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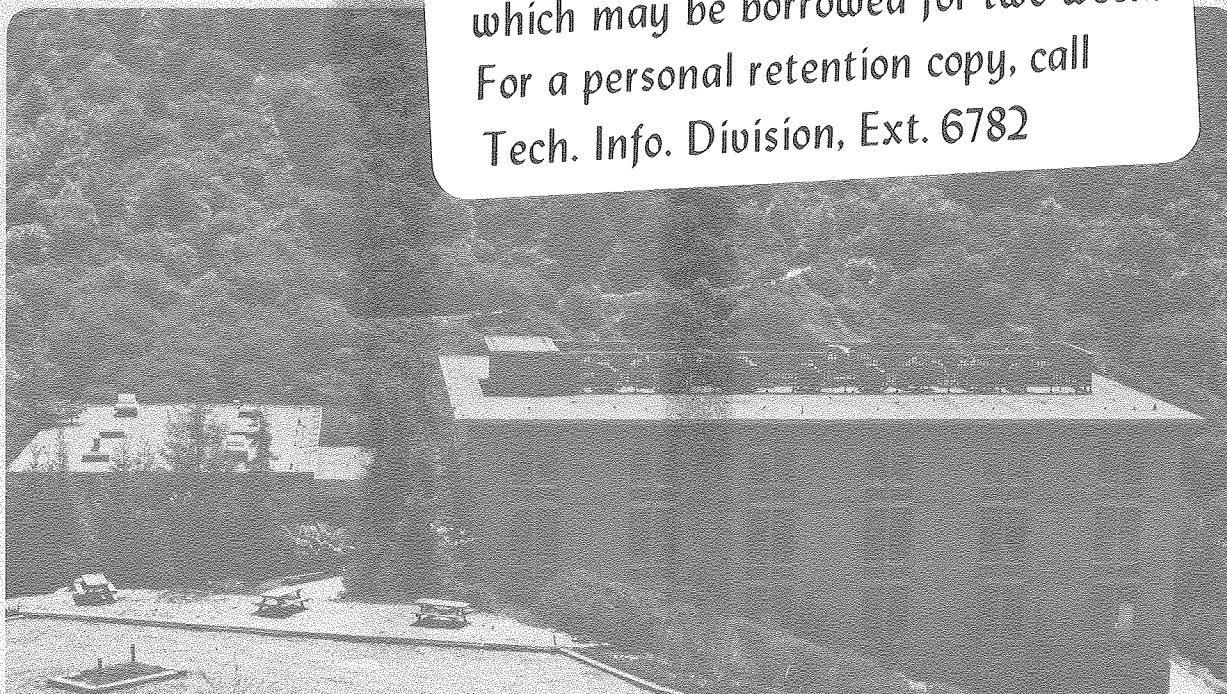
FOURIER-TRANSFORM ANALYSIS OF NORMAL PHOTOELECTRON
DIFFRACTION DATA FOR SURFACE-STRUCTURE DETERMINATION

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

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CLASSIFICATION: PHYSICS

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

(adsorbate geometry/Se-Ni system/quasi-dynamical scattering theory)

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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 3%.

Following the prediction by Liebsch (1) 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 structures (5) 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 paper, 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 \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 Tong (7) 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° Se/Ni(111) and p(2x2) 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 18 interplanar distances, and the first derivatives showed excellent agreement.

Before discussing the detailed results, we comment on 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 favor using theoretical, rather than experimental, I/E curves. First, d_{\perp} 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 calculated (7) 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 Beni (10) 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 Martens 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 Lee (12) 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 2.83Å, 4.49Å, 6.66Å and

8.66Å. The last three peaks fall within 0.08Å, of distances corresponding to $d_{\perp}+b$, $d_{\perp}+2b$ and $d_{\perp}+3b$, where d_{\perp} (=2.51Å) is the perpendicular distance from Se to the first Ni(111) surface layer, used for calculating $\chi(k)$ in Fig. 1(a) and b (=2.033Å) is the interlayer spacing in Ni(111). The first peak falls at a distance which is larger by 0.32Å than the structural value of $d_{\perp} = 2.51\text{Å}$ 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 $d = 2.22\text{Å}$ and 1.93Å 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 0.012Å.

