

Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title

FOURIER-TRANSFORM ANALYSIS OF NORMAL PHOTOELECTRON DIFFRACTION DATA FOR SURFACE-STRUCTURE DETERMINATION

Permalink

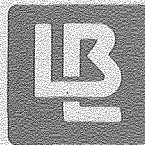
<https://escholarship.org/uc/item/3mm012dt>

Author

Hussain, Z.

Publication Date

1980-10-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

LAWRENCE
BERKELEY LABORATORY

MAR 2 1981

LIBRARY AND
DOCUMENTS SECTION

Submitted to Physical Review Letters

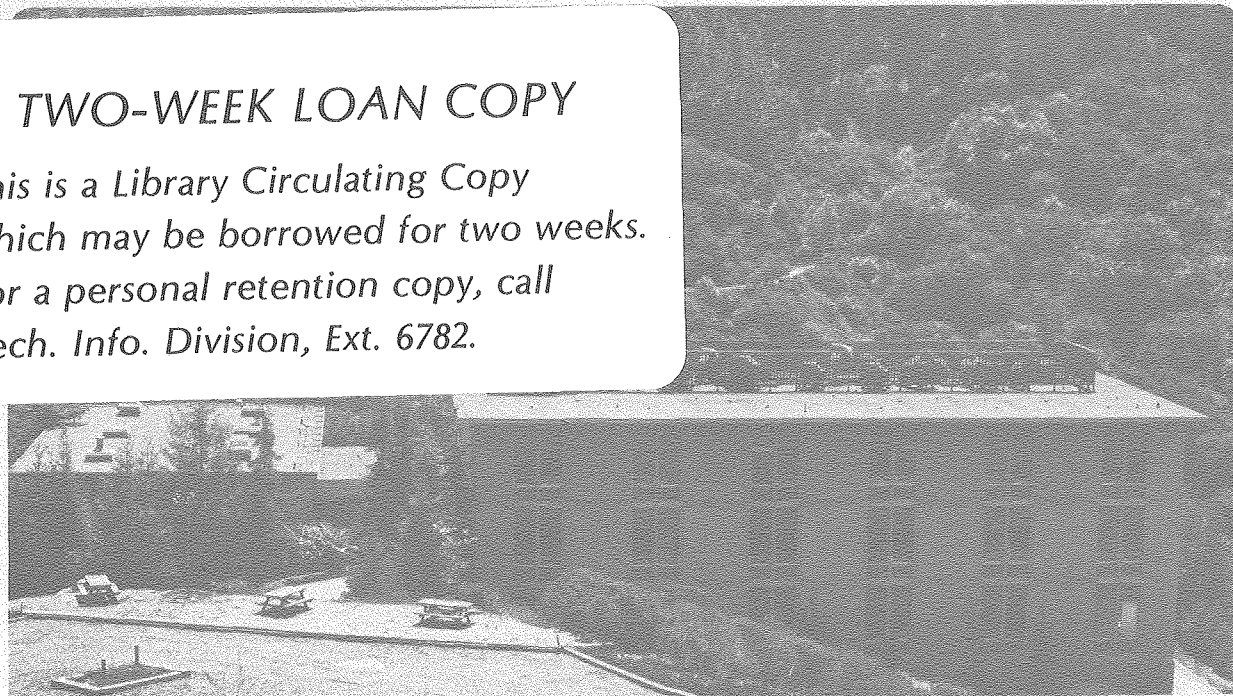
FOURIER-TRANSFORM ANALYSIS OF NORMAL PHOTOELECTRON
DIFFRACTION DATA FOR SURFACE-STRUCTURE DETERMINATION

Z. Hussain, D.A. Shirley, C.H. Li, and S.Y. Tong

October 1980

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-11686 c. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

FOURIER-TRANSFORM ANALYSIS OF NORMAL PHOTOELECTRON
DIFFRACTION DATA FOR SURFACE-STRUCTURE DETERMINATION

Z. Hussain, D.A. Shirley
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

C.H. Li,^{*} and S.Y. Tong
Surface Studies Laboratory
and
Department of Physics
University of Wisconsin
Milwaukee, Wisconsin 53201

ABSTRACT

A direct method for surface-structure determination from normal emission photoelectron diffraction (NPD) data is presented. Fourier transforms of the calculated NPD intensities yield peaks at adsorbate-substrate normal interlayer distances. Applications are demonstrated using theoretical NPD curves for the Se/Ni system calculated by dynamical theory. These results show that interplanar spacings between the overlayer and as many as four substrate layers could be determined with an accuracy of better than 2%.

