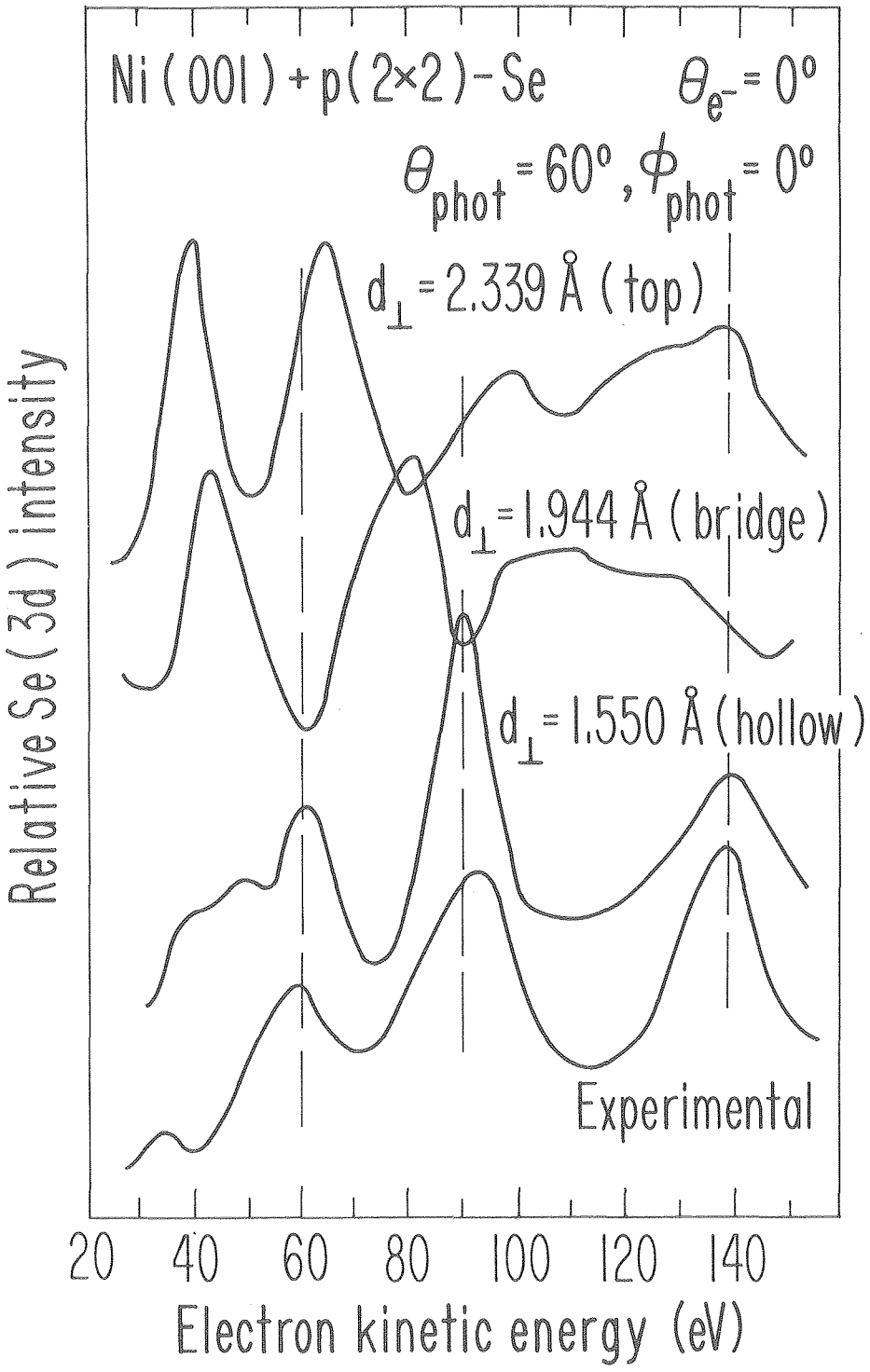