2. The first interplanar distance, d_{\perp} , is high by about 0.3Å in all three cases. We believe this discrepancy is due to the limited energy range used and the choice of $\phi_b(k)$.

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 $d_{\perp}+b$ and $d_{\perp}+2b$, with $d_{\perp} = 1.94\text{\AA}$ and $b = 1.76\text{\AA}$ for Ni(001). The first peak lies at 2.10\AA , or 0.16\AA above d_{\perp} . The broad peak at $\sim 7\text{\AA}$ does not correspond well to $d_{\perp}+3b$, and corresponding peaks for other d_{\perp} 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 18 points in all) needs no further comment. These results suggest that it is probably possible--given good data and careful analysis--to derive d_{\perp} values (probably from the 2nd and 3rd peaks) accurate to better than 3% 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_{\perp} 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 curves will yield normal interplanar spacings. The explanation lies in the fact that at high kinetic energies ($E_k > 100$ eV), the layer scattering amplitudes are sharply peaked in the forward (scattering angle $\theta = 0$) and back ($\theta = \pi$) directions (14). In band-structure terminology, the photoelectrons travels into the solid in conduction-band states which propagate in, e.g., the $[001]$ direction. They can scatter elastically into states propagating along $[00\bar{1}]$. This is a general consequence of the crystal symmetry: hence elastic scattering through π is favored. Knowledge of d_{\perp} from the adsorbate to any one substrate layer fixes the adsorption site in many cases. A tabulation of $\phi_b(k)$ as a function of the layer at which back-scattering occurs will be given elsewhere (14).

Acknowledgements

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References

1. Liebsch, A. (1974) *Phys. Rev. Lett.* 32, 1203-1206.
2. Kono, S., Fadley, C.S., Hall, N.F.T. & Hussain, Z. (1978) *Phys. Rev. Lett.* 41, 117-120.
3. Woodruff, D.P., Norman, D., Holland, B.W., Smith, N.V., Farrel, H.H. & Traum, N.M. (1978) *Phys. Rev. Lett.* 41, 1130-1133.
4. Kevan, S.D., Rosenblatt, D.H. Denley, D., Lu, B.-C. & Shirley, D.A. (1978) *Phys. Rev. Lett.* 41, 1565-1568.
5. Li, C.H. & Tong, S.Y. (1979) *Phys. Rev. Lett.* 42, 901-904.
6. Stern, E.A. (1974) *Phys. Rev. B* 10, 3027-3037.
7. Li, C.H. & Tong, S.Y. (1979) *Phys. Rev. Lett.* 43, 526-529.
8. Kevan, S.D. (May 1980) Ph.D. thesis, Lawrence Berkeley Laboratory Report LBL-11017 (unpublished).
9. Rosenblatt, D.H., Tobin, J.G., Mason, M.G., Davis, R.D., Shirley, D.A., Li, C.H. & Tong S.Y. (1981) *Phys. Rev. B* 23, 3828-3835.
10. Lee, P.A. & Beni, G. (1977) *Phys. Rev. B* 15, 2862-2883.
11. Martens, G., Rabe, P., Chwentner, N. & Werner, A. (1978) *Phys. Rev. B* 17, 1481-1488.
12. Teo, B.K. & Lee, P.A. (1979) *J. Amer. Chem. Soc.* 101, 2815-2832.
13. Lee, P.A. (1976) *Phys. Rev. B* 13, 5261-5270.
14. Tong, S.Y. & Tang, G.C., to be published.

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(2x2) 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 values of 1.55\AA (circles), 1.94\AA (triangles) and 2.34\AA (squares) (see inset in Fig. 2 (b)).

