Determination of the Anomalous Scattering Factors for Cu, Ni and Ti using the Dispersion Relation

By J. J. Hoyt and D. de Fontaine

Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720, USA

And W. K. Warburton

Stanford Synchrotron Radiation Laboratory, Stanford, California 94305, USA

(Received 15 February 1984; accepted 30 May 1984)

Abstract

X-ray absorption spectra about the K edges of Ni, Cu and Ti have been measured at the Stanford Synchrotron Radiation Laboratory. The imaginary part of the atomic scattering factor $f''$ was determined using the optical theorem and the real part $f'$ computed by the Kramers-Kronig dispersion relation. Methods for evaluating this integral as well as the effects on $f'$ of various experimental errors are investigated. The $f'$ results for Cu and Ni are compared to data from interferometry experiments.

Introduction

Many experiments involving the anomalous scattering of X-rays require a precise knowledge of the atomic scattering factor at wavelengths near an absorption edge. The earliest calculations of both the real part $f'$ and the imaginary part $f''$ of the atomic scattering factor were performed by Hönig (see James, 1965) who used hydrogenic wavefunctions. Parratt & Hempstead (1954) used the Kramers-Kronig dispersion relation and empirical forms of absorption curves to determine $f'$. More elaborate calculations based on relativistic wavefunctions were made by Cromer & Liberman (1970a, b), which appear to agree fairly well with experimental values of $f'$ at energies far from an absorption edge. These calculations suffer from the inability to predict near-edge effects, which demonstrates the need for measured anomalous scattering factors in this energy regime.

Several attempts have been made to measure anomalous scattering factors accurately for various materials. At the K edge of copper, Freund (1974) determined $f'$ by measuring the total integrated intensity of Bragg reflections from a single crystal. Using an X-ray interferometer (Bonse & Hart, 1976), Bonse and co-workers (Bonse & Materlik, 1976; Hart & Siddons, 1981; Bonse, Hartmann-Lotsch & Lotsch, 1983) simultaneously measured $f'$ and $f''$ for both nickel and copper across their K edges. Fukamachi and others (Fukamachi & Hosoya, 1975; Fukamachi, Hosoya, Kawamura & Okunuki, 1977) evaluated $f'$ near the Ga K edge in a GaP crystal and near the Ga and As edges in GaAs by measuring the ratio of the scattered X-ray intensity from Friedel-pair reflections. In addition, Fukamachi, Hosoya, Kawamura, Hunter & Nakano (1978), as well as Fuoss (1980), determined anomalous scattering factors from measurements of total reflection curves. In a recent experiment, Fontaine, Warburton, Ludwig, Hoyt & Wilson (1984) determined $f'$ for GaAs at both the Ga and As edges by measuring the index of refraction using the prism method.

Perhaps the most straightforward technique of $f'$ determination is by first measuring $f''$ from absorption spectra using the optical theorem and subsequently calculating $f'$ by the Kramers-Kronig integral. Although this method has been used in previous studies (Fukamachi et al., 1978; Fuoss, 1980; Templeton, Templeton, Phillips & Hodgson, 1980; Kawamura & Fukamachi, 1978) it remains poorly characterized and a detailed description and evaluation of the techniques used to solve the dispersion formula are needed. In the present work, different techniques for evaluating the Kramers-Kronig integral are investigated and the effect on $f'$ of various systematic errors are reported. Values of $f''$ and $f'$ at the K absorption edges of Cu, Ni and Ti are calculated and, where possible, compared to previous results.

Experimental procedures

Extended X-ray absorption edge fine structure (EXAFS) experiments were performed on beam line VII-3 (wiggler side station) at the Stanford Synchrotron Radiation Laboratory (SSRL). The monochromator used at SSRL consists of an upward reflecting pair of Si 220 single crystals. When the two crystals are exactly parallel, the Bragg reflections 220, 440, 660 etc. are operative, which means that, in addition to the
fundamental wavelength $\lambda$, higher harmonics of wavelengths $\lambda/2, \lambda/3, \ldots$ will be transmitted by the monochromator. By slightly tilting one Si crystal relative to the other, one can remove the harmonic reflections. This process, known as detuning, has the desirable effect of creating a monochromatic incident beam, but the undesirable effect of decreasing the intensity. In this experiment, two separate EXAFS curves were collected for Ni; one in which the monochromator was fully tuned and the other in which the monochromator was detuned such that the incident intensity was decreased by 75%. The effect on $f'$ of higher harmonics in the incident beam is discussed in the next section.