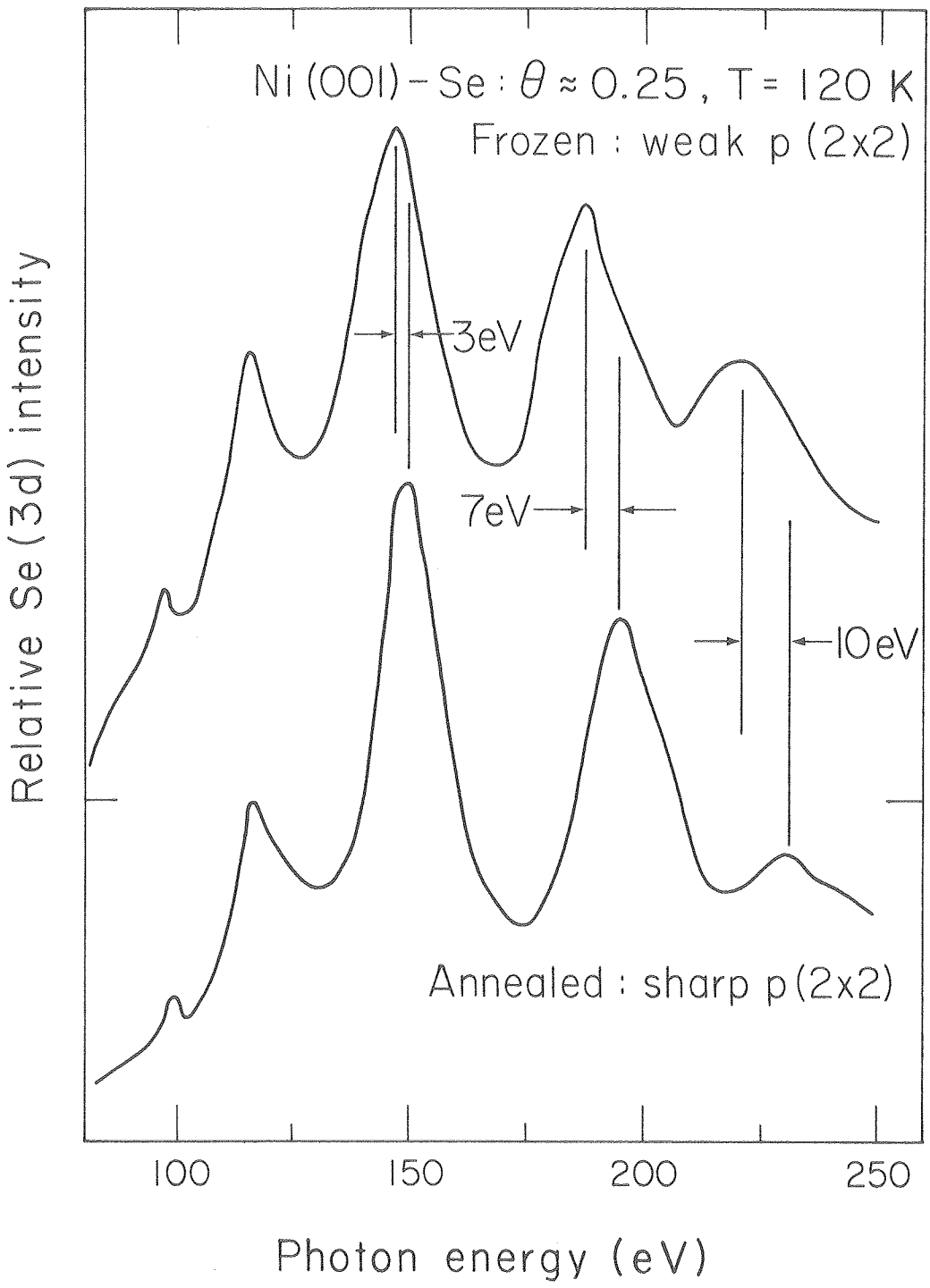
Figure 1.



