

## Powder Diffraction with Synchrotron Radiation. II. Dispersion Factors of Ni

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### Abstract

Accurate values of the absolute integrated reflections from a powder sample of Ni have been determined from measurements with synchrotron radiation as a function of scattering angle over a range of energies from 290 to 3 eV below the Ni *K*-absorption edge, 8332 eV. From these values, the dispersion factor  $f'$  has been determined by comparison of the experimental scattering factors with the theoretical values of Wang & Callaway [*Phys. Rev. B* (1977), **15**, 298-306] based upon a LCAO calculation with the KSG (Kohn & Sham and Gaspar) approximation for exchange [Kohn & Sham (1965). *Phys. Rev.* **140**, A1133-1138; Gaspar (1954). *Acta Phys. Acad. Sci. Hung.* **3**, 263-286]. The values obtained for  $f'$  as a function of energy are within about 0.2 electron units of those calculated from measured and tabulated absorption coefficients by Bonse & Hartmann-Lotsch [*Nucl. Instrum. Methods* (1984), **222**, 185-188] and within about 0.5 electron units of their direct measurements by interferometric techniques in the range 30 to 3 eV below threshold. The variation of  $f'$  with scattering angle is negligibly small (less than 0.2 electron units on average). The present experiment demonstrates that powder techniques provide a simple and convenient method for the measurement of  $f'$  for many materials that are not available in forms suitable for the application of other techniques such as interferometry.

### I. Introduction

Recently, there has been renewed interest in the X-ray dispersion factors  $f'$  and  $f''$  now that tunable synchrotron radiation has made possible scattering experiments under near-resonant conditions. On the one hand, theoretical calculations of  $f'$  and  $f''$  can now be checked by direct measurements and, on the other, reliable values can be obtained for measurements that require anomalous dispersion techniques.

Most of the recent measurements of  $f'$  are based on X-ray interferometry (Bonse & Hartmann-Lotsch, 1984; Siddons & Hart, 1983). Results are available for a number of elements that can be obtained as thin

uniform foils (Co, Ni, Cu, Fe, Zn, Se, W, Au). The measurements are supposedly very precise, but some of the results are clearly contradictory. The values calculated from the absorption coefficients through the Kramers-Kronig relations are generally in fair agreement with the measured values of  $f'$ , but again there is some disagreement in certain cases.

The angular dependence of  $f'$  and  $f''$  has been debated for a long time. Hönl-type calculations, which have been supported by measurements (Hildebrandt, Stephenson & Wagenfeld, 1973), suggest that  $f'$  depends only very slightly on  $\sin \theta/\lambda$ , in contrast to calculations, which show noticeable effects for both  $f'$  and  $f''$  (Hazell, 1975). Interferometric measurements give  $f'$  at zero angle, as do measurements of the critical angle or calculations from the absorption coefficient through the Kramers-Kronig relations (Bonse & Hartmann-Lotsch, 1984; Dreier, Rabe, Malzfeldt & Niemann, 1984; Hoyt, de Fontaine & Warburton, 1984). To our knowledge, there are no recent experiments on pure elements in which  $f'$  has been determined as a function of angle although single-crystal measurements on Gd and Sm complexes (Templeton, Templeton, Phizackerley & Hodgson, 1982) have been reported.

The accurate determination of the absolute integrated reflections from a powder sample of Ni with 1.54 Å radiation, which is reported in paper I (Suortti, Hastings & Cox, 1985), has encouraged us to extend measurements to wavelengths very close to the *K*-absorption edge of Ni. In addition to giving an independent determination of  $f'$ , measurements of reflections at different scattering angles should reveal any angular dependence that would be of significance in diffraction experiments.

### II. Structure factor

In the following we will separate the atomic scattering amplitude  $f$  into the nonresonant part  $f_0$  and the components  $f_D$  and  $f_Q$ , which correspond to dipole and quadrupole transitions, respectively. The multipole expansion converges very rapidly, and the higher terms can be neglected. The dispersion terms are complex, so that  $f_D = f'_D + if''_D$  and  $f_Q = f'_Q + if''_Q$ . The dipole and quadrupole terms have their own angular dependence, and these will be considered separately in the following. Polarization of the incident beam

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also affects the scattering amplitude, but the angular dependence due to this is usually incorporated in the 'polarization factor'. For the component with the electric vector perpendicular to the plane of diffraction, the atomic scattering amplitude is (Wagenfeld, 1975)

$$f_{\sigma} = (f_0 + f'_D + if''_D) + (f'_Q + if''_Q) \cos 2\theta, \quad (1a)$$

and, for the parallel component,

$$f_{\pi} = (f_0 + f'_D + if''_D) \cos 2\theta + (f'_Q + if''_Q) \cos 4\theta. \quad (1b)$$