* Present address: Department of Physics, National Tsing Hua University, Hsinchu, Taiwan, Republic of China.

Following the prediction by Liebsch¹ that diffraction effects are present in photoemission from adsorbate-atom core levels, such effects have been observed in several experimental configurations.²⁻⁴ In each case comparison of experimental results with curves derived from microscopic theory based on certain surface structures⁵ showed good agreement, thereby establishing photoelectron diffraction (PD) as a technique for structure determination. Unfortunately, PD data analysis appeared to require a scattering-theory computation of complexity up to the LEED level for each trial structure. In this Letter, however, we propose a direct method for analysis of normal photoelectron diffraction (NPD) data which is independent of model calculations. This method is based on Fourier transformation of NPD intensity curves to yield peaks in the transform at perpendicular distances $d_{\perp} + nb$, $n = 0, 1, 2, \dots$. Here d_{\perp} is the adsorbate-substrate spacing and b is the substrate interlayer spacing. Fourier-transform NPD (FTNPD) is thus comparable to EXAFS in its simplicity of analysis. The validity of FTNPD is tested by extensive Fourier analysis of theoretical NPD curves. Arguments are presented to show that FTNPD is less dependent on phase shifts than is EXAFS, and the reasons for perpendicular distances dominating the transform are discussed.

First we note some similarities between NPD and EXAFS, in which both differ from LEED. The intensity-versus-energy (I/E) curve in NPD is similar in appearance to either a LEED I/V curve or an EXAFS absorption curve. However, like the latter, NPD is atom-specific. In fact, both the NPD and EXAFS I/E curves result from (photoelectric) excitation of an atomic core level. Most of the diffractive structure in an NPD (EXAFS) curve carries information about the distance from the source atom to other planes (atoms). For both NPD and EXAFS, the diffractive structure

appears as sinusoidal modulation of the photoexcitation curve, and for both cases phase coherence between the scattered wave and the primary unscattered wave is provided by their common origin--the source atom. A different mechanism exists in LEED, which is not atom-specific and for which coherence must be provided by long-range order over $10^2 - 10^3 \text{ \AA}$ in the sample. Just as in EXAFS, where multiple scattering effects are unimportant and/or average out and single-scattering theory prevails,⁶ the modulation pattern in NPD at higher kinetic energies depends largely on single back scattering. In fact Li and Tong⁷ have shown that only a single backscattering event need be considered to calculate NPD curves for kinetic energies in the 100-400 eV range. Finally, in NPD, as in EXAFS, the periodicity in k space of the sinusoidal modulation increases with decreasing d_{\perp} where the theoretical curves are calculated over a small range of d_{\perp} . These similarities suggest that Fourier transformation of NPD I/E curve might yield distances directly, as in EXAFS.

To test this hypothesis we have taken the "experimental" approach of computing I/E NPD curves for the Se(3d) orbital in two known structures: $\sqrt{3} \times \sqrt{3} R30^\circ$ Se/Ni(111) and $p(2 \times 2)$ Se/Ni(001). These I/E curves were then Fourier transformed to ascertain whether the "input" interplanar spacings would yield features in the transforms. By varying the value of d_{\perp} for each structure we also tested the first derivative relationship of the input and derived distances. As discussed below, the agreement was very good to excellent in a total of six structures, or 21 interplanar distances, and the first derivatives showed excellent agreement.

Before discussing the detailed results, two aspects of our approach

deserve comment. First, it would be aesthetically more satisfying to derive structural features from a Fourier analysis of the theoretical I/E curves analytically, rather than computationally. Unfortunately an analytical theory has thus far proved to be evasive, although further work on this problem is continuing. Perhaps the results presented below will stimulate additional theoretical activity.

The other aspect is the use of theoretical rather than experimental I/E curves. This choice is supported by two facts. Wherever comparison is available between experiment and theory--about ten cases--the agreement is very good.⁸ Also for at least two cases, Fourier transforms of experimental data show peaks at appropriate distances in spite of very limited data ranges,⁹ in accord with the conclusions given below. Two factors strongly favored using theoretical, rather than experimental, I/E curves. First, d_1 could be varied at will, providing a much more sensitive test. Second, the "data" range could be extended in energy at will, again making the test more stringent and meaningful. The results indicate the value of making extra efforts to extend the experimental range of NPD.