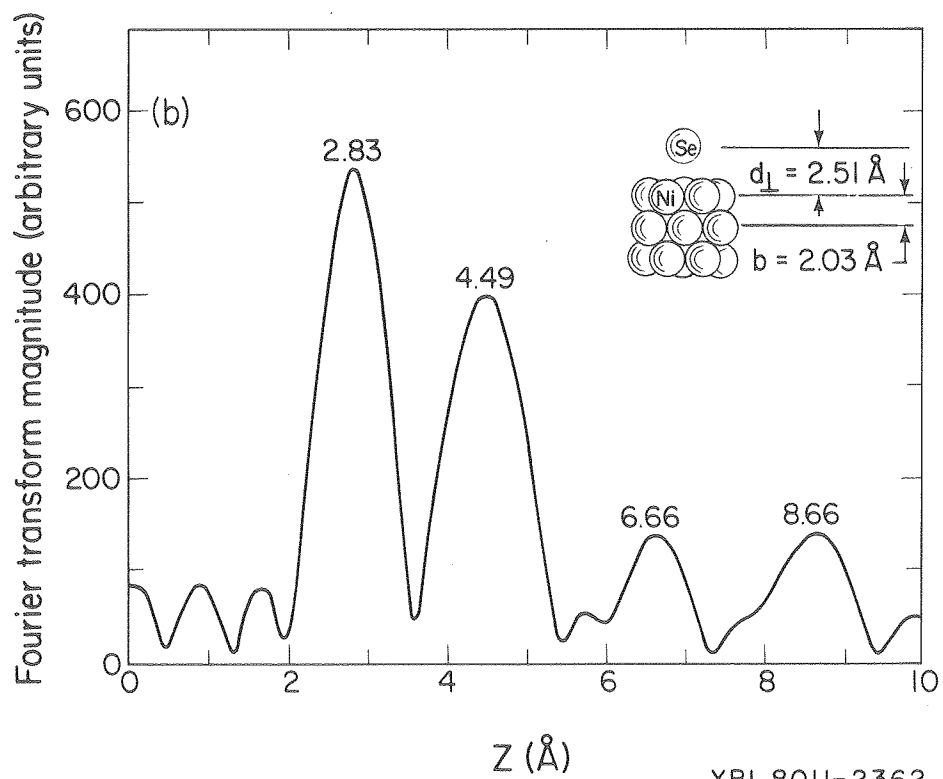
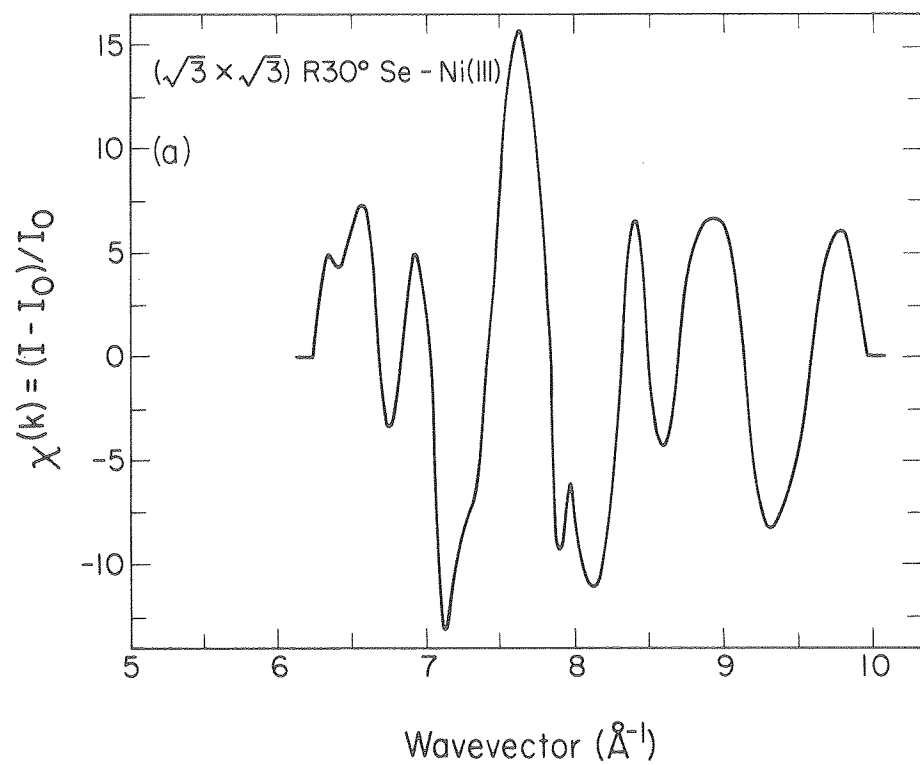
