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variance with the predictions of Wagenfeld's (1975) non-relativistic model.

4.2.6.2.4. *Intercomparison of theories*

A discussion of the validity of the non-relativistic dipole approximation for the calculation of forward Rayleigh scattering amplitudes has been given by Roy & Pratt (1982). They compared their relativistic multipole calculations with the relativistic dipole approximation and with the non-relativistic dipole approximation for two elements, silver and lead. They concluded that a relativistic correction to the form factor of order $(Z\alpha)^2$ persists in the high-energy limit, and that this constant correction accounts for much of the deviation from the non-relativistic dipole approximation at all energies above threshold. In addition, their results illustrate that cancelling occurs amongst the relativistic, retardation, and higher multipole contributions to the scattering amplitude. This implies that care must be taken in assessing where to terminate the series that describes the multipolarity of the scattering process.

In a later paper, Roy, Kissel & Pratt (1983) discussed the elastic photon scattering for small momentum transfers and the validity of the form-factor theories. In this paper, which compares the relativistic modified form factor with experimental results for lead and a relativistic form factor and the tabulation by Hubbell, Veigele, Briggs, Brown, Cromer & Howerton (1975), it is shown that the modified relativistic form-factor approach gives better agreement with experiment for high momentum transfers ($< 104 \text{ \AA}^{-1}$) than the non-relativistic, form-factor theories.

Kissel *et al.* (1980) used the S -matrix technique to calculate the real part of the forward-scattering amplitude $f'(\omega, 0)$ for the inert gases at the wavelength of Mo $K\alpha_1$. These values are compared with the predictions of the relativistic dipole theory (RDP) and the relativistic multipole theory (RMP) in Table 4.2.6.2(a). In most cases, the agreement between the S matrix and the RMP theory is excellent, considering the differences in the methodology of the two sets of calculations. Table 4.2.6.2(b) shows comparisons of the real part of the forward-scattering amplitude $f''(\omega, 0)$ calculated for the atoms aluminium, silicon, zinc, germanium, silver, samarium, tantalum and lead using the approach of Kissel *et al.* (1980) with that of Cromer & Liberman (1970, 1981), with tabulations by Wagenfeld (1975), and with values taken from the tables in this section. Although reasonably satisfactory agreement exists between the relativistic values, large differences exist between the non-relativistic value (Wagenfeld, 1975) and the relativistic values. The major difference between the relativistic values occurs because of differences in estimation of the self-consistent-field term, which is proportional to E_{tot}/mc^2 . The Cromer & Liberman (1970) relativistic dipole value is $+\frac{5}{3}(E_{\text{tot}}/mc^2)$, whereas the tabulation in this section uses the relativistic multipole value of $(+E_{\text{tot}}/mc^2)$. This causes a vertical shift of the curve, but does not alter its shape. Should better estimates of the self-energy term be found, the correction is simply that of adding a constant to each value of $f'(\omega, 0)$ for each atomic species. There is a significant discrepancy between the Kissel *et al.* (1980) result for ^{62}Sm and the other theoretical values. This is the only major point of difference, however, and the results are better in accord with the relativistic multipole approach than with the relativistic dipole approach. Note that the relativistic multipole approach does not include the Stibius-Jensen correction, which alters the shape of the curve.

In §4.2.6.3.3, some examples are given to illustrate the extent to which predictions of these theories agree with experimental data for $f''(\omega, 0)$.

That there is little to choose between the different theoretical approaches where the calculation of $f''(\omega, 0)$ is concerned is illustrated in Table 4.2.6.3. In most cases, the agreement between the scattering matrix, relativistic dipole, and relativistic multipole values is within 1%. In contrast, there are some significant differences between the relativistic and the non-relativistic values of $f''(\omega, 0)$. The extent of the discrepancies is greater the higher the atomic number, as one might expect from the assumptions made in the formulation of the non-relativistic model. Some detailed comparisons of theoretical and experimental data for linear attenuation coefficients [proportional to $f''(\omega, 0)$] have been given by Creagh & Hubbell (1987) for silicon, and for copper and carbon by Gerward (1982, 1983). These tend to confirm the assertion that, at the 1% level of accuracy, there is little to choose between the various relativistic models for computing scattering cross sections.

Further discussion of this is given in §4.2.6.3.3.

4.2.6.3. *Modern experimental techniques*

The atomic scattering factor enters directly into expressions for such macroscopic material properties as the *refractive index*, n , and the *linear attenuation coefficient*, μ_1 . The refractive index depends on the dielectric susceptibility χ through

$$n = (1 + \chi)^{1/2}, \quad (4.2.6.35)$$

where

$$\chi = -\frac{r_e \lambda^2}{\pi} \sum_j N_j f_j(\omega, \Delta) \quad (4.2.6.36)$$

and N_j is the number density of atoms of type j .

The imaginary part of the dispersion correction $f''(\omega, \Delta)$ for the case where $\Delta = 0$ is related to the atomic scattering cross section through equation (4.2.6.23).

Experimental techniques that measure refractive indices or X-ray attenuation coefficients to determine the dispersion corrections involve measurements for which the scattering vector, Δ , is zero or close to it. Data from these experiments may be compared *directly* with data sets such as Cromer & Liberman (1970, 1981).

Other techniques measure the intensities of Bragg reflections from crystalline materials or the variation of intensities within one particular Laue reflection (*Pendellösung*). For these cases, $\Delta = g_{hkl}$, the reciprocal-lattice vector for the reflection or reflections measured. These techniques can be compared only indirectly with existing relativistic tabulations, since these have been developed for the $\Delta = 0$ case. Data are available for elements having atomic numbers less than 20 in the non-relativistic case (Wagenfeld, 1975).

The following sections will discuss some modern techniques for the measurement of dispersion corrections, and an inter-comparison will be made between experimental data and theoretical calculations for a representative selection of atoms and at two extremes of photon energies: near to and remote from an absorption edge of those atoms.

4.2.6.3.1. *Determination of the real part of the dispersion correction: $f'(\omega, 0)$*

X-ray interferometer techniques are now used extensively for the measurement of the refractive index of materials and hence

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Table 4.2.6.2(a). Comparison between the *S*-matrix calculations of Kissel (K) (1977) and the form-factor calculations of Cromer & Liberman (C & L) (1970, 1981, 1983) and Creagh & McAuley (C & M) for the noble gases and several common metals; $f'(\omega, 0)$ values are given for two frequently used photon energies

Energy (keV)	Element	RDP (C & L)	<i>S</i> matrix (K)	RMP (C & M)
17.479 (Mo $K\alpha_1$)	Ne	0.021	0.024	0.026
	Ar	0.155	0.170	0.174
	Kr	-0.652	-0.478	-0.557
	Xe	-0.684	-0.416	-0.428
22.613 (Ag $K\alpha_1$)	Al	0.032	0.039	0.041
	Zn	0.260	0.323	0.324
	Ta	-0.937	-0.375	-0.383
	Pb	-1.910	-1.034	-1.162

$f'(\omega, 0)$. All the interferometers are transmission-geometry LLL devices (Bonse & Hart, 1965, 1966*a,b,c,d*, 1970), and initially they were used to measure the X-ray refractive indices of such materials as the alkali halides, beryllium and silicon using the characteristic radiation emitted by sealed X-ray tubes. Measurements were made for such characteristic emissions as Ag $K\alpha_1$, Mo $K\alpha_1$, Cu $K\alpha_1$ and Cr $K\alpha_1$ by a variety of authors (Creagh & Hart, 1970; Creagh, 1970; Bonse & Hellkötter, 1969; Bonse & Materlik, 1972).

The ready availability of synchrotron-radiation sources led to the adaptation of the simple LLL interferometers to use this new radiation source. Bonse & Materlik (1975) reported measurements at DESY, Hamburg, made with a temporary adaptation of a diffraction-beam line. Recent advances in X-ray interferometry have led to the establishment of a permanent interferometer station at DESY (Bonse, Hartmann-Lotsch & Lotsch, 1983*b*). This, and many of the earlier interferometers invented by Bonse, makes its phase measurements by the rotation of a phase-shifting plate in the beams emanating from the first wafer of the interferometer.