The intensity of the scattered radiation is obtained when the components are weighted by the polarization ratio of the incident beam,  $K = P_{\pi}/P_{\sigma}$ . Accordingly,

$$|F|^2 = (f_{\sigma} f_{\sigma}^* + K f_{\pi} f_{\pi}^*) / (1 + K), \quad (2)$$

and after substitution from (1a) and (1b),

$$\begin{aligned} |F|^2 = & [(1 + K \cos^2 2\theta) / (1 + K)] |f_0 + f_D|^2 \\ & + 2a \cos 2\theta (1 + K \cos 4\theta) / (1 + K) \\ & + b (\cos^2 2\theta + K \cos^2 4\theta) / (1 + K), \end{aligned} \quad (3)$$

where

$$|f_0 + f_D|^2 = (f_0 + f'_D)^2 + (f''_D)^2, \quad (4a)$$

$$a = f'_Q (f_0 + f'_D) + f''_D f''_Q, \quad (4b)$$

$$b = (f'_Q)^2 + (f''_Q)^2. \quad (4c)$$

The results of Hildebrandt *et al.* (1973) indicate that  $f''_0/f''_D$  is typically 0.01 to 0.05. The same is presumably true for the real parts, and so  $a \gg b$ . The angular dependence of the first term in (3) is just the normal 'polarization factor' and hence the angle-dependent dispersion effects are dominated by the second term in (3), and this differs from zero only when  $f'_Q$  or  $f''_Q$  do.

The expressions above are valid only for pure elements. Clearly, these results can be extended to compounds.

### III. Measurements

The details of absolute intensity measurements from a powder sample are reported in paper I. In the present case three reflections of Ni were used: 111, 311 and 331. At energies just below the Ni *K* edge (8332 eV) the scattering angles are about 43, 89 and 134°, respectively, so that the angle-dependent second term in (3) should be clearly different in the three cases.

Measurements were made at nine energies ranging from 290 to 3 eV below the Ni *K* edge. In order to eliminate possible systematic errors from fill to fill of the storage ring, measurements at any single energy were made only during a given fill. We were able to obtain measurements on all three reflections at five of the selected energies, and on two at the other four

energies. The energy of the incident photons was calculated from the angular positions of the reflections, and the known lattice parameter of Ni (3.5239 Å), the precision of this determination being about 0.1 eV. The energy bandwidth transmitted by the double-crystal sagittally focusing monochromator was about 4.5 eV. The scans of the reflections were very similar in shape at the different energies, and the background and tails of the reflections were analyzed in the same way as for the measurements reported in paper I.

The absolute scale was fixed by the integrated reflections of the Ni standard at the Cu *K* $\alpha$  wavelength. The calculated and measured parameters that relate the measured integrated counts to the integrated reflections through (3) of paper I yield essentially the same scale, and these values of the parameters are used in the subsequent calculations. The parameters change with wavelength, and the details of the calculation of the relative values are as follows.

The wavelength dependences of the conversion factor of the monitor and the reflectivity of the analyzer were discussed in paper I. Absorption in air is proportional to  $E^{-2.8}$  (Suortti, 1971). The various factors compensate each other, so that  $n_0 A \Delta\varphi \Delta\psi K_{\text{pol}}$  changes only by a few percent in the region of interest.

The structure factor  $f_{hkl}$  is related to the integrated reflection  $P_{hkl}$  through (4) of paper I. Immediately below the *K*-absorption edge the attenuation coefficient of the sample is due to scattering and photoelectric absorption in the higher shells together with resonant Raman scattering (RRS). The former contribution can be extrapolated from the tabulated values (*International Tables for X-ray Crystallography*, 1974). The RRS cross section  $\sigma_{K,RRS}$  can be calculated when the radiative width of the *K* shell,  $\Gamma_K$ , is known (Suortti, 1979).

$$\sigma_{K,RRS} = \Gamma_K \sigma_K (\Omega_K + E_F) / \pi (\Omega_K + E_F - h\omega_1). \quad (5)$$

Here  $(\Omega_K + E_F)$  is the excitation energy of the *K* electron,  $h\omega_1$  the energy of the incident X-ray photon, and  $\sigma_K(\Omega_K + E_F)$  the *K*-shell contribution to the absorption cross section at the *K* edge. This approximate form is valid when  $\Omega_K + E_F - h\omega_1 > 3\Gamma_K$ . The following values were used:  $\Gamma_K = 0.59$  eV (Walters & Bhalla, 1971) and  $\sigma_K(\Omega_K + E_F) = 286$  cm<sup>2</sup> g<sup>-1</sup> (*International Tables for X-ray Crystallography*, 1974).