The incident-beam intensity $I_0$ and the transmitted-beam intensity $I$ were monitored using standard SSRL N$_2$-filled ionization chambers. The samples were standard SSRL thin foils (thickness $\approx 12-5 \mu m$) of pure Ni, Cu and Ti. The measured ratio $I_0/I$ was corrected for the effect of air absorption as follows. Without a sample in place, the intensities in the forward ionization chamber $I_a^a$ and in the rear ionization chamber $I_a^b$ were measured every 500 eV in the range 6 to 10 keV. A polynomial fit to $I_a^b/I_a^a$ as a function of incident-beam energy generated a calibration curve. The corrected ratio of transmitted to incident intensity through the sample $I_a^b/I_a^a$ is expressed as $I_0/I_0$. The atomic cross section, $\sigma$, can then be calculated by

$$\sigma = \frac{1}{t} \frac{A}{\rho N} \ln \left[ \frac{I_0^s}{I_0^s} \right],$$

where $A$ is the atomic number, $\rho$ the density, $N$ is Avagadro’s number and $t$ is the sample thickness.

Since the thicknesses of the thin foils are not well known, a simple correction to the measured atomic cross sections is necessary. This involves multiplying the entire data set by a scaling factor $k$, that is $\sigma_{corr} = k\sigma_{exp}$. The scaling factor is determined by the ratio of a standard value of the atomic cross section (i.e. a previously published value) to the experimental one found using (1). $k$ was calculated using a standard value at a single energy well below the K-absorption edge. The effect on $f'$ of using two different standards to calculate the scaling factor is presented in the following section.

Values of $f''$ were obtained from the absorption spectra $\sigma(\omega)$ through the use of the optical theorem

$$f''(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\sigma(\omega)}{\omega_0^2 - \omega^2} d\omega,$$

a formula first obtained by Darwin (see James, 1965). In this equation $\sigma(\omega)$ is the atomic cross section as a function of the incident X-ray frequency $\omega$, $m$ and $e$ are the mass and charge of an electron and $c$ is the speed of light. $f'$ was then computed using the equation

$$f'(\omega_0) = \frac{1}{\pi} \int_0^{\omega_0} \frac{\sigma(\omega)}{\omega_0^2 - \omega^2} d\omega,$$

which is one form of the Kramers–Kronig relationships. Here the symbol $\oint$ denotes the Cauchy principal value of the integral.

Since this integral is singular at the point $\omega = \omega_0$, a modification is necessary before proceeding with the numerical integration. Equation (3) is therefore rewritten as

$$f'(\omega_0) = \frac{2}{\pi} \int_a^b \frac{\sigma(\omega)}{\omega_0^2 - \omega^2} d\omega + \frac{2}{\pi} \int_a^b \frac{\sigma(\omega)}{\omega_0^2 - \omega^2} d\omega,$$

Here the second term contains the singularity where the limits $a$ and $b$ represent adjacent data points above and below the singularity. The first and last terms of (4) contain no singularities and can easily be integrated numerically. An integration technique for a set of data points using cubic interpolation (Gill & Miller, 1972) was employed in the present work.