In contrast, the LLL interferometer designed by Hart (1968) uses the movement of the position of lattice planes in the third wafer of the interferometer relative to the standing-wave field formed by the recombination of two of the diffracted beams within the interferometer. Measurements made with and without the specimen in position enabled both the refractive index and the linear attenuation coefficient to be determined. The use of energy-dispersive detection meant that these parameters could be determined for harmonics of the fundamental frequency to which the interferometer was tuned (Cusatis & Hart, 1975, 1977). Subsequently, measurements have been made by Siddons & Hart (1983) and Hart & Siddons (1981) for zirconium, niobium, nickel, and molybdenum. Hart (1985) planned to provide detailed dispersion curves for a large number of elements capable of being rolled into thin foils.

Both types of interferometers have yielded data of high quality, and accuracies better than 0.2 electrons have been claimed for measurements of $f'(\omega, 0)$ in the neighbourhood of the *K*- and *L*-absorption edges of a number of elements. The energy window has been claimed to be as low as 0.3 eV in width. However, on the basis of the measured values, it would seem that the width of the energy window is more likely to be about 2 eV for a primary wavelength of 5 keV.

Table 4.2.6.2(b). A comparison of the real part of the forward-scattering amplitudes computed using different theoretical approaches: KPR (Kissel et al., 1980); C & L (Cromer & Liberman, 1970, 1981); W (Wagenfeld, 1975); and C & M (this data set)

Atom	Radiation	$f'(\omega, 0)$				
		KPR	C & L		W	C & M
			1970	1981		
¹³ Al	Cr $K\alpha_1$	13.320	13.328	13.316	13.376	13.326
	Cu $K\alpha_1$	13.209	13.204	13.203	13.235	13.213
	Ag $K\alpha_1$	13.039	13.032	13.020	13.078	13.041
¹⁴ Si	Cr $K\alpha_1$		14.333	14.354	14.441	14.365
	Cu $K\alpha_1$		14.244	14.242	14.282	14.254
	Ag $K\alpha_1$		14.042	14.029	14.071	14.052
³⁰ Zn	Cr $K\alpha_1$	29.161	29.316	29.314		29.383
	Cu $K\alpha_1$	28.369	28.388	28.383		28.451
	Ag $K\alpha_1$	30.323	30.260	30.232		30.324
³² Ge	Cr $K\alpha_1$		31.538	31.538	30.20	31.614
	Cu $K\alpha_1$		30.837	30.837	31.92	30.911
	Ag $K\alpha_1$		32.228	32.228	32.14	32.302
⁴⁷ Ag	Cu $K\alpha_1$	47.075	46.940	46.936		47.131
⁶² Sm	Ag $K\alpha_1$	58.307	56.304	56.299		56.676
⁷³ Ta	Ag $K\alpha_1$	72.625	72.063	71.994		72.617
⁸² Pb	Ag $K\alpha_1$	80.966	80.090	80.012		80.832

Apparently, the ångström-ruler design is the better of the two interferometer types, since the interferometer to be mounted at the EU storage ring is to be of this type (Buras & Tazzari, 1985).

Interferometers of this type have the advantage of enabling direct measurements of both refractive index and linear attenuation coefficients to be made. The determination of the energy scale and the assessment of the energy bandpass of such a system are two factors that may influence the accuracy of this type of interferometer.

One of the oldest techniques for determining refractive indices derives from measurement of the deviation produced when a prism of the material under investigation is placed in the photon beam. Recently, a number of groups have used this technique to determine the X-ray refractive index, and hence $f'(\omega, 0)$.

Deutsch & Hart (1984*a,b*) have designed a novel double-crystal transmission spectrometer for which they were able to detect to high accuracy the angular rotation of one element with respect to the other by reference to the *Pendellösung* maxima that are observed in the wave field of the primary wafer. In this second paper, data gained for beryllium and lithium fluoride wedges are discussed.

Several Japanese groups have used more conventional monochromator systems having Bragg-reflecting optics to determine the refractive indices of a number of materials. Hosoya, Kawamura, Hunter & Hakano (1978; cited by Bonse & Hartmann-Lotsch, 1984) made determinations of $f'(\omega, 0)$ in the region of the *K*-absorption edge for copper. More recently, Ishida & Katoh (1982) have described the use of a multiple-reflection diffractometer for the determination of X-ray refrac-

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Table 4.2.6.3. A comparison of the imaginary part of the forward-scattering amplitudes $f''(\omega, 0)$ computed using different theoretical approaches: KPR (Kissel *et al.*, 1980); C & L (Cromer & Liberman, 1981); W (Wagenfeld, 1975); and C & M (this data set)

Atom	Radiation	$f''(\omega, 0)$			
		KPR	C & L	W	C & M
¹³ Al	Cr $K\alpha_1$	0.514	0.522		0.512
	Cu $K\alpha_1$	0.243	0.246		0.246
	Ag $K\alpha_1$	0.031	0.031		0.031
¹⁴ Si	Cr $K\alpha_1$		0.694	0.70	0.692
	Cu $K\alpha_1$		0.330	0.33	0.330
	Ag $K\alpha_1$		0.043	0.047	0.043
³⁰ Zn	Cr $K\alpha_1$	1.370	1.373		1.371
	Cu $K\alpha_1$	0.678	0.678		0.678
	Ag $K\alpha_1$	0.932	0.938		0.938
³² Ge	Cr $K\alpha_1$		1.786	1.84	1.784
	Cu $K\alpha_1$		0.886	0.87	0.886
	Ag $K\alpha_1$		1.190	1.23	1.190
⁴⁷ Ag	Cu $K\alpha_1$	4.242	4.282		4.282
⁶² Sm	Cu $K\alpha_1$	12.16	12.218		12.218
⁷³ Ta	Ag $K\alpha_1$	4.403	4.399		4.399
⁸² Pb	Ag $K\alpha_1$	6.937	6.929		6.929

tive indices. Later, Katoh *et al.* (1985a,b) described its use for the measurement of $f'(\omega, 0)$ for lithium fluoride and potassium chloride at a wavelength near that of Mo $K\alpha_1$ and for germanium in the neighbourhood of its K -absorption edge.

Measurements of the linear attenuation coefficient μ_l over an extended energy range can be used as a basis for the determination of the real part of the dispersion correction $f'(\omega, 0)$ because of the Kramers–Kronig relation, which links $f'(\omega, 0)$ and $f''(\omega, 0)$. However, as Creagh (1980) has pointed out, even if the integration can be performed accurately [implying the knowledge of $f''(\omega, 0)$ over several decades of photon energies and the exact energy at which the absorption edge occurs], there will still be some ambiguity in the result because there still has to be the inclusion of the appropriate relativistic correction term.

The experimental procedures that must be adopted to ensure that the linear attenuation coefficients are measured correctly have been given in Subsection 4.2.3.2. One other problem that must be addressed is the accuracy to which the photon energy can be measured. Accuracy in the energy scale becomes paramount in the neighbourhood of an absorption edge where large variations in $f'(\omega, 0)$ occur for very small changes in photon energy $\hbar\omega$.

Despite these difficulties, Creagh (1977, 1978, 1982) has used the technique to determine $f'(\omega, 0)$ and $f''(\omega, 0)$ for several alkali halides and Gerward, Thuesen, Stibius-Jensen & Alstrup (1979) used the technique to measure these dispersion corrections for germanium. More recently, the technique has been used by Dreier *et al.* (1984) to determine $f'(\omega, 0)$ and $f''(\omega, 0)$ for a number of transition metals and rare-earth atoms. The experi-

mental configuration used by them was a conventional XAFS system. Similar techniques have been used by Fuoss & Bienenstock (1981) to study a variety of amorphous materials in the region of an absorption edge.

Henke *et al.* (1982) used the Kramers–Kronig relation to compute the real part of the dispersion correction for most of the atoms in the Periodic Table, given their measured scattering cross sections. This data set was computed specifically for the soft X-ray region ($\hbar\omega < 1.5$ keV).