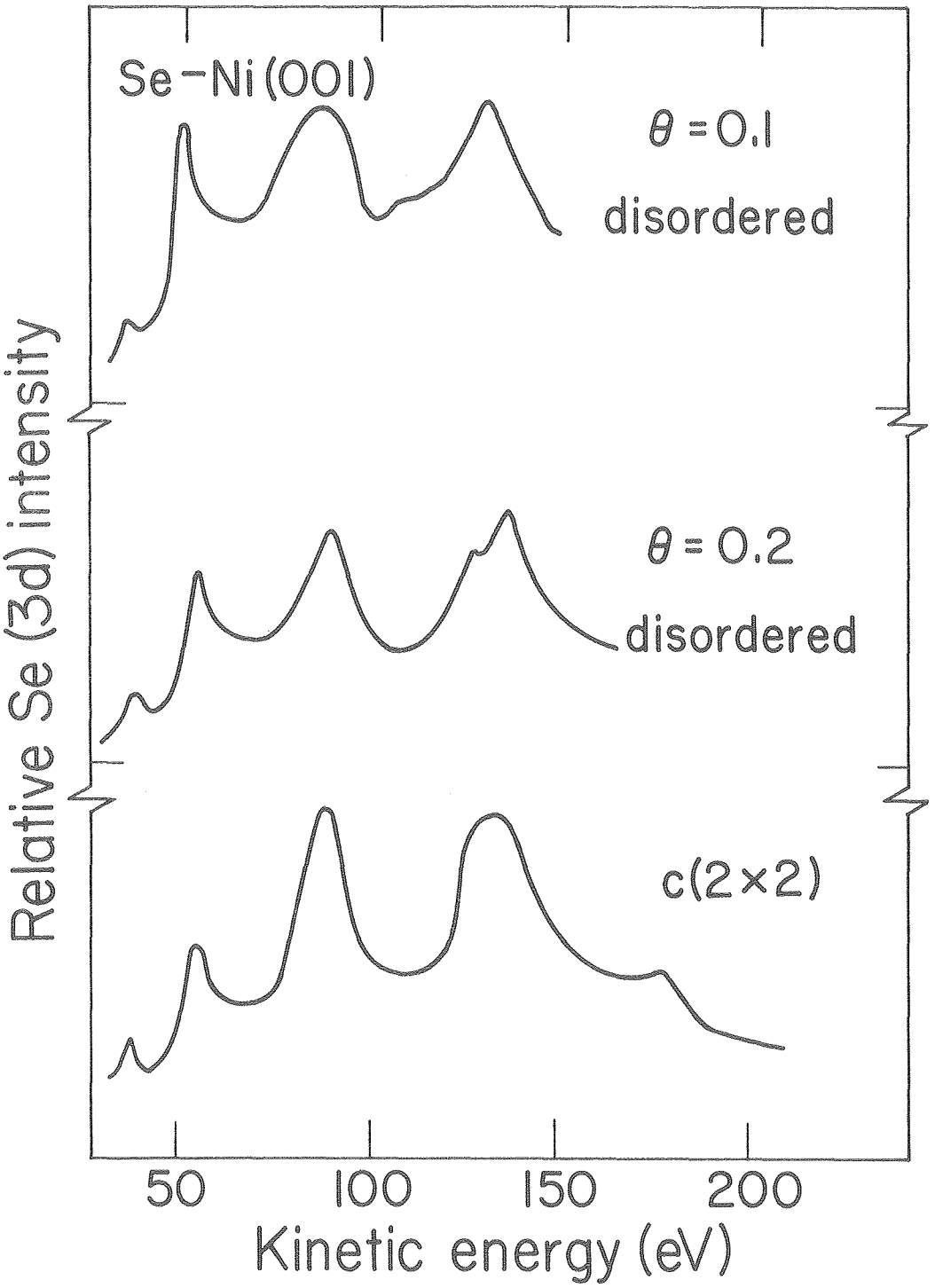
XBL7911-13241

Figure 2.