The second term of (4) can be calculated by expanding the $f''$ function in a Taylor series about $\omega_0$ and integrating term by term. The integral is first rewritten as

$$f'(\omega_0) = \frac{2}{\pi} \left[ \int_a^b \frac{\sigma(\omega)}{\omega_0^2 - \omega^2} d\omega + \frac{1}{\omega_0^2} \int_a^b \frac{\sigma(\omega)}{\omega_0^2 - \omega^2} d\omega \right].$$

Expanding $f''(\omega)$ in a Taylor series about $\omega_0$,

$$f''(\omega) = f''(\omega_0) + \frac{d f''}{d \omega} \bigg|_{\omega_0} (\omega - \omega_0)$$

$$+ \frac{1}{2} \frac{d^2 f''}{d \omega^2} \bigg|_{\omega_0} (\omega - \omega_0)^2 + \ldots,$$

one obtains for the interval $a \rightarrow b$:

$$f'_{a \rightarrow b} = \left[ \frac{2}{\pi} \left[ \int_a^b \frac{f''(\omega)}{\omega_0^2 + \omega} d\omega - \int_a^b f''(\omega_0) \frac{d\omega}{\omega_0^2 - \omega_0^2} \right] \right].$$
The first integral contains no singularities and can be integrated numerically. The Cauchy principal value of the second integral exists and is equal to

$$\int_a^b \frac{d\omega}{\omega - \omega_0} = (\ln|b - \omega_0| - \ln|a - \omega_0|) \quad (8)$$

Thus,

$$f'_{a \rightarrow b} = \frac{1}{\pi} \left[ \int_a^b \frac{f''(\omega)}{\omega + \omega_0} d\omega - \left\{ \ln|b - \omega_0| - \ln|a - \omega_0| \right\} \right. \left. \right] - \frac{d \hat{f''}}{d\omega} \bigg|_{\omega_0} (b - a) - \sum_{n=2}^\infty \frac{1}{n!} \frac{d^n \hat{f''}}{d\omega^n} \bigg|_{\omega_0} (b - \omega_0)^n \quad (9)$$

In practice, the $f''(\omega)$ data about $\omega_0$ were fit using a polynomial of degree $n = 5$ and $f'$ calculated by substituting (9) into (4).

**Evaluation of the technique**

The evaluation of (4) is not a trivial matter. A typical EXAFS spectrum measures absorption events in a range of about 500–1000 eV on the high- and low-wavelength sides of a given edge, whereas the Kramers–Kronig integral contains limits of zero to infinite energy. Clearly, a method for obtaining $f''$ as a function of energy at wavelengths far from the edge must be employed. In this section two such techniques are discussed. In addition, the effect of $f'$ on the limits of integration will be analyzed.

Also discussed in this section are: the effect on the calculated $f'$ owing to two different thickness-correction schemes, the effect on $f'$ owing to the presence of higher harmonics in the incident X-ray beam; and an estimate of the precision in $f''$ calculated by the dispersion relation.

**McMaster vs Cromer & Liberman extrapolations**

The integral in (3) has limits from zero to infinity and thus an extrapolation of $f''$ to very high and very low energies must be made. Two methods are considered. The first involves fitting the calculated $f''$ values of Cromer & Liberman (1970a) to an equation of the form $f'' \propto E^n$, where $E$ is the energy and $n$ is a constant. The second method employs the polynomial fits for the absorption coefficient as a function of energy, which are published in the McMaster tables. In both cases the form of the equation will differ for energies above and below the edge.

Fig. 1 shows the difference in $f'$ for pure nickel using the McMaster fit and the Cromer & Liberman fit to extrapolate the $f''$ data to energies far below and far above the $K$ edge. The lower limit of integration was set at the $L_\gamma$-edge energy and an upper limit of 100 times the $K$-edge energy was used in the comparison. A nearly constant offset of $\sim 0.2$ electrons is observed, with the lower values of $f'$ predicted when the McMaster fit is employed.

**Limits of integration**

The effect of $f'$ on the limits of integration was examined for a sample of pure nickel using the McMaster extrapolation. Fig. 2 shows $f'$ vs. energy with the upper limit set at 5, 10, 50, 100 and 200 times the $K$-edge energy (for Ni 8333 eV) while holding the lower limit constant at the $L_\gamma$-edge energy (1012 eV). In this figure the lower curve is the result of three separate calculations using upper limits of 50, 100 and 200 times the $K$-edge energy. The coincidence of these three curves demonstrates that the calculated $f'$ converges to its final value with the upper limit of integration set at about 50 times the $K$-edge energy. Fig. 2 is plotted on an expanded scale to observe the effect more clearly.