Figures 1(a) and 2(a) show the theoretically calculated⁷ normalized NPD intensity

$$\chi(k) = (I - I_0) / I_0$$

plotted against k for the two Se/Ni systems. The intensity I_0 is a smooth atomic Se(3d) background, and I is the total intensity expected in an NPD experiment. In deriving $\chi(k)$ from calculated I/E curves (taking E as the electron kinetic energy), the free-electron relation

$$|\vec{k}| = \left[\frac{2m}{\hbar^2} (E + V_0) \right]^{1/2}$$

was assumed. Thus the effective inner potential V_0 sets the zero of the energy scale. In Fourier transform EXAFS data analysis, V_0 is taken as an adjustable parameter: we have followed this practice. Lee and Beni¹⁰ showed for EXAFS data analysis that the imaginary part of the Fourier transform, $\text{Im}F(r)$, is a symmetric function peaked at the neighbor distance, which should coincide with the peak of the absolute value, $F(r)$, of the transform. The condition that $\text{Im}F(k)$ and $F(r)$ should peak at the same distance is commonly used to choose the "zero" of the energy scale in EXAFS. An alternate method for determining the bond distances reliably in EXAFS by Fourier analysis has been discussed by Martins et al.¹¹ In their method V_0 is adjusted to optimize k-independence of the derived nearest-neighbor distance. We have adapted both methods for Fourier-analyzing the NPD, $\chi(k)$ curves, with similar results. The backscattering phase shift $\phi_b(k)$ and amplitude $A_b(k)$ dependence were eliminated before the transform; i.e.,

$$F(r) = \frac{1}{2\pi} \int \left[\frac{\chi(k) e^{-i\phi_b(k)}}{A_b(k)} \right] e^{-i2kr} g(k) dk \quad (1)$$

The $\phi_b(k)$ and $A_b(k)$ values calculated by Teo and Lee¹² for Ni were used. The square window function $g(k)$ was chosen to select a data range whose cutoff points fell at nodes in $\chi(k)$, and the lower limit was generally chosen to be above 100 eV kinetic energy, where the theory used to calculate the I/E curve is on firm ground.

Fig. 1(b) shows $F(r)$ according to Eq. 1 of the $\chi(k)$ shown in Fig. 1(a). The value of V_0 was set at 0 eV, which optimized the match of $F(r)$ with $\text{Im}F(r)$, as discussed above. Four prominent peaks occur in $F(r)$, at 2.83\AA , 4.49\AA , 6.66\AA and 8.66\AA . The last three peaks fall within $.08\text{\AA}$, of distances corresponding to $d_{\perp}+b$, $d_{\perp}+2b$ and $d_{\perp}+3b$, where d_{\perp} ($=2.51\text{\AA}$) is the perpendicular distance from Se to the first Ni(111) surface layer, used for calculating $\chi(k)$ in Fig. 1(a) and b ($=2.033\text{\AA}$) is the interlayer spacing in Ni(111). The first peak falls at a distance which is larger by 0.32\AA than the structural value of $d_{\perp} = 2.51\text{\AA}$ used in calculating $\chi(k)$ in Fig. 1(a). A similar discrepancy in the position of the first peak only occurs in $F(r)$ derived via Eq. (1) from $\chi(k)$ curves calculated using $d_{\perp} = 2.22\text{\AA}$ and 1.93\AA for the same $\sqrt{3} \times \sqrt{3}$ R30° Se(3d) - Ni(111) system. Figure 3 shows the distances Z_F , derived from $F(r)$, plotted against the input "structural" distances Z_S for all three d_{\perp} values. We conclude from this plot that:

1. The agreement between Z_F and Z_S is excellent for the 2nd, 3rd, and 4th interplanar distances; i.e., $d_{\perp}+nb$, with $n = 1,2,3$. A least-squares fit through these nine points gives a slope of 1.010 and an intercept of 0.012\AA .

2. The first interplanar distance, d_{\perp} , is high by about 0.3\AA in all three cases. Among the possible reasons for this discrepancy are effects of multiple scattering, and the choice of $g(k)$.

3. Of most importance, the derivatives of Z_F with respect to Z_S are near unity, and the dominant peaks in Z_F arise only from normal interplanar distances. Thus Z_F faithfully yields these distances and no others.