Linear attenuation coefficient measurements yield $f'(\omega, 0)$ directly and $f''(\omega, 0)$ indirectly through use of the Kramers–Kronig integral. Data from these experiments do not have the reliability of those from refractive-index measurements because of the uncertainty in knowing the correct value for the relativistic correction term.

None of the previous techniques is useful for small photon energies. These photons would experience considerable attenuation in traversing both the specimen and the experimental apparatus. For small photon energies or large atomic numbers, reflection techniques are used, the most commonly used technique being that of total external reflection. As Henke *et al.* (1982) have shown, when reflection occurs at a smooth (vacuum–material) interface, the refractive index of the reflecting material can be written as a single complex constant, and measurement of the angle of total external reflection may be related directly to the refractive index and therefore to $f'(\omega, \Delta)$. Because the X-ray refractive indices of materials are only slightly less than unity, the scattering wavevector Δ is small, and the scattering angle is only a few degrees in magnitude. Assuming that there is not a strong dependence of $f'(\omega, \Delta)$ with Δ , one may consider that this technique provides an estimate of $f'(\omega, 0)$ for a photon energy range that cannot be surveyed using more precise techniques. A recent review of the use of reflectometers to determine $f'(\omega, 0)$ has been given by Lengeler (1994).

4.2.6.3.2. Determination of the real part of the dispersion correction: $f'(\omega, \Delta)$

This classification includes those experiments in which measurements of the geometrical structure factors F_{hkl} for various Bragg reflections are undertaken. Into this category fall those techniques for which the period of standing-wave fields (*Pendellösung*) and reflectivity of perfect crystals in Laue or Bragg reflection are measured. Also included are those techniques from which the atomic scattering factors are inferred from measurements of Bijvoet- or Friedel-pair intensity ratios for noncentrosymmetric crystal structures.

4.2.6.3.2.1. Measurements using the dynamical theory of X-ray diffraction

The development of the dynamical theory of X-ray diffraction (see, for example, Section 5 in *IT B*, 1995) and recent advances in techniques for crystal growth have enabled experimentalists to determine the geometrical structure factor F_{hkl} for a variety of materials by measuring the spacing between minima in the internal standing wave fields within the crystal (*Pendellösung*).

Two classes of *Pendellösung* experiment exist: those for which the ratio $(\lambda/\cos\theta)$ is kept constant and the thickness of the samples varies; and those for which the specimen thickness remains constant and $(\lambda/\cos\theta)$ is allowed to vary.

Of the many experiments performed using the former technique, measurements by Aldred & Hart (1973a,b) for

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silicon are thought to be the most accurate determinations of the atomic form factor $f(\omega, \Delta)$ for that material. From these data, Price, Maslen & Mair (1978) were able to refine values of $f'(\omega, \Delta)$ for a number of photon energies. Recently, Deutsch & Hart (1985) were able to extend the determination of the form factor to higher values of momentum transfer ($\hbar\Delta$). This technique requires for its success the availability of large, strain-free crystals, which limits the range of materials that can be investigated.

A number of experimentalists have attempted to measure *Pendellösung* fringes for parallel-sided specimens illuminated by white radiation, usually from synchrotron-radiation sources. [See, for example, Hashimoto, Kozaki & Ohkawa (1965) and Aristov, Shmytko & Shulakov (1977).] A technique in which the *Pendellösung* fringes are detected using a solid-state detector has been reported by Takama, Kobayashi & Sato (1982). Using this technique, Takama and his co-workers have reported measurements for silicon (Takama, Iwasaki & Sato, 1980), germanium (Takama & Sato, 1984), copper (Takama & Sato, 1982), and aluminium (Takama, Kobayashi & Sato, 1982). A feature of this technique is that it can be used with small crystals, in contrast to the first technique in this section. However, it does not have the precision of that technique.

Another technique using the dynamical theory of X-ray diffraction determines the integrated reflectivity for a Bragg-case reflection that uses the expression for integrated reflectivity given by Zachariasen (1945). Using this approach, Freund (1975) determined the value of the atomic scattering factor $f(\omega, \mathbf{g}_{222})$ for copper. Measurements of intensity are difficult to make, and this method is not capable of yielding results having the precisions of the *Pendellösung* techniques.

4.2.6.3.2.2. Friedel- and Bijvoet-pair techniques

The Bijvoet-pair technique (Bijvoet *et al.*, 1951) is used extensively by crystallographers to assist in the resolution of the phase problem in the solution of crystal structures. Measurements of as many as several hundred values for the diffracted intensities I_{hkl} for a crystal may be made. When these are analysed, the Cole & Stemple (1962) observation that the ratio of the intensities scattered in the Bijvoet or Friedel pair is independent of the state of the crystal is assumed to hold. This is a necessary assumption since in a large number of structure analyses radiation damage occurs during the course of an experiment.

For simple crystal structures, Hosoya (1975) has outlined a number of ways in which values of $f'(\omega, \mathbf{g}_{hkl})$ and $f''(\omega, \mathbf{g}_{hkl})$ may be extracted from the Friedel-pair ratios. Measurements of these corrections for atoms such as gallium, indium, arsenic and selenium have been made.

In more complicated crystal structures for which the positional parameters are known, attempts have been made to determine the anomalous-scattering corrections by least-squares-refinement techniques. Measurements of these corrections for a number of atoms have been made, *inter alia*, by Engel & Sturm (1975), Templeton & Templeton (1978), Philips, Templeton, Templeton & Hodgson (1978), Templeton, Templeton, Philips & Hodgson (1980), Philips & Hodgson (1985), and Chapuis, Templeton & Templeton (1985). There are a number of problems with this approach, not the least of which are the requirement to measure intensities accurately for a large period of time and the assumption that specimen perfection does not affect the intensity ratio. Also, factors such as crystal shape and primary and secondary extinction may adversely affect the ability to measure intensity ratios correctly. One problem that has to be addressed in this type of

determination is the fact that $f'(\omega, 0)$ and $f''(\omega, 0)$ are related to one another, and cannot be refined separately.

4.2.6.3.3. Comparison of theory with experiment

In this section, discussion will be focused on (i) the scattering of photons having energies considerably greater than that of the K -absorption edge of the atom from which they are scattered, and (ii) scattering of photons having energies in the neighbourhood of the K -absorption edge of the atom from which they are scattered.

4.2.6.3.3.1. Measurements in the high-energy limit ($\omega/\omega_K \rightarrow 0$)

In this case, there is some possibility of testing the validity of the relativistic dipole and relativistic multipole theories since, in the high-energy limit, the value of $f'(\omega, 0)$ must approach a value related to the total self energy of the atom (E_{tot}/mc^2). That there is an atomic number dependent systematic error in the relativistic dipole approach has been demonstrated by Creagh (1984). The question of whether the relativistic multipole approach yields a result in better accord with the experimental data is answered in Table 4.2.6.4, where a comparison of values of $f'(\omega, 0)$ is made for three theoretical data sets (this work; Cromer & Liberman, 1981; Wagenfeld, 1975) with a number of experimental results. These include the 'direct' measurements using X-ray interferometers (Cusatis & Hart, 1975; Creagh, 1984), the Kramers-Kronig integration of X-ray attenuation data (Gerward *et al.*, 1979), and the angle-of-the-prism data of Deutsch & Hart (1984*b*). Also included in the table are 'indirect' measurements: those of Price *et al.* (1978), based on *Pendellösung* measurements, and those of Grimvall & Persson (1969). These latter data estimate $f'(\omega, \mathbf{g}_{hkl})$ and not $f'(\omega, 0)$. Table 4.2.6.4 details values of the real part of the dispersion correction for LiF, Si, Al and Ge for the characteristic wavelengths $\text{Ag}K\alpha_1$, $\text{Mo}K\alpha_1$ and $\text{Cu}K\alpha_1$. Of the atomic species listed, the first three are approaching the high-energy limit at $\text{Ag}K\alpha_1$, whilst for germanium the K -shell absorption edge lies between $\text{Mo}K\alpha_1$ and $\text{Ag}K\alpha_1$.