Also investigated was the effect of changing the lower limit of integration in the dispersion formula. Here the value of the lower limit was set at the $L_{\gamma}$, $L_{\gamma\gamma}$, $L_{\gamma\gamma\gamma}$ and $M$-edge energies (for Ni 1012, 872, 855 and 130 eV, respectively). The $L$-absorption edges were assumed to be infinitely sharp and the $L$-edge jump heights were those given in the McMaster tables. In the case of the lower limit equal to the $M$-edge energy, a power law for absorption by $M$ electrons (Parratt & Hempstead, 1954) of the form $\mu \propto E^{5/2}$ was used to extrapolate data below the $L_{\gamma\gamma\gamma}$ edge. It was found that the calculated $f'$ values were the same for the four different lower limits of integration tested. This result arises essentially from the fact that this region is relatively far from the singularity $\omega_0$ in the
dispersion formula and also the range of energy ($\sim 1000$ eV) excluded from the integral is small compared to the entire range of integration.

In summary, it can be seen that adequate convergence of the integral in (3) can be obtained with the upper limit ' $\infty$ ' replaced by $\sim 50 \times E_K$ and the lower limit of zero replaced by $E_L$.

**Thickness**

Since the thickness of the sample is not well known, a simple correction to the data was performed, as described in the preceding section. The measured absorption coefficient at an energy well below the $K$ edge was compared to a standard value. The standard value, to be consistent with the schemes above, was either that taken from the McMaster tables or calculated by the Cromer & Liberman algorithm. The single value of $k$, that is the ratio of the standard to the experimentally determined absorption coefficient, was used to correct the entire data set.

Fig. 3 shows the effect of mixing the two thickness corrections and 'extrapolation' schemes. The top curve shows $f'$ vs energy for Ni using a McMaster fit for both (thickness correction and 'extrapolation') and the bottom curve shows the effect of using a McMaster 'extrapolation', but with a thickness correction based on the standard value calculated by the Cromer & Liberman algorithm. Not only is the McMaster curve lower at all energies, but the two curves do not have the same shape; the McMaster fit predicts a sharper drop in $f'$ in the vicinity of the $K$ edge. The difference in the shape of the two curves is very slight and would be negligible in most anomalous scattering experiments. Comparison of Figs. 1 and 3 clearly indicates that the thickness correction accounts for most of the discrepancy between the two procedures.

**Harmonics**

Fig. 4 shows the effect on $f'$ of having higher harmonics in the incident X-ray beam (see above) when collecting the absorption data. The top curve is the case of the monochromator in the fully tuned condition, i.e. higher harmonics are present, whereas the lower curve shows the case of the incident intensity detuned by $75\%$. The difference in $f'$ for the two cases is about 0.1 electrons at the minimum of the curves. For the thin samples (thickness $\approx 12.5$ $\mu$m) studied here, the calculated $f'$ is relatively insensitive to the presence of higher harmonics. With thicker samples, however, one could expect the effect to become much greater just as EXAFS data is similarly distorted (Heald & Stern, 1977).

**Precision**

Owing to statistical fluctuations in the counting of X-rays, the $f''$ vs energy curves are not smooth. The effect of these fluctuations on $f'$ was estimated by the
following procedure. A polynomial (degree 5) was fit to five points on both high- and low-energy sides of a given $f''$ point. A random-number generator with a Gaussian distribution was used to calculate a new set of $f''$ data. The standard deviation of the distribution was set equal to the difference between the actual and fitted $f''$ point and the mean was taken as the fitted $f''$ data. Ten new data sets were generated with the $f'$ values and standard deviation in $f'$ calculated for each energy. The resulting error band is shown in Fig. 5 on an expanded scale. The uncertainty in $f'$ appears to be about $\pm 0.3$ electrons, which is negligible compared to the systematic errors described above.

In summary, the major sources of error in this technique are the extrapolation procedure and the thickness correction. The calculated values of $f'$ using the two extrapolation procedures differ by a constant $0.1-0.2$ electrons. Clearly, a much more important source of inaccuracy is due to the thickness correction; a change in the correction procedure causes the $f'$ vs energy curve to change shape as well as shift vertically by about $0.2-0.3$ electrons.