The structure factors derived from equation (4), paper I cannot be compared with the theoretical values unless corrections for specimen effects are made. These were studied in detail when the Ni powder standard used in the present study was developed, and those results are used to correct for the extra absorption due to specimen granularity and for preferred orientation (Suortti & Jennings, 1977). Those results also showed that losses due to extinction

and amorphous scattering could be neglected. The effects of thermal motion are taken into account by multiplying  $f_{\text{exp}}^2$  by  $\exp(+2B \sin^2 \theta / \lambda^2)$ , and the results are given in Table 1.

#### IV. Results and discussion

The dispersion factors are obtained by a comparison of the experimental scattering factors with the theoretical values. The most sophisticated calculation seems to be that by Wang & Callaway (1977), who used the LCAO method with the KSG approximation for exchange. The difference between the experimental and theoretical static scattering factors are plotted in Fig. 1 for the three reflections.

Below the  $K$  edge, the imaginary part  $f''$  is only about 0.5 electron units, and (3) and (4) can be further simplified to:

$$\begin{aligned} f_{\text{exp}}^2 &= |F|^2 K_{\text{pol}} \\ &\approx (f_0 + f'_D)^2 + 2 \left( \cos 2\theta \frac{1 + K \cos 4\theta}{1 + K \cos^2 2\theta} \right) \\ &\quad \times f'_Q (f_0 + f'_D), \end{aligned} \quad (6)$$

and, as the second term is much smaller than the first one,

$$f_{\text{exp}} - f_0 \approx f'_D + \cos 2\theta \frac{1 + K \cos 4\theta}{1 + K \cos^2 2\theta} f'_Q. \quad (7)$$

The value of the angular factor in the second term is about 0.7 for 111, 0.0 for 311, and  $-0.7$  for 331, and so  $f'_Q$  can be determined from the differences in  $f_{\text{exp}} - f_0$ .

The figures show that if there are any differences in  $f_{\text{exp}} - f_0$  between the three reflections, they are very small, about 0.2 electron units at most. This is only a few percent of  $f'_D$ , in agreement with the calculated and observed ratio  $f'_Q/f'_D$  of the imaginary parts (Hildebrandt *et al.*, 1973). It can be concluded that although the present experiment does not give any definite value for the angle-dependent part of  $f'$ , it gives an upper limit and this limit is so low that it rules out any speculations that there may be significant effects of this kind.

Most of the experimental points lie 0.2 to 0.3 electron units above the dotted line, which shows  $f'$  as calculated from measured and tabulated absorption coefficients (Bonse & Hartmann-Lotsch, 1984). The error bars shown on the data points are due to the possible error in the absolute scale and uncertainties in the theoretical scattering factors. In addition, a 10% uncertainty in the calculated  $\sigma_{K,RRS}$  is included on the points closest to the absorption edge. Direct measurements of  $f'$  in forward scattering (Bonse & Hartmann-Lotsch, 1984) give values that are 0.2 to 0.3 electron units below the calculated line in the

region where  $\Delta E = (\Omega_K + E_F - h\omega_1)$  lies in the range 30 to 3 eV. Thus, there seems to be an overall difference of 0.5 electron units between the two measurements, which in fact represents a very satisfactory agreement.