The high-energy-limit case is considered first: both the relativistic dipole and relativistic multipole theories underestimate $f'(\omega, 0)$ for LiF whereas the non-relativistic theory overestimates $f'(\omega, 0)$ when compared with the experimental data. For silicon, however, the relativistic multipole yields values in good agreement with experiment. Further, the values derived from the work of Takama *et al.* (1982), who used a *Pendellösung* technique to measure the atomic form factor of aluminium are in reasonable agreement with the relativistic multipole approach. Also, some relatively imprecise measurements by Creagh (1985) are in better accordance with the relativistic multipole values than with the relativistic dipole values.

Further from the high-energy limit (smaller values of ω/ω_K), the relativistic multipole approach appears to give better agreement with theory. It must be reported here that measurements by Katoh *et al.* (1985*a*) for lithium fluoride at a wavelength of 0.77366 Å yielded a value of 0.018 in good agreement with the relativistic multipole value 0.017.

At still smaller values of (ω/ω_K), the non-relativistic theory yields values considerably at variance with the experimental data, except for the case of LiF using $\text{Cu}K\alpha_1$ radiation. The relativistic multipole approach seems, in general, to be a little better than the relativistic approach, although agreement between experiment and theory is not at all good for germanium. Neither

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of the experiments cited here, however, has claims to high accuracy.

In Table 4.2.6.5, a comparison is made of measurements of $f''(\omega, 0)$ derived from the results of the IUCr X-ray Attenuation Project (Creagh & Hubbell, 1987, 1990) with a number of theoretical predictions. The measurements were made on carbon, silicon and copper specimens at the characteristic wavelengths $\text{Cu } K\alpha_1$, $\text{Mo } K\alpha_1$ and $\text{Ag } K\alpha_1$. The principal conclusion that can be drawn from perusal of Table 4.2.6.5 is that only minor, non-systematic differences exist between the predictions of the several relativistic approaches and the experimental results. In contrast, the non-relativistic theory fails for higher values of atomic number.

4.2.6.3.3.2. Measurements in the vicinity of an absorption edge

The advent of the synchrotron-radiation source as a routine experimental tool and the deep interest that many crystallographers have in both XAFS and the anomalous-scattering determinations of crystal structures have stimulated considerable interest in the determination of the dispersion corrections in the neighbourhood of absorption edges. In this region, the interaction of the ejected photoelectron with electrons belonging to neighbouring atoms causes the modulations that are referred to as XAFS. Both $f''(\omega, 0)$ (which is directly proportional to the X-ray scattering cross section) and $f'(\omega, 0)$ [which is linked to $f''(\omega, 0)$ through the Kramers-Kronig integral] exhibit these modulations. It is at this point that one must realize that the theoretical tabulations are for the interactions of photons with *isolated* atoms. At best, a comparison of theory and experiment can show that they follow the same trend.

Measurements have been made in the neighbourhood of the absorption edges of a variety of atoms using the 'direct' techniques interferometry, Kramers-Kronig, refraction of a prism and critical-angle techniques, and by the 'indirect' refinement techniques. In Table 4.2.6.6, a comparison is made of experimental values taken at or near the absorption edges of copper, nickel and niobium with theoretical predictions. These have not been adjusted for any energy window that might be thought to exist in any particular experimental configuration. The theoretical values for niobium have been calculated at the energy at which the experimentalists claimed the experiment was conducted.

Despite the considerable experimental difficulties and the wide variety of experimental apparatus, there appears to be close agreement between the experimental data for each type of atom. There appears to be, however, for both copper and nickel, a large discrepancy between the theoretical values and the experimental values. It must be remembered that the experimental values are averages of the value of $f'(\omega, 0)$, the average being taken over the range of photon energies that pass through the device when it is set to a particular energy value. Furthermore, the exact position of the wavelength chosen may be in doubt in absolute terms, especially when synchrotron-radiation sources are used. Therefore, to be able to make a more realistic comparison between theory and experiment, the theoretical data gained using the relativistic multipole approach (this work) were averaged over a rectangular energy window of 5 eV width in the region containing the absorption edge. The rectangular shape arises because of the shape of the reflectivity curve and 5 eV was chosen as a result of (i) analysis of the characteristics of the interferometers used by Bonse *et al.* and Hart *et al.*, and (ii) a statement concerning the experimental bandpass of the interferometer used by Bonse & Henning (1986). It must also be borne in mind that mechanical vibrations and

Table 4.2.6.4. Comparison of measurements of the real part of the dispersion correction for LiF, Si, Al and Ge for characteristic wavelengths $\text{Ag } K\alpha_1$, $\text{Mo } K\alpha_1$ and $\text{Cu } K\alpha_1$ with theoretical predictions; the experimental accuracy claimed for the experiments is shown thus: (10) = 10% error

Sample	Reference	$f'(\omega, 0)$		
		$\text{Cu } K\alpha_1$	$\text{Mo } K\alpha_1$	$\text{Ag } K\alpha_1$
LiF	Theory			
	This work	0.075	0.017	0.010
	Cromer & Liberman (1981)	0.068	0.014	0.006
	Wagenfeld (1975)	0.080	0.023	0.015
	Experiment			
Creagh (1984)	0.085 (5)	0.020 (10)	0.014 (10)	
Deutsch & Hart (1984b)	-	0.0217 (1)	0.0133 (1)	
Si	Theory			
	This work	0.254	0.817	0.052
	Cromer & Liberman (1981)	0.242	0.071	0.042
	Wagenfeld (1975)	0.282	0.101	0.071
	Experiment			
	Cusatis & Hart (1975)	-	0.0863 (2)	0.0568 (2)
	Price <i>et al.</i> (1978)	-	0.085 (7)	0.047 (7)
	Gerward <i>et al.</i> (1979)	0.244 (7)	0.099 (7)	0.070 (7)
Creagh (1984)	0.236 (5)	0.091 (5)	0.060 (5)	
Deutsch & Hart (1984b)	-	0.0847 (1)	0.0537 (1)	
Al	Theory			
	This work	0.213	0.0645	0.041
	Cromer & Liberman (1981)	0.203	0.0486	0.020
	Wagenfeld (1975)	0.235	0.076	0.553
	Experiment			
	Creagh (1985)	-	0.065 (20)	0.044 (20)
Takama <i>et al.</i> (1982)	0.20 (5)	0.07 (5)	0.035 (10)	
Ge	Theory			
	This work	-1.089	0.155	0.302
	Cromer & Liberman (1981)	-1.167	0.062	0.197
	Wagenfeld (1975)	-1.80	-0.08	0.14
	Experiment			
	Gerward <i>et al.</i> (1979)	-1.04	0.30	0.43
Grimvall & Persson (1969)	-1.79	0.08	0.27	

thermal fluctuations can broaden the energy window and that 5 eV is not an overestimate of the width of this window. Note that for elements with atomic numbers less than 40 the experimental width is greater than the line width.

For the Bonse & Henning (1986) data, two values are listed for each experiment. Their experiment demonstrates the effect the state of polarization of the incoming photon has on the value of $f'(\omega, 0)$. Similar X-ray dichroism has been shown for sodium bromate by Templeton & Templeton (1985) and Chapuis *et al.* (1985). The theoretical values are for averaged polarization in

4.2. X-RAYS

Table 4.2.6.5. Comparison of measurements of $f'(\omega, 0)$ for C, Si and Cu for characteristic wavelengths $Ag K\alpha_1$, $Mo K\alpha_1$ and $Cu K\alpha_1$ with theoretical predictions; the measurements are from the IUCr X-ray Attenuation Project Report (Creagh & Hubbell, 1987, 1990), corrected for the effects of Compton, Laue–Bragg, and small-angle scattering

Sample	Reference	$f'(\omega, 0)$		
		Cu $K\alpha_1$	Mo $K\alpha_1$	Ag $K\alpha_1$
^{6}C	Theory			
	This work	0.0091	0.0016	0.0009
	Cromer & Liberman (1981)	0.0091	0.0016	0.0009
	Wagenfeld (1975)	–	–	–
	Scofield (1973)	0.0093	0.0016	0.0009
	Storm & Israel (1970)	0.0090	0.0016	0.0009
	Experiment IUCr Project	0.0093	0.0016	0.0009
^{14}Si	Theory			
	This work	0.330	0.070	0.043
	Cromer & Liberman (1981)	0.330	0.0704	0.0431
	Wagenfeld (1975)	0.330	0.071	0.044
	Scofield (1973)	0.332	0.0702	0.0431
	Storm & Israel (1970)	0.331	0.0698	0.0429
	Experiment IUCr Project	0.332	0.0696	0.0429
^{29}Cu	Theory			
	This work	0.588	1.265	0.826
	Cromer & Liberman (1981)	0.589	1.265	0.826
	Scofield (1973)	0.586	1.256	0.826
	Experiment IUCr Project	0.588	1.267	0.826

the incident photon beam. Another important feature is the difference of 0.16 electrons between the Kramers–Kronig and the interferometer values. Bonse & Henning (1986) did not add the relativistic correction term to their Kramers–Kronig values. Inclusion of this term would have reduced the quoted values by 0.20, bringing the two data sets into close agreement with one another.