**Results**

Presented in this section are the anomalous scattering factors $f'$ and $f''$ of Ni, Cu and Ti about their K-absorption edges. The $f'$ results for Cu and Ni are compared to previous data determined by the X-ray interferometry technique.

As pointed out by Gerward, Thueben, Stibius Jensen & Alstrup (1979), a complete relativistic treatment of the atomic scattering $f$ shows that the Kramers–Kronig relationship is not strictly valid when the dispersion correction is defined as $f-f_0$ ($f_0$ being the Thomson scattering factor). Cromer & Liberman (1970a) treated this problem and showed that an extra term

$$-f_0^+ + (f^- - f_0^-) = 5 \frac{E_{TOT}}{3mc^2}$$

(19) must be added to the value of $f'$ calculated by the Kramers–Kronig relation. Cromer & Liberman have calculated $5 \frac{E_{TOT}}{3mc^2}$ in the dipole approximation. This term is equal to $-0.146$ electrons for Cu, $-0.135$ electrons for Ni and $-0.075$ electrons for Ti. This additional term is included in all the results that follow.

**Nickel**

Fig. 6 shows the variation of $f''$ with energy for nickel as calculated by the optical theorem in the vicinity of the K-absorption edge. The $f''$ value at the Cu $K\alpha$ energy (8047.7 eV) calculated here ($0.53$ electrons) agrees fairly well with that calculated by Cromer & Liberman ($0.51$ electrons). Fig. 7 shows $f'$ as a function of energy for pure Ni. The form of the Kramers–Kronig relation (equation 3) suggests that

---

**Fig. 5.** Estimate of the error band in $f'$ calculated for pure nickel. Uncertainty is about $\pm 0.03$ electrons.

**Fig. 6.** $f''$ vs energy for pure nickel about the Ni K-absorption edge.

**Fig. 7.** $f'$ vs energy for pure Ni compared to Bonse & Hart's (1976) interferometry data.
$f'(E)$ should behave essentially like the derivative of the $f''$ vs energy curve (Fuoss, 1980). This can be clearly seen in the case of Ni. The two minima in $f'$ at the K-edge energy correspond to the two inflection points in the edge jump of Fig. 7. For comparison, the X-ray interferometry data of Bonse & Materlik (1976) are also plotted. The agreement at energies far from the edge is fairly good, for example at the Cu Kα energy (not shown) these authors cite a value of $f' = -3.014$ whereas $f' = -3.07$ was calculated in the present work. Above the K edge the interferometry data fall consistently below the computed $f'$ values by about 0.3–0.4 electrons. A constant offset in the absolute magnitude of $f'$ is often observed when two different experimental measures of $f'$ are compared. For example, Bonse & Hartmann-Lotsch (1984) found a similar 0.4 electron difference between their Kramers-Kronig transformed data and their interferometry results. For an important class of anomalous scattering experiments, namely the determination of partial structure functions in multicomponent solutions, a constant systematic error in the $f'$ calculation is not critical (Simon, Lyon & de Fontaine, 1984).

**Copper and titanium**

Figs. 8–11 show $f'$ and $f''$ as a function of X-ray energy for pure copper and pure titanium about their K edges. In both cases the lower limit of the Kramers-Kronig integral was taken as the L$\alpha$ edge energy and the upper limit was 100 times the K-edge energy. Also, in Fig. 10 the Bonse interferometer results for copper and the data of Freund who used the method of integrated intensities are plotted. The agreement in this case appears to be much better than...
that of Ni and the alignment with energy of the EXAFS structure above the absorption edge is excellent. The discrepancy between the present $f'$ values and the interferometry results is not constant with energy, the former being about 0.1 electrons greater at low energies, 0.4 electrons larger at the edge and 0.2 electrons lower at high energies. It is unclear what errors in the Kramers–Kronig integration procedure could produce such discrepancies since the major errors identified have all produced a nearly constant offset in $f'$.