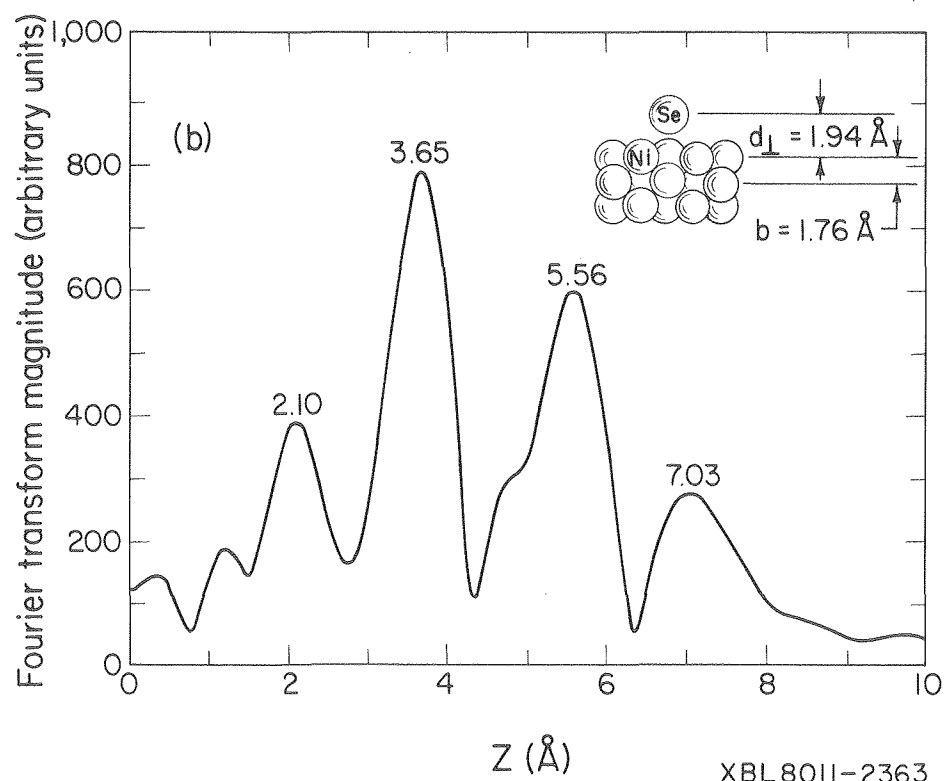