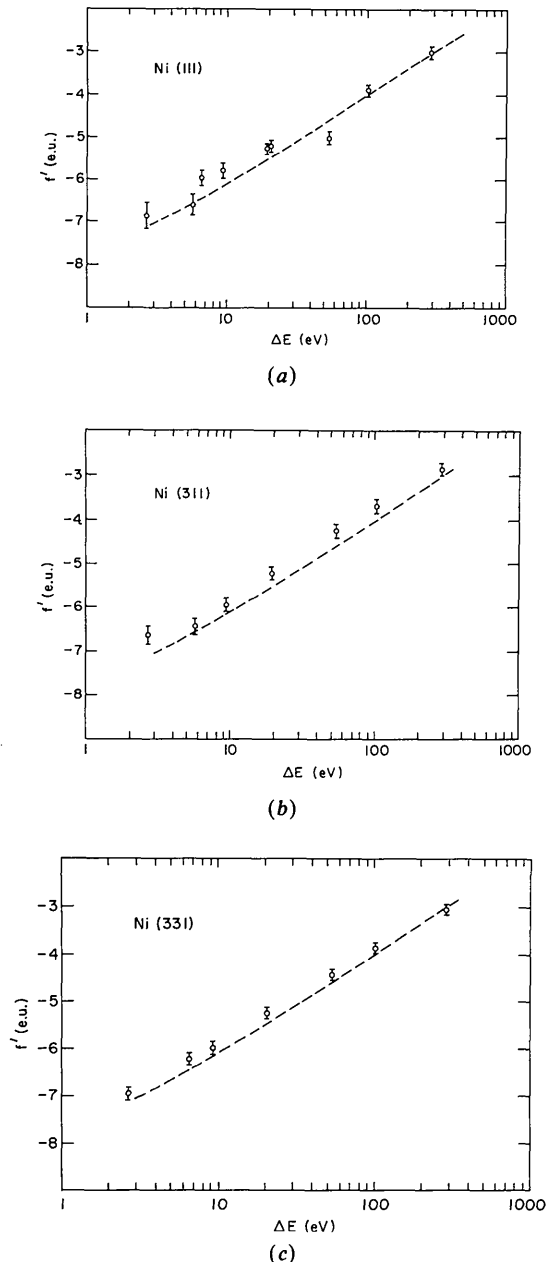


Fig. 1. Real part of the dispersion factor,  $f' = f_{\text{exp}} - f_{\text{th}}$ , as a function of the difference between the edge energy and the incident energy,  $\Delta E = \Omega_K + E_F - h\omega_1$ , for three reflections from Ni. (a) 111, (b) 311, (c) 331. The dotted line is the calculated  $f'$  from the absorption coefficient (Bonse & Hartmann-Lotsch, 1984). The error bars allow for a 1% uncertainty due to the absolute scale and  $f_{\text{th}}$ , and for a possible error in the calculation of  $\mu_{K,RRS}$ .

Table 1. *Absolute scattering factors of Ni near the K-absorption edge*

The difference between the edge energy,  $\Omega_K + E_F$ , and that of the incident photons,  $h\omega_1$ , is given by  $\Delta E$ . The integrated reflections have been corrected for preferred orientation and specimen granularity (Suortti & Jennings, 1977), as well as by a Debye-Waller factor with  $B = 0.36 \text{ \AA}^2$ . The theoretical scattering factors,  $f_{\text{th}}$ , are from a calculation by Wang & Callaway (1977).

$\Delta E(\text{eV})$	(111)		(311)		(331)	
	$f_{\text{exp}}$	$f'$	$f_{\text{exp}}$	$f'$	$f_{\text{exp}}$	$f'$
289	17.42	-3.00	10.72	-2.86	7.46	-3.06
102	16.54	-3.88	9.89	-3.69	6.65	-3.87
54	15.40	-5.02	9.32	-4.26	6.13	-4.39
20.6	15.21	-5.21			5.25	-5.27
19.4	15.16	-5.26	8.54	-5.24		
9.4	14.63*	-5.79	7.61*	-5.97	4.53*	-5.99
6.6	14.46*	-5.96			4.28*	-6.24
5.7	13.79*	-6.63	7.12*	-6.46		
2.7	13.56*	-6.86	6.94	-6.64	3.57*	-6.95
$f_{\text{th}}$	20.42		13.58		10.52	

\* The width of the incident energy band is included in the calculation of  $\mu = \mu_{L,M} + \mu_{K,RRS}$ .

Perhaps the most significant finding of the present study, along with the observation that  $f'$  is not angle dependent, is the close agreement between the measured values of  $f'$  and those calculated from the absorption coefficients. Obviously  $f'$  can be calculated reliably, if absorption data are available over a large range of wavelengths. However, the use of the Kramers-Kronig relations requires that the energy scale is known precisely, and it should be remembered that the absorption edge for a given element may shift appreciably due to chemical bonding.

Extension of the procedure described above to other systems requires the determination of the absolute scale of the integrated reflections using a standard sample, and calculation of the structure factors of the compound being studied from (4) of paper I. However, much work must be done before meaningful dispersion factors can be extracted from this method. Firstly, the intensity standard should be available in the wavelength region being used for the measurements, because the changes in the parameters of equation (3), paper I cannot be extrapolated too far. Secondly, specimen effects should be studied carefully before any structure factors are calculated, which involves subsidiary measurements as discussed by Suortti & Jennings (1977). Nevertheless, the present method can be applied to elements, and with a suitably modified analysis to a large number of compounds, which may not be available in the forms that are needed for other methods.

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