Katoh *et al.* (1985b) have made measurements spanning the K -absorption edge of germanium using the deviation by a prism method, and these data have been shown to be in excellent agreement with the theory on which these tables are based (Creagh, 1993). In contrast, the theoretical approach of Pratt, Kissell & Bergstrom (1994) does not agree so well, especially near to, and at higher photon energies, than the K -edge energy. Also, Chapuis *et al.* (1985) have measured the dispersion corrections for holmium in $[HoNa(edta)] \cdot 8H_2O$ for the characteristic emission lines $Cu K\alpha_1$, $Cu K\alpha_2$, $Cu K\beta$, and $Mo K\alpha_1$ using a refinement technique. Their results are in reasonable agreement with the relativistic multipole theory, *e.g.* for $f'(\omega, \Delta)$ at the wavelength of $Cu K\alpha_1$ experiment gives $-(16.0 \pm 0.2)$ whereas the relative multipole approach yields -15.0 . For $Cu K\alpha_2$, experiment yields $-(13.9 \pm 0.3)$ and theory gives -13.67 . The discrepancy between theory and experiment may well be explained by the oxidation state of the holmium ion, which is in the form Ho^{3+} . The oxidation state of an atom affects both the position of the absorption edge and the magnitude of the

relativistic correction. Both of these will have a large influence on the value of $f'(\omega, \Delta)$ in the neighbourhood of the absorption edge. Another problem that may be of some significance is the natural width of the absorption edge, about 60 eV. What is remarkable is the extent of the agreement between theory and experiment given the nature of the experiment. In these experiments, the intensities of many reflections (usually nearly 1000) are analysed and compared. Such a procedure can be followed only if there is no dependence of $f'(\omega, \Delta)$ on Δ .

It had often been thought that the dispersion corrections should exhibit some functional dependence on scattering angle. Indeed, some texts ascribe to these corrections the same functional dependence on angle of scattering as the form factor. A fundamental dependence was also predicted theoretically on the basis of non-relativistic quantum mechanics (Wagenfeld, 1975). This prediction is not supported by modern approaches using relativistic quantum mechanics [see, for example, Kissel *et al.* (1980)]. Reference to Tables 4.2.6.4 and 4.2.6.6 shows that the agreement between experimental values derived from diffraction experiments and those derived from ‘direct’ experiments is excellent. They are also in excellent agreement with the recent calculations, using relativistic quantum mechanics, so that it may be inferred that there is indeed no functional dependence of the dispersion corrections on scattering angle. Moreover, Suortti, Hastings & Cox (1985) have recently demonstrated that $f'(\omega, \Delta)$ was independent of Δ in a powder-diffraction experiment using a nickel specimen.

4.2.6.3.3.3. Accuracy in the tables of dispersion corrections

Experimentalists must be aware of two potential sources of error in the values of $f'(\omega, 0)$ listed in Table 4.2.6.5. One is computational, arising from the error in calculating the relativistic correction. Stibius-Jensen (1980) has suggested that this error may be as large as $\pm 0.25(E_{tot}/mc^2)$. This means, for example, that the real part of the dispersion correction $f'(\omega, 0)$ for lead at the wavelength of 0.55936 Å is $-(1.168 \pm 0.146)$. The effect of this error is to shift the dispersion curve vertically without distorting its shape. Note, however, that the direction of the shift is either up or down for all atoms: the effect of multipole cancellation and retardation will be in the same direction for all atoms.

The second possible source of error occurs because the position of the absorption edge varies somewhat depending on the oxidation state of the scattering atom. This has the effect of displacing the dispersion curve laterally. Large discrepancies may occur for those regions in which the dispersion corrections are varying rapidly with photon energy, *i.e.* near absorption edges.

It must also be borne in mind that in the neighbourhood of an absorption edge polarization effects may occur. The tables are valid only for average polarization.

4.2.6.3.3.4. Towards a tensor formalism

The question of how best to describe the interaction of X-rays with crystalline materials is quite difficult to answer. In the form factor formalism, the atoms are supposed to scatter as though they are isolated atoms situated at fixed positions in the unit cell. In the vast majority of cases, the polarization on scattering is not detected, and only the scattered intensities are measured. From the scattered intensities, the distribution of the electron density within the unit cell is calculated, and the difference between the form-factor model and that calculated from the intensities is taken as a measure of the nature and location of chemical bonds between atoms in the unit cell.

4. PRODUCTION AND PROPERTIES OF RADIATIONS

Table 4.2.6.6. Comparison of $f'(\omega_A, 0)$ for copper, nickel, zirconium, and niobium for theoretical and experimental data sets; in this table: BR \equiv Bragg reflection; IN \equiv interferometer; KK \equiv Kramers–Kronig; CA = critical angle; and REF = reflectivity; measurements have been made for the K-absorption edges of copper and nickel and near the K-absorption edges of zirconium and niobium; claimed experimental errors are not worse than 5%

Reference	Method	$f'(\omega_A, 0)$			
		Cu	Ni	Nb	Zr
Experiment					
Freund (1975)	BR	−8.2			
Begum, Hart, Lea & Siddons (1986)	IN	−7.84	−7.66		
Bonse & Materlik (1972)	IN		−8.1		
Bonse, Hartmann-Lotsch & Lotsch (1983a)	IN	−8.3			
Hart & Siddons (1981)	IN	−9.3	−9.2	−4.396	−6.670
Kawamura & Fukimachi (1978; cited in Bonse & Hartmann-Lotsch, 1984)	KK		−7.9		
Dreier <i>et al.</i> (1984)	KK	−8.2	−7.8		−7.83
	IN	−8.3	−8.1		
Bonse & Hartmann-Lotsch (1984)	KK	−8.3	−7.7		
Fukamachi <i>et al.</i> (1978; cited in Bonse & Hartmann-Lotsch, 1984)	KK	−8.8			
	CA	−10.0			
Bonse & Henning (1986)	IN			−7.37; −7.73	
	KK			−7.21; −7.62	
Stanglmeier, Lengeler, Weber, Gobel & Schuster (1992)	REF	−8.5	−8.1		
Creagh (1990, 1993)	REF	−8.2	−7.7		−6.8
Theory					
Cromer & Liberman (1981)		−13.50	−9.45	−4.20; −7.39	−6.207
This work		−9.5	−9.40	−4.04; −7.23	−6.056
Averaged values (5 eV) window		−9.0	−7.53	−8.18	−6.04

This is the zeroth-order approximation to a solution, but it is in fact the only way crystal structures are solved *ab initio*.

The existence of chemical bonding imposes additional restrictions on the symmetry of lattices, and, if the associated influence this has on the complexity of energy levels is taken into account, significant changes in the scattering factors may occur in the neighbourhood of the absorption edges of the atoms comprising the crystal structure. The magnitudes of the dispersion corrections are sensitive to the chemical state, particularly oxidation state, and phenomena similar to those observed in the XAFS case (Section 4.2.4) are observed.