Discussion

Other experiments that attempt to measure anomalous scattering factors are often quite difficult to perform. Some require elaborate experimental equipment, such as an X-ray interferometer, while others require careful sample preparation, for example, total reflection measurements or the prism method. With the increasing availability of synchrotron sources and with EXAFS data now being collected routinely, the technique described above is both very rapid and simple to perform. An adequately thin foil is the only sample requirement. For most applications of anomalous scattering the calculation of $f'$ via the dispersion relation appears to be the most practical.

An important systematic error present in the Kramers–Kronig inversion is caused by the method of extrapolating $f''$ data at remote energies. One way to minimize this error is by taking data at a much wider range on either side of the absorption edge. Since the integrand in the dispersion formula (equation 3) contains the term $\omega_0^2 - \omega^2$ in the denominator, as a wider range of data is collected the contribution of the extrapolated data becomes increasingly less important. Eventually, the two curves (Fig. 3) will converge. However, the only effect that is due to the choice of fitting technique, McMaster vs Cromer & Liberman, is a change in the relative scale of $f'$ but no change in the form of the curve. Such offsets are often found when two experimental measures of $f'$ are compared. The error from the thickness correction more troublesome. In this case, the shape of the $f'$ curve is also changed slightly, dropping more rapidly in the vicinity of the edge for the McMaster correction.

Concerning the discrepancy between the present results and those of Bonse et al. (1983), it should be pointed out that the interferometry technique also employs a determination of sample thickness which can introduce uncertainty into the measured $f'$ values. The procedure is to measure the phase shift using the first harmonic (twice the energy) and use a calculated value of $f'$ at this energy to obtain the thickness. Since the first harmonic is far from an absorption edge, $f'$ (2E) can be calculated accurately from dispersion theory, a procedure similar to the thickness normaliza-

Conclusion

The application of the Kramers–Kronig dispersion relation to the calculation of the real part $f'$ of the atomic scattering factor has been examined in detail. The modification of the integrand in the dispersion formula allows one to avoid the problem of numerically integrating in the region of a singularity. An analysis of the effect on $f'$ of the limits of integration in the dispersion formula has established that appropriate choices for the upper and lower limits are 50 times the $K$-edge energy and the $L_2$-edge energy, respectively. Two techniques to extrapolate absorption spectra to very high and very low energies have been investigated. The two methods employ either published absorption data by McMaster et al. (1969)
or calculated $f''$ values due to Cromer & Liberman (1970a). The comparison between the two techniques has demonstrated that the calculated $f'$ differs by a constant of the order of 0.1–0.2 electrons over the entire range of energy investigated. Negligibly small uncertainties in $f'$ have been observed owing to the presence of higher harmonics in the incident X-ray beam and statistical fluctuations in the counting of X-rays.

In many EXAFS experiments, the foil thickness is not known accurately; to remedy this situation two procedures for normalizing absorption data have been developed. The measured absorption at an energy below the edge is compared with a standard value. The chosen standards were taken from either the McMaster et al. (1969) tables or the Cromer & Liberman (1970a) algorithm. The difference in $f'$ when comparing the two thickness corrections amounts approximately to 0.2–0.3 electrons and represents the largest uncertainty associated with the determination of $f'$ via the dispersion relation. Despite this error, the $f'$ vs energy curves for Ni and Cu presented in this experiment agree very well with data from earlier studies.

Determination of anomalous scattering factors by the optical theorem and the dispersion relation has many advantages. With the advent of synchrotron radiation the collection of absorption spectra is quite simple and very fast. The method of computation of $f''$ and $f'$ is straightforward and the precision in $f'$ appears to be excellent. The major disadvantage of this technique is its inability to predict an absolute scale of $f'$ accurately. The same problem afflicts, at the present time, virtually all other experiments that measure anomalous scattering factors.

The authors wish to thank Professor D. H. Templeton, Dr J. P. Simon, Dr O. Lyon and Dr A. Fontaine for their valuable advice and continued support. This work was supported by the National Science Foundation. A portion of this work was done at SSRL, which is supported by the Department of Energy, Office of Basic Energy Science, and the NIH Biotechnology Resource Program.

References