A parallel analysis for the p(2x2) Se/Ni(001) system is illustrated in Fig. 2, and Fig. 4 shows Z_F plotted against Z_S . In this case V_0 was optimized at 5 eV. Fig. 2b shows $F(r)$, for which the second peak (at 3.65\AA) and the third peak (at 5.56\AA) agree within 0.1\AA with the Z_S values for d_1+b and d_1+2b , with $d_1 = 1.94\text{\AA}$ and $b = 1.76\text{\AA}$ for Ni(001). The first peak lies at 2.10\AA , or 0.16\AA above d_1 . The broad peak at $\sim 7\text{\AA}$ does not correspond well to d_1+3b , and corresponding peaks for other d_1 values are also misshapen. They were omitted from Fig. 4. With these qualifications the p(2x2) Se/Ni(001) results were similar to those for the Ni(111) face. The remarkably close agreement between Z_F and Z_S for the two structures (six cases, or 21 points in all) needs no further comment. These results suggest that it is probably possible--given good data and careful analysis--to derive d_1 values (probably from the 2nd and 3rd peaks) accurate to $\sim 2\%$ by Fourier transformation of NPD data. In fact a Fourier transform analysis of NPD data from oxygen and sulfur overlayers on Ni(001) support this conclusion.⁹

In comparing Fourier-transform NPD with surface EXAFS, a complementarity is obvious: the determination of both d_1 from NPD and the nearest-neighbor distance from surface EXAFS would be especially desirable. NPD has the advantages over surface EXAFS that $\chi(k)$ is about an order of magnitude larger and that there is no contribution to the interference term from the source atom phase shift, which cancels in the direct and scattered waves.¹³

It seems clear that Fourier transformation of NPD I/E curves will yield normal interplanar spacings. In seeking a qualitative explanation, we note that lattice symmetry implies a necessary energy degeneracy between

(for example) electronic states propagating in the (100) and the ($\bar{1}00$) directions. Elastic scattering from one to the other is allowed. In contrast the needed degeneracy would in general be absent for oblique elastic scattering. Thus scattering of photoelectrons from a state propagating normally into the substrate into one propagating normally outward is favored. Therefore, the magnitude of photoelectron diffraction modulations is greater by a factor of 3-5 for normal emission as compared to non-normal emission.¹⁴ Further tests are needed, including experimental data sets extending to high kinetic energies.