The XAFS interaction arising from the presence of neighbouring atoms is proportional to $f''(\omega, 0)$ and therefore is related to $f'(\omega, 0)$ through the Kramers–Kronig integral. It is not surprising that these modulations are observed in diffracted intensities in those X-ray diffraction experiments where the photon energy is scanned through the absorption edge of an atomic species in the crystal lattice. Studies of this type are referred to as diffraction absorption fine structure (DAFS) experiments. A recent review of work performed using counter techniques has been given by Sorenson (1994). Creagh & Cookson (1995) have described the use of imaging-plate techniques to study the structure and site symmetry using the DAFS technique. This technique has the ability to discriminate between different lattice sites in the unit cell occupied by an atomic species. XAFS cannot make this discrimination. The DAFS modulations are small perturbations to the diffracted intensities. They are, however, significantly larger than the tensor effects described in the following paragraphs.

In the case where the excited state lacks high symmetry and is oriented by crystal bonding, the scattering can no longer be

Table 4.2.6.7. List of wavelengths, energies, and linewidths used in compiling the table of dispersion corrections (a) Agarwal (1979); (b) Deutsch & Hart (1982)

Radiation	Wavelength (Å)	Energy (keV)	Linewidth (eV)
⁷⁹ Au $K\alpha_1$	0.180195	68.803	46 (a)
⁷⁴ W $K\alpha_1$	0.209010	59.318	43 (a)
⁷³ Ta $K\alpha_1$	0.215947	57.412	42 (a)
⁴⁷ Ag $K\alpha_1$	0.559360	22.165	7 (a)
⁴² Mo $K\alpha_1$	0.709260	17.480	4 (a)
²⁹ Cu $K\alpha_1$	1.540520	8.04792	2.61 (b)
²⁷ Co $K\alpha_1$	1.788965	6.9302	1.8
²⁶ Fe $K\alpha_1$	1.93597	6.4040	1.6
²⁴ Cr $K\alpha_1$	2.289620	5.4149	1.5
²² Ti $K\alpha_1$	2.748510	4.5108	1.4

described by a scalar scattering factor but must be described by a symmetric second-rank tensor. The consequences of this have been described by Templeton (1994). It follows therefore that material media can be optically active in the X-ray region. Hart (1994) has used his unique polarizing X-ray optical devices to study, for example, Faraday rotation in such materials as iron, in the region of the iron K -absorption edge, and cobalt(III) bromide monohydrate in the region of the cobalt K -absorption edge.

The theory of anisotropy in anomalous scattering has been treated extensively by Kirfel (1994), and Morgenroth, Kirfel

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Table 4.2.6.8. *Dispersion corrections for forward scattering*

Wavelength (Å)	2.748510	2.289620	1.935970	1.788965	1.540520	0.709260	0.559360	0.215947	0.209010	0.180195
Li	f' =	0.0035	0.0023	0.0015	0.0013	0.0008	-0.0003	-0.0004	-0.0006	-0.0006
	f'' =	0.0013	0.0008	0.0006	0.0005	0.0003	0.0001	0.0000	0.0000	0.0000
Be	f' =	0.0117	0.0083	0.0060	0.0052	0.0038	0.0005	0.0001	-0.0005	-0.0005
	f'' =	0.0050	0.0033	0.0023	0.0019	0.0014	0.0002	0.0001	0.0000	0.0000
B	f' =	0.0263	0.0190	0.0140	0.0121	0.0090	0.0013	0.0004	-0.0009	-0.0009
	f'' =	0.0139	0.0094	0.0065	0.0055	0.0039	0.0007	0.0004	0.0000	0.0000
C	f' =	0.0490	0.0364	0.0273	0.0237	0.0181	0.0033	0.0015	-0.0012	-0.0013
	f'' =	0.0313	0.0213	0.0148	0.0125	0.0091	0.0016	0.0009	0.0001	0.0001
N	f' =	0.0807	0.0606	0.0461	0.0403	0.0311	0.0061	0.0030	-0.0020	-0.0020
	f'' =	0.0606	0.0416	0.0293	0.0248	0.0180	0.0033	0.0019	0.0002	0.0002
O	f' =	0.1213	0.0928	0.0716	0.0630	0.0492	0.0106	0.0056	-0.0025	-0.0026
	f'' =	0.1057	0.0731	0.0518	0.0440	0.0322	0.0060	0.0036	0.0004	0.0004
F	f' =	0.1700	0.1324	0.1037	0.0920	0.0727	0.0171	0.0096	-0.0027	-0.0028
	f'' =	0.1710	0.1192	0.0851	0.0725	0.0534	0.0103	0.0061	0.0007	0.0007
Ne	f' =	0.2257	0.1793	0.1426	0.1273	0.1019	0.0259	0.0152	-0.0025	-0.0028
	f'' =	0.2621	0.1837	0.1318	0.1126	0.0833	0.0164	0.0098	0.0012	0.0011
Na	f' =	0.2801	0.2295	0.1857	0.1670	0.1353	0.0362	0.0218	-0.0028	-0.0031
	f'' =	0.3829	0.2699	0.1957	0.1667	0.1239	0.0249	0.0150	0.0019	0.0017
Mg	f' =	0.3299	0.2778	0.2309	0.2094	0.1719	0.0486	0.0298	-0.0030	-0.0034
	f'' =	0.5365	0.3812	0.2765	0.2373	0.1771	0.0363	0.0220	0.0028	0.0026
Al	f' =	0.3760	0.3260	0.2774	0.2551	0.2130	0.0645	0.0406	-0.0020	-0.0026
	f'' =	0.7287	0.5212	0.3807	0.3276	0.2455	0.0514	0.0313	0.0040	0.0037
Si	f' =	0.3921	0.3647	0.3209	0.2979	0.2541	0.0817	0.0522	-0.0017	-0.0025
	f'' =	0.9619	0.6921	0.5081	0.4384	0.3302	0.0704	0.0431	0.0056	0.0052
P	f' =	0.3821	0.3898	0.3592	0.3388	0.2955	0.1023	0.0667	-0.0002	-0.0012
	f'' =	1.2423	0.8984	0.6628	0.5731	0.4335	0.0942	0.0580	0.0077	0.0071
S	f' =	0.3167	0.3899	0.3848	0.3706	0.3331	0.1246	0.0826	0.0015	0.0003
	f'' =	1.5665	1.1410	0.8457	0.7329	0.5567	0.1234	0.0763	0.0103	0.0096
Cl	f' =	0.1832	0.3508	0.3920	0.3892	0.3639	0.1484	0.0998	0.0032	0.0017
	f'' =	1.9384	1.4222	1.0596	0.9202	0.7018	0.1585	0.0984	0.0134	0.0125
Ar	f' =	-0.0656	0.2609	0.3696	0.3880	0.3843	0.1743	0.1191	0.0059	0.0041
	f'' =	2.3670	1.7458	1.3087	1.1388	0.8717	0.2003	0.1249	0.0174	0.0162
K	f' =	-0.5083	0.0914	0.3068	0.3532	0.3868	0.2009	0.1399	0.0089	0.0067
	f'' =	2.8437	2.1089	1.5888	1.3865	1.0657	0.2494	0.1562	0.0219	0.0204
Ca	f' =	-1.3666	-0.1987	0.1867	0.2782	0.3641	0.2262	0.1611	0.0122	0.0097
	f'' =	3.3694	2.5138	1.9032	0.6648	1.2855	0.3064	0.1926	0.0273	0.0255
Sc	f' =	-5.4265	-0.6935	-0.0120	0.1474	0.3119	0.2519	0.1829	0.0159	0.0130
	f'' =	4.0017	2.9646	2.2557	1.9774	1.5331	0.3716	0.2348	0.0338	0.0315
Ti	f' =	-2.2250	-1.6394	-0.3318	-0.0617	0.2191	0.2776	0.2060	0.0212	0.0179
	f'' =	0.5264	3.4538	2.6425	2.3213	1.8069	0.4457	0.2830	0.0414	0.0387
V	f' =	-1.6269	-4.4818	-0.8645	-0.3871	0.0687	0.3005	0.2276	0.0259	0.0221
	f'' =	0.6340	0.4575	3.0644	2.6994	2.1097	0.5294	0.3376	0.0500	0.0468
Cr	f' =	-1.2999	-2.1308	-1.9210	-0.9524	-0.1635	0.3209	0.2496	0.0314	0.0272
	f'' =	0.7569	0.5468	3.5251	3.1130	2.4439	0.6236	0.3992	0.0599	0.0561
Mn	f' =	-1.0732	-1.5980	-3.5716	-2.0793	-0.5299	0.3368	0.2704	0.0377	0.0330
	f'' =	0.8956	0.6479	0.4798	3.5546	2.8052	0.7283	0.4681	0.0712	0.0666
Fe	f' =	-0.8901	-1.2935	-2.0554	-3.3307	-1.1336	0.3463	0.2886	0.0438	0.0386
	f'' =	1.0521	0.7620	0.5649	0.4901	3.1974	0.8444	0.5448	0.0840	0.0787
Co	f' =	-0.7307	-1.0738	-1.5743	-2.0230	-2.3653	0.3494	0.3050	0.0512	0.0454
	f'' =	1.2272	0.8897	0.6602	0.5731	3.6143	0.9721	0.6296	0.0984	0.0921
Ni	f' =	-0.5921	-0.9005	-1.2894	-1.5664	-3.0029	0.3393	0.3147	0.0563	0.0500
	f'' =	1.4240	1.0331	0.7671	0.6662	0.5091	1.1124	0.7232	0.1146	0.1074
Cu	f' =	-0.4430	-0.7338	-1.0699	-1.2789	-1.9646	0.3201	0.3240	0.0647	0.0579
	f'' =	1.6427	1.1930	0.8864	0.7700	0.5888	1.2651	0.8257	0.1326	0.1242
Zn	f' =	-0.3524	-0.6166	-0.9134	-1.0843	-1.5491	0.2839	0.3242	0.0722	0.0648
	f'' =	1.8861	1.3712	1.0193	0.8857	0.6778	1.4301	0.9375	0.1526	0.1430
Ga	f' =	-0.2524	-0.4989	-0.7701	-0.9200	-1.2846	0.2307	0.3179	0.0800	0.0721
	f'' =	2.1518	1.5674	1.1663	1.0138	0.7763	1.6083	1.0589	0.1745	0.1636
Ge	f' =	-0.1549	-0.3858	-0.6412	-0.7781	-1.0885	0.1547	0.3016	0.0880	0.0796
	f'' =	2.4445	1.7841	1.3291	1.1557	0.8855	1.8001	1.1903	0.1987	0.1863
As	f' =	-0.0687	-0.2871	-0.5260	-0.6523	-0.9300	0.0499	0.2758	0.0962	0.0873
	f'' =	2.7627	2.0194	1.5069	1.3109	1.0051	2.0058	1.3314	0.2252	0.2112
Se	f' =	0.0052	-0.1919	-0.4179	-0.5390	-0.7943	-0.0929	0.2367	0.1047	0.0954
	f'' =	3.1131	2.2784	1.7027	1.4821	1.1372	2.2259	1.4831	0.2543	0.2386
Br	f' =	0.0592	-0.1095	-0.3244	-0.4363	-0.6763	-0.2901	0.1811	0.1106	0.1026
	f'' =	3.4901	2.5578	1.9140	1.6673	1.2805	2.4595	1.6452	0.2858	0.2682
Kr	f' =	0.1009	-0.0316	-0.2303	-0.3390	-0.5657	-0.5574	0.1067	0.1180	0.1082
	f'' =	3.9083	2.8669	2.1472	1.8713	1.4385	2.7079	1.8192	0.3197	0.3003