XBL805-1071

Figure 3.



XBL 794-1376

Figure 4.

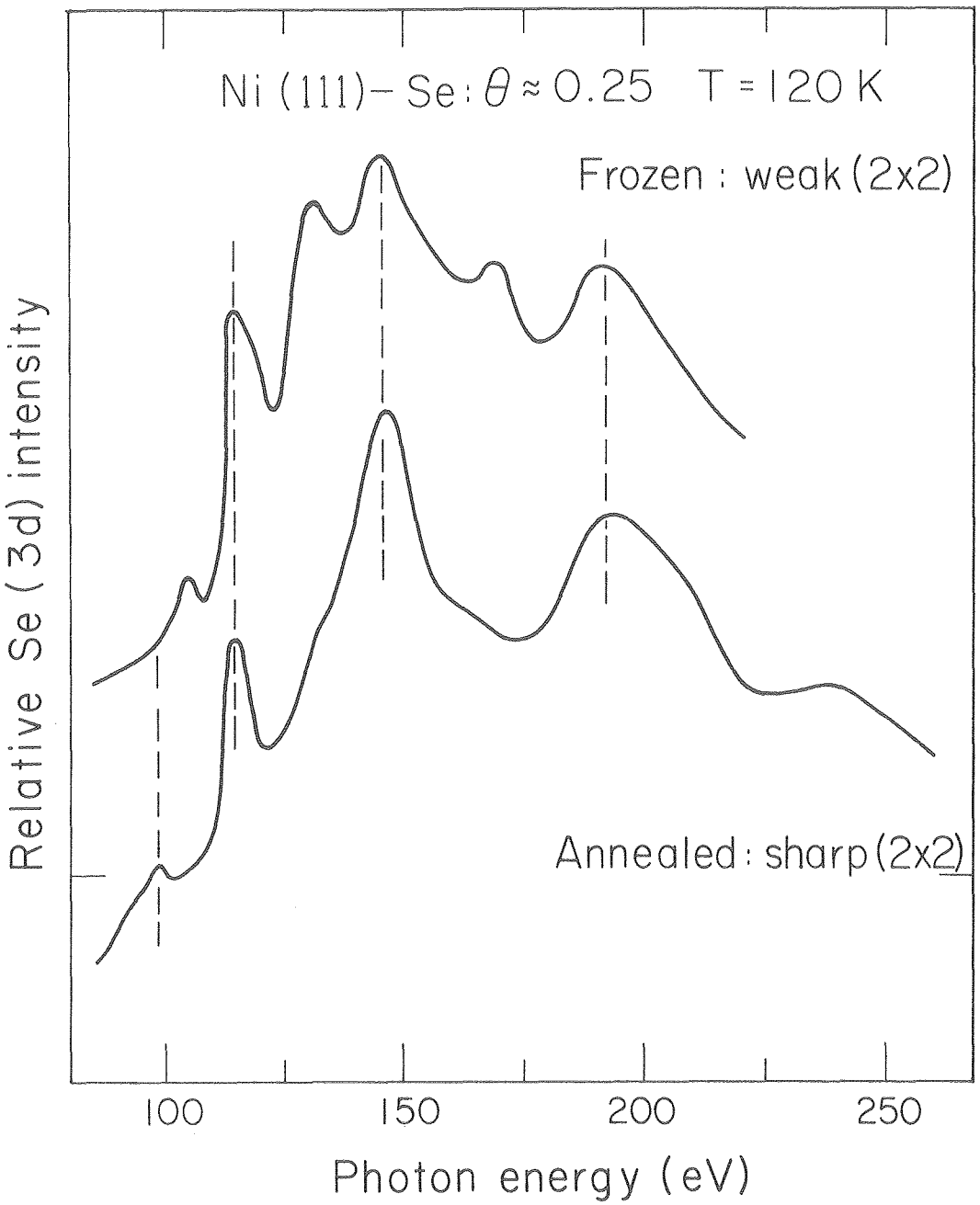


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Figure 5.