Acknowledgements

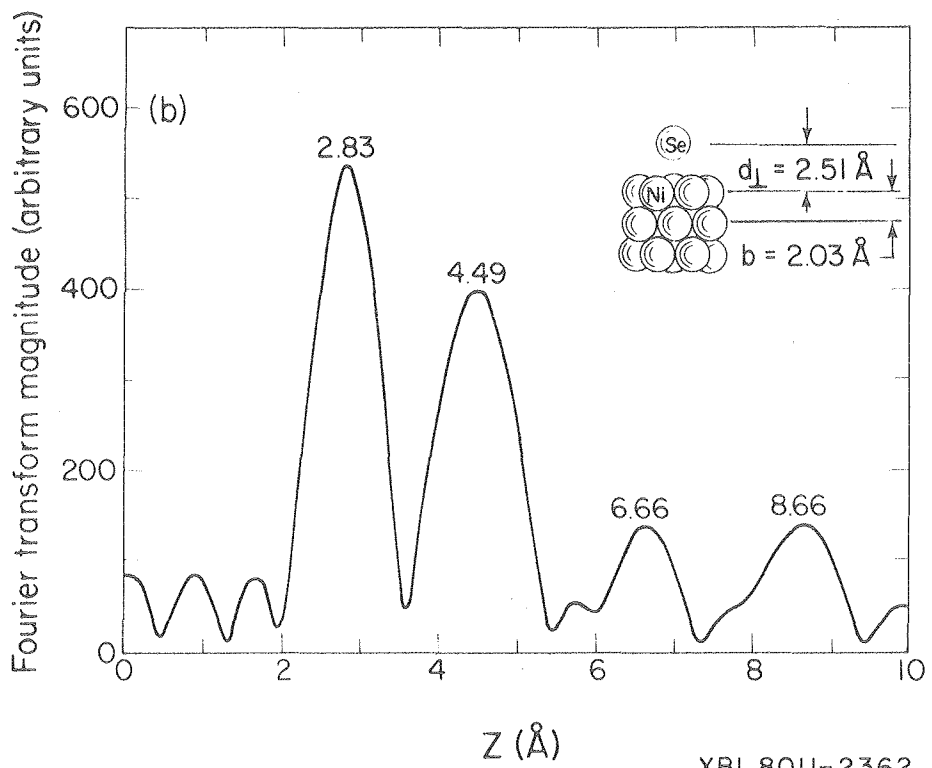
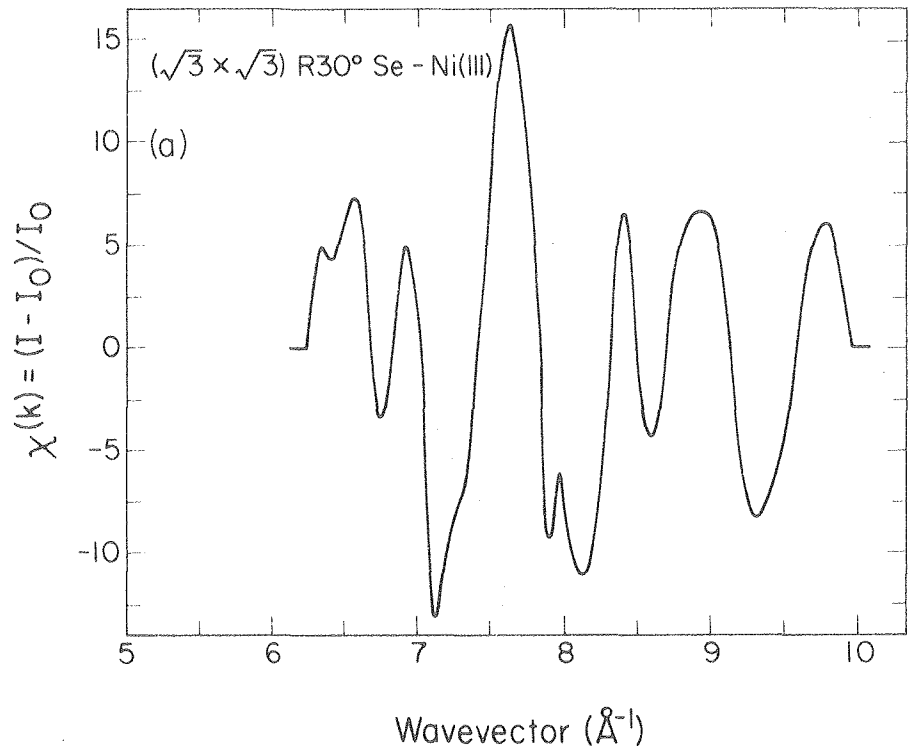
This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract No. W-7405-Eng-48. Work done at Milwaukee was supported by National Science Foundation No. DMR77-28112 and Petroleum Research Fund No. 11584-AC5,6.

References

1. A. Liebsch, Phys. Rev. Lett. 32, 1203 (1974); Phys. Rev. B 13, 544 (1976).
2. S. Kono, C.S. Fadley, N.F.T. Hall, and Z. Hussain, Phys. Rev. Lett. 41, 117 (1978).
3. D.P. Woodruff, D. Norman, B.W. Holland, N.V. Smith, H.H. Farrell, and N.M. Traum, Phys. Rev. Lett. 41, 1130 (1978).
4. S.D. Kevan, D.H. Rosenblatt, D. Denley, B.-C. Lu, and D.A. Shirley, Phys. Rev. Lett. 41, 1565 (1978).
5. C. H. Li and S. Y. Tong, Phys. Rev. Lett. 42, 901 (1979).
6. E.A. Stern, Phys. Rev. B 10, 3027 (1974).
7. C.H. Li and S.Y. Tong, Phys. Rev. Lett. 43, 526 (1979).
8. S.D. Kevan, Ph.D. thesis, Lawrence Berkeley Laboratory Report LBL-11017, May 1980 (unpublished).
9. D.H. Rosenblatt, J.G. Tobin, M.G. Mason, R.F. Davis, and D.A. Shirley, Lawrence Berkeley Laboratory Report LBL-11447, September 1980, submitted to Physical Review B.
10. P.A. Lee and G. Beni, Phys. Rev. B 15, 2862 (1977).
11. G. Martins, P. Rabe, N. Chwentner, and A. Werner, Phys. Rev. B 17, 1418 (1978).
12. B.K. Teo and P.A. Lee, J. Amer. Chem. Soc. 101, 2815 (1979).
13. P.A. Lee, Phys. Rev. B 13, 5261 (1976).
14. S.D. Kevan, D.H. Rosenblatt, D.R. Denley, B.-C. Lu, and D.A. Shirley, Phys. Rev. B 20, 4133 (1979).