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Table 4.2.6.8. Dispersion corrections for forward scattering (cont.)

Wavelength (Å)	2.748510	2.289620	1.935970	1.788965	1.540520	0.709260	0.559360	0.215947	0.209010	0.180195	
Rb	$f' =$	0.1056	0.0247	-0.1516	-0.2535	-0.4688	-0.9393	0.0068	0.1247	0.1146	0.0717
	$f'' =$	4.3505	3.1954	2.3960	2.0893	1.6079	2.9676	2.0025	0.3561	0.3346	0.2514
Sr	$f' =$	0.1220	0.1037	-0.0489	-0.1448	-0.3528	-1.5307	-0.1172	0.1321	0.1219	0.0769
	$f'' =$	4.8946	3.6029	2.7060	2.3614	1.8200	3.2498	2.2025	0.3964	0.3726	0.2805
Y	$f' =$	0.0654	0.1263	0.0138	-0.0720	-0.2670	-2.7962	-0.2879	0.1380	0.1278	0.0819
	$f'' =$	5.4198	3.9964	3.0054	2.6241	2.0244	3.5667	2.4099	0.4390	0.4128	0.3112
Zr	$f' =$	-0.0304	0.1338	0.0659	-0.0066	-0.1862	-2.9673	-0.5364	0.1431	0.1329	0.0863
	$f'' =$	5.9818	4.4226	3.3301	2.9086	2.2449	0.5597	2.6141	0.4852	0.4562	0.3443
Nb	$f' =$	-0.1659	0.1211	0.1072	0.0496	-0.1121	-2.0727	-0.8282	0.1471	0.1371	0.0905
	$f'' =$	6.5803	4.8761	3.6768	3.2133	2.4826	0.6215	2.8404	0.5342	0.5025	0.3797
Mo	$f' =$	-0.3487	0.0801	0.1301	0.0904	-0.0483	-1.6832	-1.2703	0.1487	0.1391	0.0934
	$f'' =$	7.2047	5.3484	4.0388	3.5326	2.7339	0.6857	3.0978	0.5862	0.5517	0.4177
Tc	$f' =$	-0.6073	-0.0025	0.1314	0.1164	0.0057	-1.4390	-2.0087	0.1496	0.1406	0.0960
	$f'' =$	7.8739	5.8597	4.4331	3.8799	3.0049	0.7593	3.3490	0.6424	0.6047	0.4582
Ru	$f' =$	-0.9294	-0.1091	0.1220	0.1331	0.0552	-1.2594	-5.3630	0.1491	0.1409	0.0981
	$f'' =$	8.5988	6.4069	4.8540	4.2509	3.2960	0.8363	3.6506	0.7016	0.6607	0.5014
Rh	$f' =$	-1.3551	-0.2630	0.0861	0.1305	0.0927	-1.1178	-2.5280	0.1445	0.1373	0.0970
	$f'' =$	9.3504	6.9820	5.2985	4.6432	3.6045	0.9187	0.5964	0.7639	0.7195	0.5469
Pd	$f' =$	-1.9086	-0.4640	0.0279	0.1128	0.1215	-0.9988	-1.9556	0.1387	0.1327	0.0959
	$f'' =$	10.1441	7.5938	5.7719	5.0613	3.9337	1.0072	0.6546	0.8302	0.7822	0.5955
Ag	$f' =$	-2.5003	-0.7387	-0.0700	0.0634	0.1306	-0.8971	-1.6473	0.1295	0.1251	0.0928
	$f'' =$	10.9916	8.2358	6.2709	5.5027	4.2820	1.1015	0.7167	0.9001	0.8484	0.6469
Cd	$f' =$	-3.5070	-1.1086	-0.2163	-0.0214	0.1185	-0.8075	-1.4396	0.1171	0.1147	0.0881
	$f'' =$	11.9019	8.9174	6.8017	5.9728	4.6533	1.2024	0.7832	0.9741	0.9185	0.7013
In	$f' =$	-5.1325	-1.5975	-0.4165	-0.1473	0.0822	-0.7276	-1.2843	0.1013	0.1012	0.0816
	$f'' =$	12.6310	9.6290	7.3594	6.4674	5.0449	1.3100	0.8542	1.0519	0.9922	0.7587
Sn	$f' =$	-7.5862	-2.2019	-0.6686	-0.3097	0.0259	-0.6537	-1.1587	0.0809	0.0839	0.0728
	$f'' =$	13.5168	10.3742	7.9473	6.9896	5.4591	1.4246	0.9299	1.1337	1.0697	0.8192
Sb	$f' =$	-9.2145	-3.0637	-0.9868	-0.5189	-0.0562	-0.5866	-1.0547	0.0559	0.0619	0.0613
	$f'' =$	12.7661	11.1026	8.5620	7.5367	5.8946	1.5461	1.0104	1.2196	1.1512	0.8830
Te	$f' =$	-11.6068	-4.2407	-1.4022	-0.7914	-0.1759	-0.5308	-0.9710	0.0216	0.0316	0.0435
	$f'' =$	-10.1013	11.8079	9.2067	8.1113	6.3531	1.6751	1.0960	1.3095	1.2366	0.9499
I	$f' =$	-13.9940	-5.6353	1.9032	1.1275	-0.3257	-0.4742	-0.8919	-0.0146	-0.0001	0.0259
	$f'' =$	3.4071	12.6156	9.8852	8.7159	6.8362	1.8119	1.1868	1.4037	1.3259	1.0201
Xe	$f' =$	-9.6593	-8.1899	-2.6313	-1.5532	-0.5179	-0.4205	-0.8200	-0.0565	-0.0367	0.0057
	$f'' =$	3.7063	11.7407	10.5776	9.3585	7.3500	1.9578	1.2838	1.5023	1.4195	1.0938
Cs	$f' =$	-8.1342	-10.3310	-3.5831	-2.1433	-0.7457	-0.3680	-0.7527	-0.1070	-0.0809	0.0194
	$f'' =$	4.0732	12.8551	11.2902	10.0454	7.9052	2.1192	1.3916	1.6058	1.5179	1.1714
Ba	$f' =$	-7.2079	-11.0454	-4.6472	-2.7946	-1.0456	-0.3244	-0.6940	-0.1670	-0.1335	-0.0494