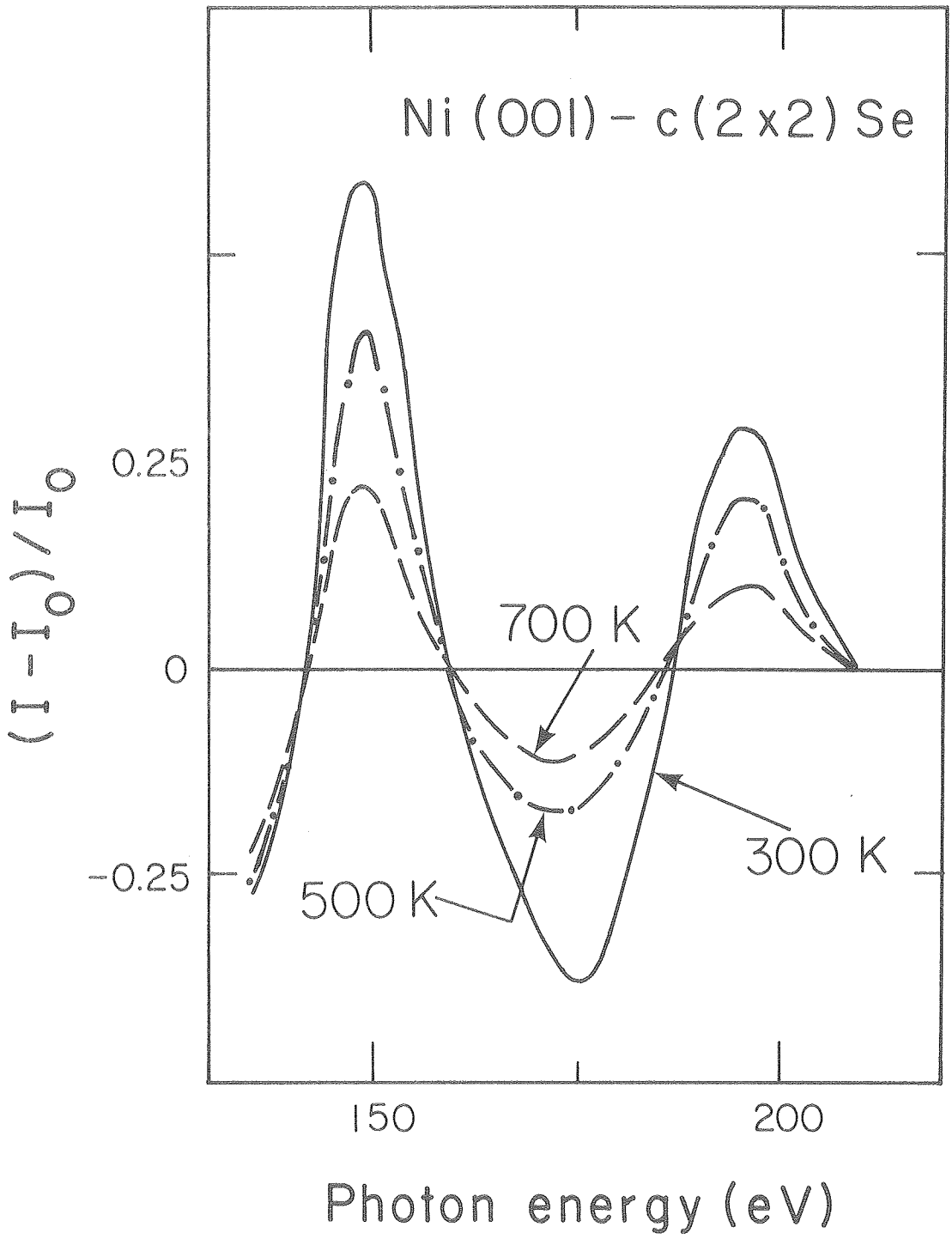

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Figure 6.