Figure Captions

- Figure 1. (a) Theoretically calculated normalized NPD intensity versus k for $(\sqrt{3} \times \sqrt{3})$ R30° Se(3d) - Ni(111) with $d_{\perp} = 2.51\text{\AA}$ and inner potential $V_0 = 0$ eV. (b) Magnitude of the Fourier transform $|F(r)|$ according to Eq. (1) of the data in (a). Schematic representation of the adsorption geometry is shown in the inset.
- Figure 2. Same as Fig. 1, except showing $p(2 \times 2)$ Se(3d) - Ni(001) system with $d_{\perp} = 1.94\text{\AA}$ and $V_0 = 5$ eV.
- Figure 3. Fourier-transform derived distances Z_F plotted against input structural distances Z_S for three d_{\perp} values of 1.93\AA (circles), 2.22\AA (triangles), and 2.51\AA (squares) (see inset in Fig. 1 (b)). A linear curve with slope = 1.0 is drawn to facilitate comparison between Z_F and Z_S .
- Figure 4. Same as Fig. 3, except for three d_{\perp} values of 1.55\AA (circles), 1.94\AA (triangles) and 2.34\AA (squares) (see inset in Fig. 2 (b)).



XBL8011-2362

Figure 1

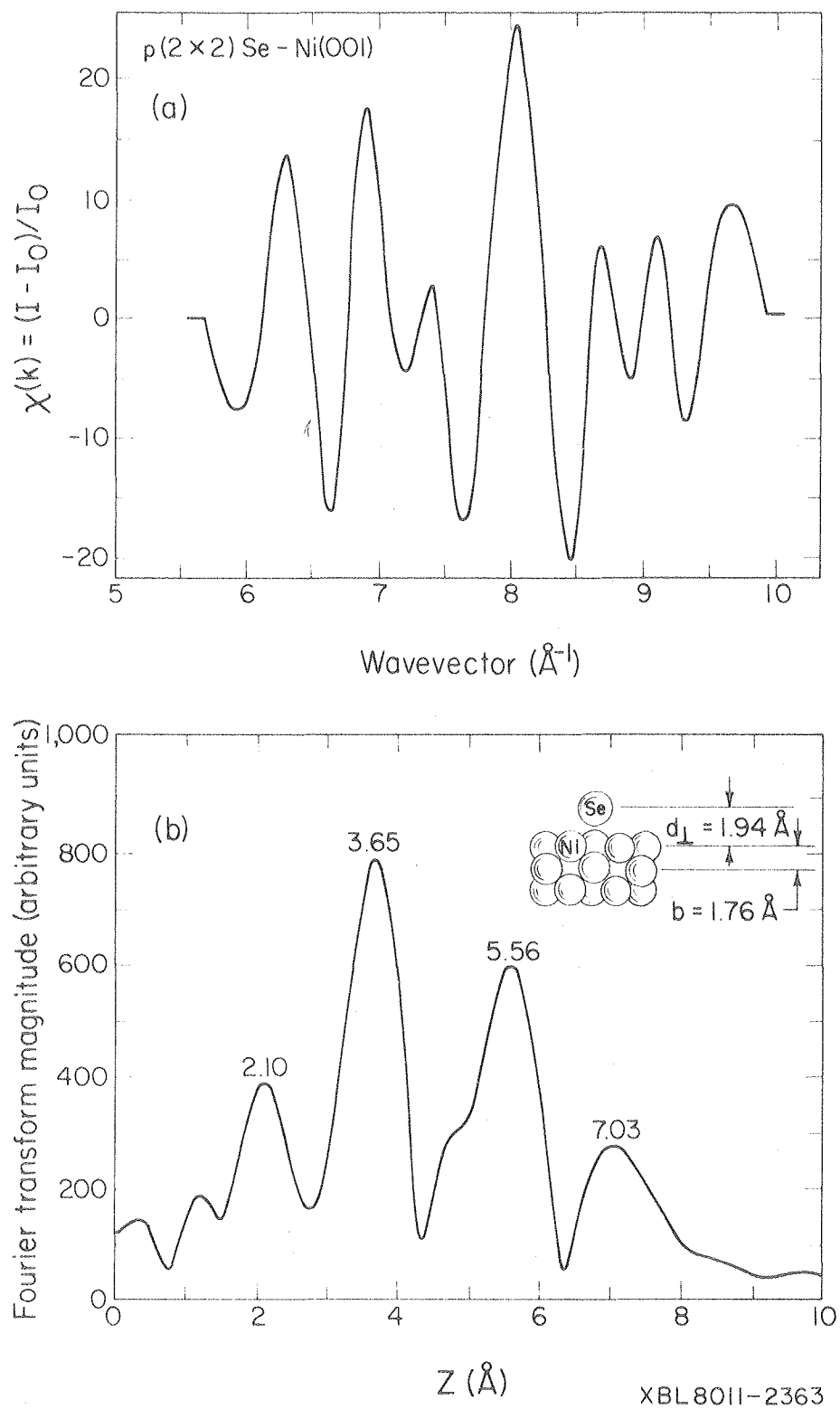
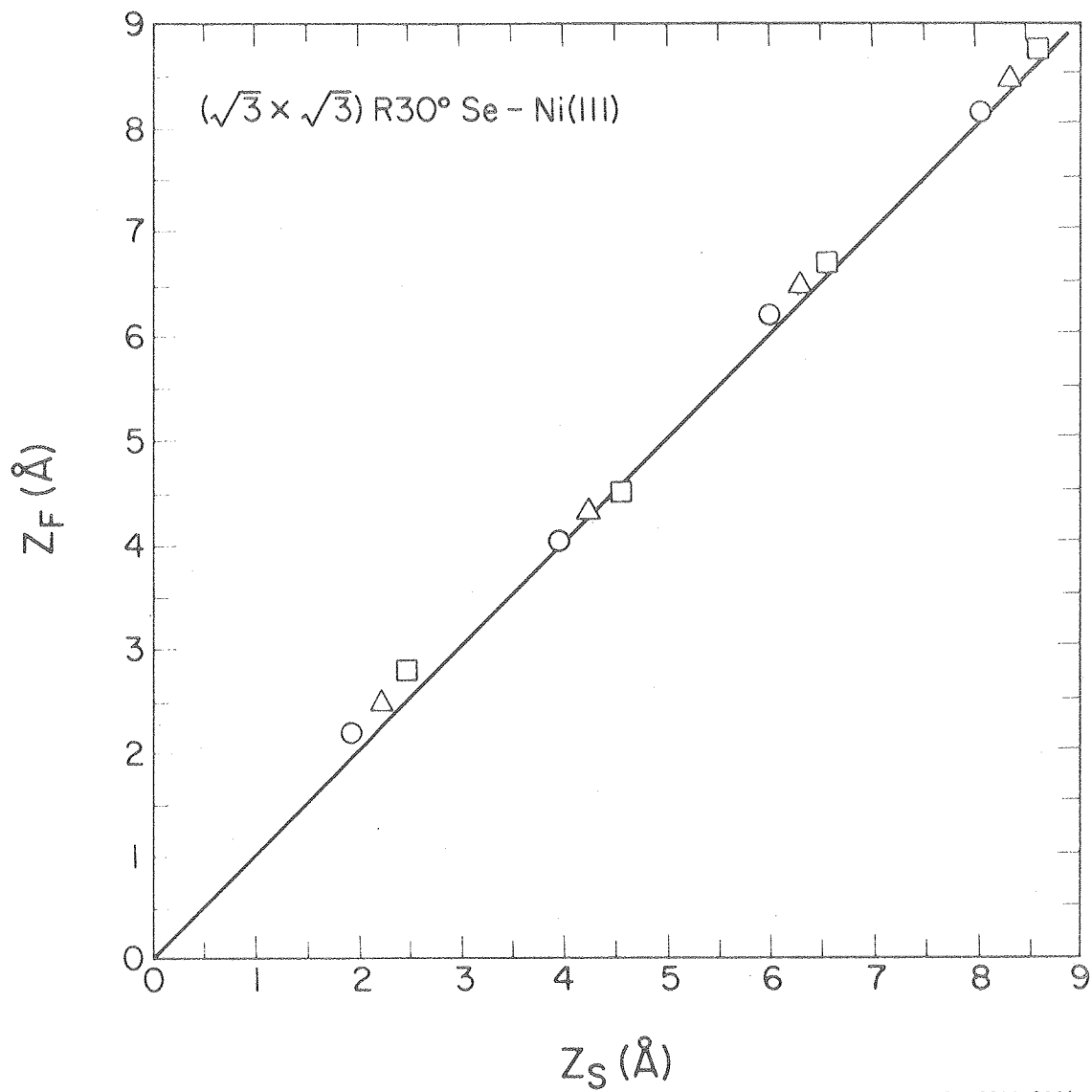