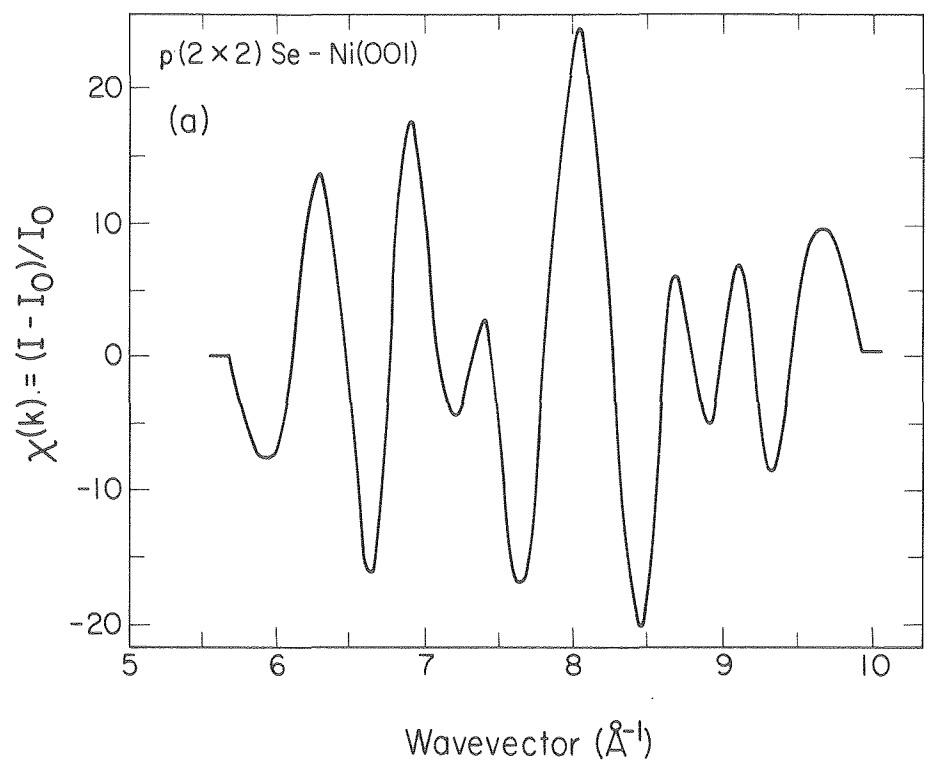
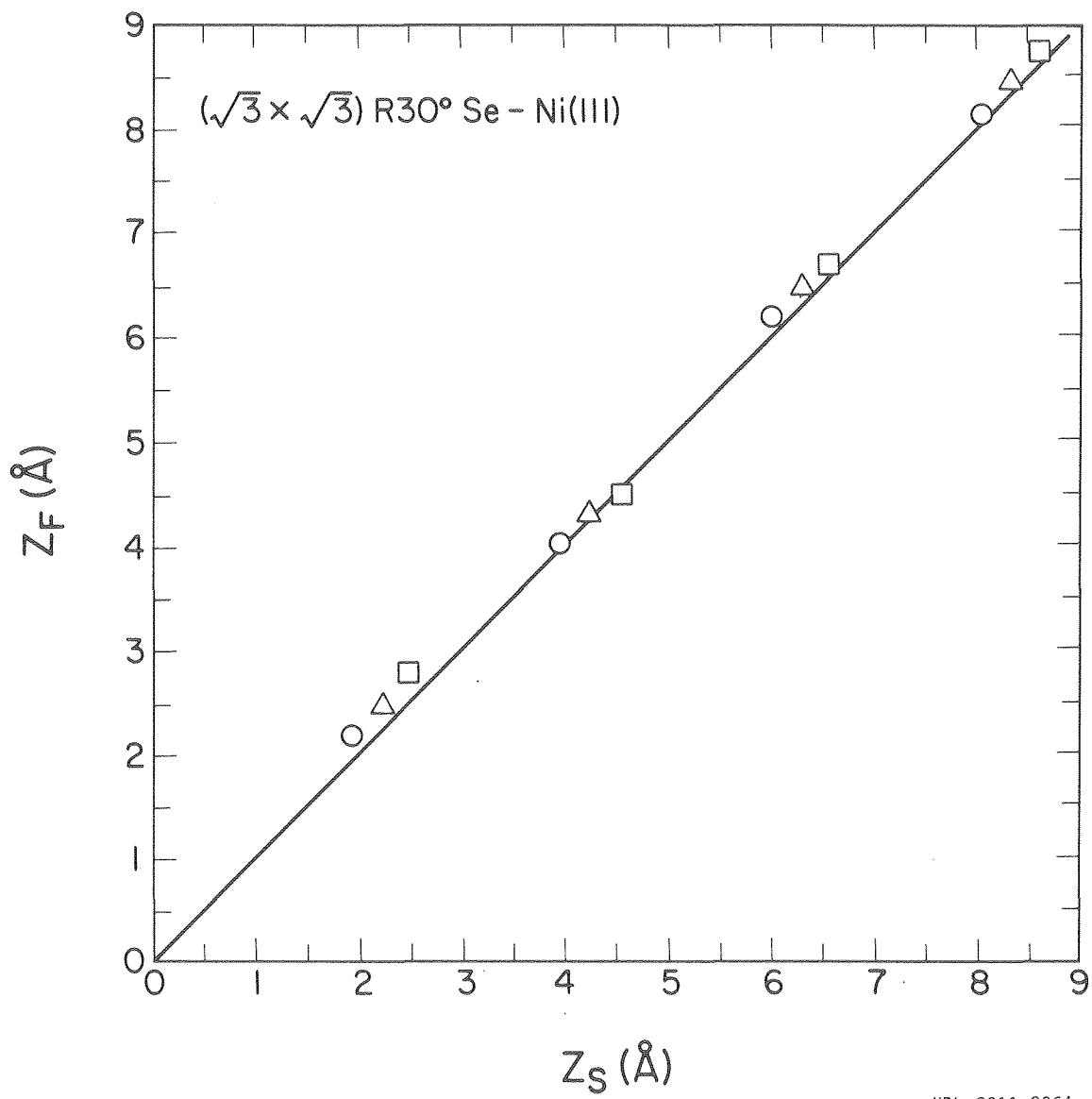