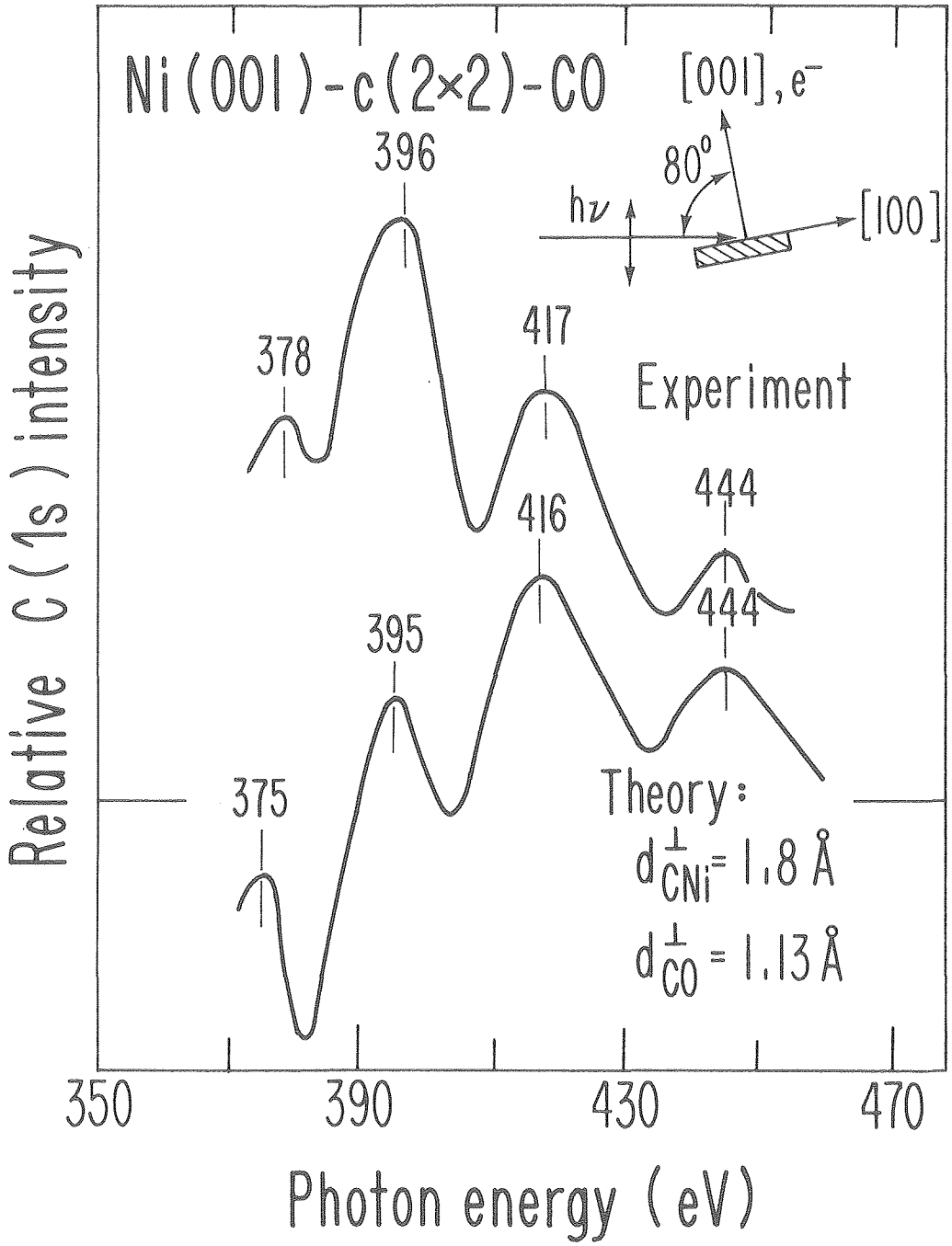

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Figure 7.