Figure 2



XBL 8011-2364

Figure 3

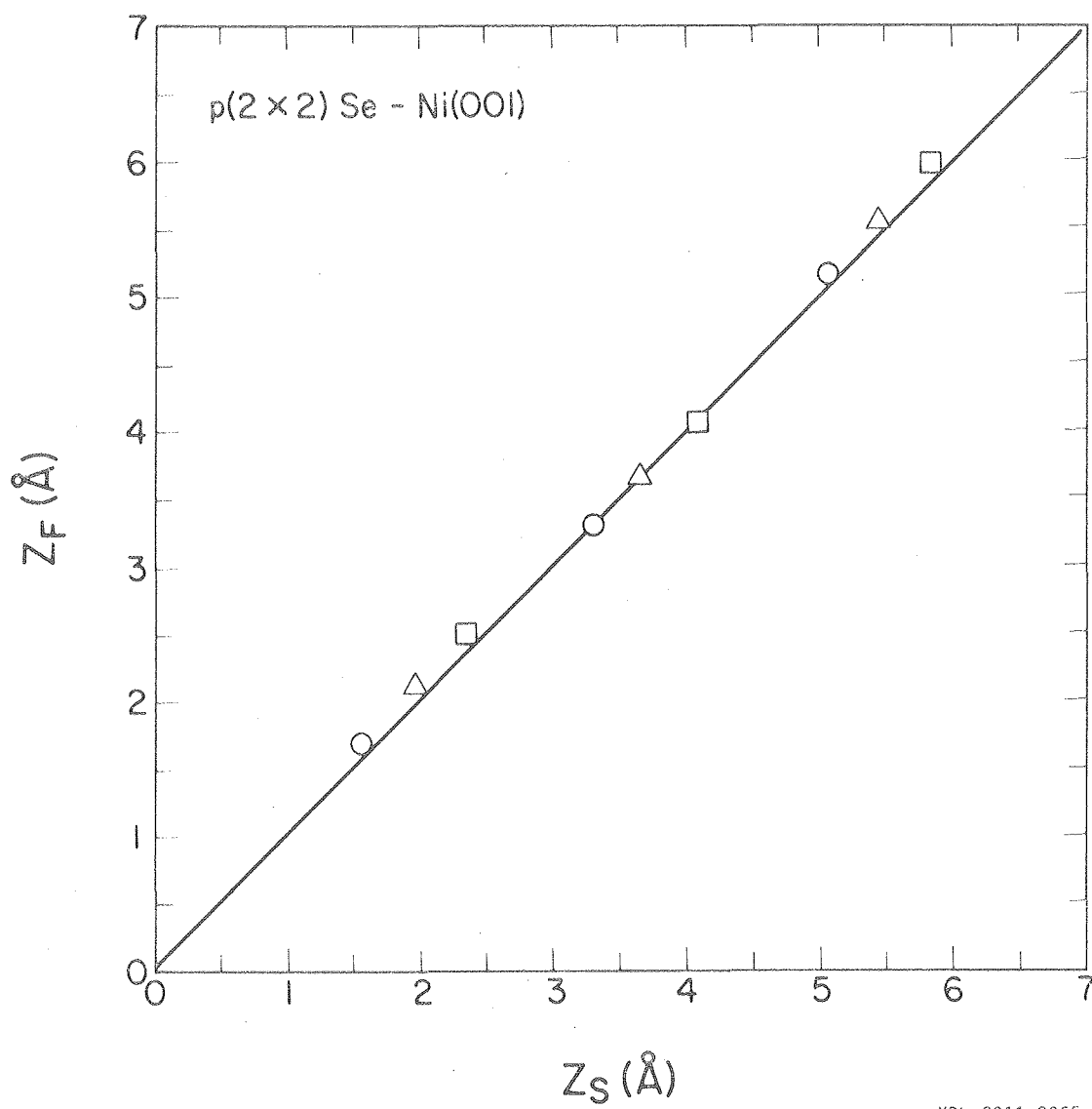


Figure 4

XBL 8011-2365