Figure 1



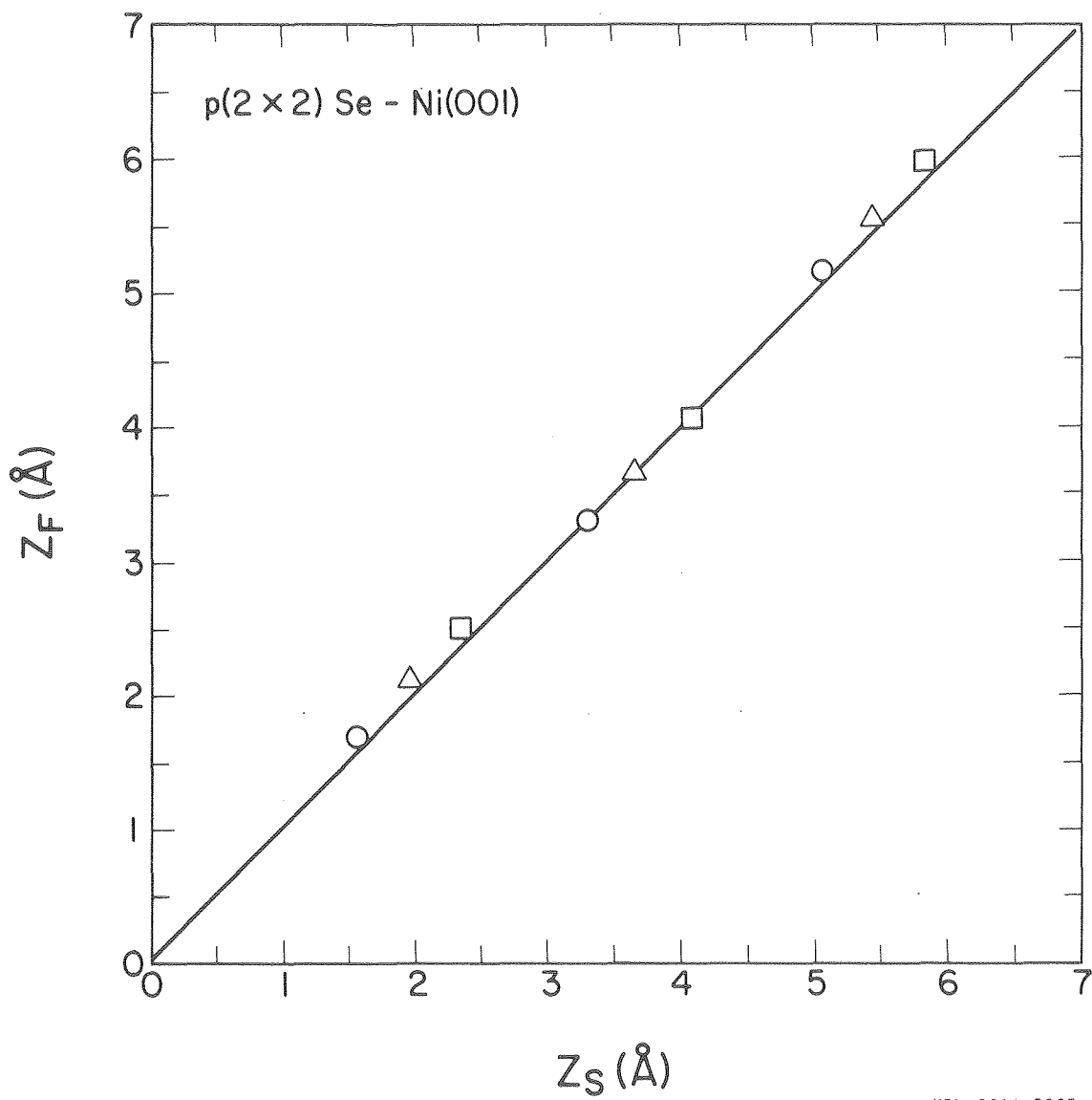
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Figure 2



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Figure 3



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Figure 4