	$f'' =$	4.4110	10.0919	12.0003	10.7091	8.4617	2.2819	1.5004	1.7127	1.6194	1.2517
La	$f' =$	-6.5722	-12.8190	-6.3557	-3.6566	-1.4094	-0.2871	-0.6411	-0.2363	-0.1940	-0.0835
	$f'' =$	4.7587	3.5648	12.8927	11.4336	9.0376	2.4523	1.6148	1.8238	1.7250	1.3353
Ce	$f' =$	-6.0641	-9.3304	-8.0962	-4.8792	-1.8482	-0.2486	-0.5890	-0.3159	-0.2633	-0.1222
	$f'' =$	5.1301	3.8433	11.8734	12.1350	9.6596	2.6331	1.7358	1.9398	1.8353	1.4227
Pr	$f' =$	-5.6727	-7.9841	-10.9279	-6.7923	-2.4164	-0.2180	-0.5424	-0.4096	-0.3443	-0.1666
	$f'' =$	5.5091	4.1304	9.2394	12.8653	10.2820	2.8214	1.8624	2.0599	1.9496	1.5136
Nd	$f' =$	-5.3510	-7.1451	-10.5249	-8.1618	-3.1807	-0.1943	-0.5012	-0.5194	-0.4389	-0.2183
	$f'' =$	5.9005	4.4278	9.9814	11.9121	10.9079	3.0179	1.9950	2.1843	2.0679	1.6077
Pm	$f' =$	-5.0783	-6.5334	-13.2062	-10.0720	-4.0598	-0.1753	-0.4626	-0.6447	-0.5499	-0.2776
	$f'' =$	6.3144	4.7422	3.6278	9.2324	11.5523	3.2249	2.1347	2.3143	2.1906	1.7056
Sm	$f' =$	-4.8443	-6.0570	-9.3497	-10.2609	-5.3236	-0.1638	-0.4287	-0.7989	-0.6734	-0.3455
	$f'' =$	6.7524	5.0744	3.8839	9.9412	12.2178	3.4418	2.2815	2.4510	2.3197	1.8069
Eu	$f' =$	-4.6288	-5.6630	-7.9854	-13.5405	-8.9294	-0.1578	-0.3977	-0.9903	-0.8137	-0.4235
	$f'' =$	7.2035	5.4178	4.1498	3.6550	11.1857	3.6682	2.4351	2.5896	2.4526	1.9120
Gd	$f' =$	-4.5094	-5.3778	-7.1681	-9.3863	-8.8380	-0.1653	-0.3741	-1.2279	-1.0234	-0.5140
	$f'' =$	7.6708	5.7756	4.4280	3.9016	11.9157	3.9035	2.5954	2.7304	2.5878	2.0202
Tb	$f' =$	-4.3489	-5.0951	-6.5583	-8.0413	-9.1472	-0.1723	-0.3496	-1.5334	-1.2583	-0.6165
	$f'' =$	8.1882	6.1667	4.7292	4.1674	9.1891	4.1537	2.7654	2.8797	2.7310	2.1330
Dy	$f' =$	-4.1616	-4.8149	-6.0597	-7.1503	-9.8046	-0.1892	-0.3302	-1.9594	-1.5632	-0.7322
	$f'' =$	8.6945	6.5527	5.0280	4.4320	9.8477	4.4098	2.9404	3.0274	2.8733	2.2494
Ho	$f' =$	-4.0280	-4.5887	-5.6628	-6.5338	-14.9734	-0.2175	-0.3168	-2.6705	-1.9886	-0.8709
	$f'' =$	9.2302	6.9619	5.3451	4.7129	3.7046	4.6783	3.1241	3.1799	3.0218	2.3711
Er	$f' =$	-3.9471	-4.4106	-5.3448	-6.0673	-9.4367	-0.2586	-0.3091	-5.5645	-2.6932	-1.0386
	$f'' =$	9.7921	7.3910	5.6776	5.0074	3.9380	4.9576	3.3158	0.6167	3.1695	2.4949
Tm	$f' =$	-3.9079	-4.2698	-5.0823	-5.6969	-8.0393	-0.3139	-0.3084	-2.8957	-5.6057	-1.2397
	$f'' =$	10.3763	7.8385	6.0249	5.3151	4.1821	5.2483	3.5155	0.6569	0.6192	2.6240
Yb	$f' =$	-3.8890	-4.1523	-4.8591	-5.3940	-7.2108	-0.3850	-0.3157	-2.4144	-2.9190	-1.4909
	$f'' =$	10.9742	8.2969	6.3813	5.6309	4.4329	5.5486	3.7229	0.6994	0.6592	2.7538

4.2. X-RAYS

Table 4.2.6.8. Dispersion corrections for forward scattering (cont.)

Wavelength (Å)	2.748510	2.289620	1.935970	1.788965	1.540520	0.709260	0.559360	0.215947	0.209010	0.180195	
Lu	f'	-3.9056	-4.0630	-4.6707	-5.1360	-6.6179	-0.4720	-0.3299	-2.1535	-2.4402	-1.8184
	f''	11.5787	8.7649	6.7484	5.9574	4.6937	5.8584	3.9377	0.7436	0.7010	2.8890
Hf	f'	-4.0452	-4.0564	-4.4593	-4.9466	-6.1794	-0.5830	-0.3548	-1.9785	-2.1778	-2.2909
	f''	12.2546	9.2832	7.1518	6.3150	4.9776	6.1852	4.1643	0.7905	0.7454	3.0246
Ta	f'	-4.0905	-3.9860	-4.3912	-4.7389	-5.7959	-0.7052	-0.3831	-1.8534	-2.0068	-3.1639
	f''	12.9479	9.8171	7.5686	6.6850	5.2718	6.5227	4.3992	0.8392	0.7915	3.1610
W	f'	-4.1530	-3.9270	-4.2486	-4.5529	-5.4734	-0.8490	-0.4201	-1.7565	-1.8819	-3.8673
	f''	13.6643	10.3696	8.0005	7.0688	5.5774	6.8722	4.6430	0.8905	0.8388	0.6433
Re	f'	-4.2681	-3.9052	-4.1390	-4.4020	-5.2083	-1.0185	-0.4693	-1.6799	-1.7868	-2.8429
	f''	14.3931	10.9346	8.4435	7.4631	5.8923	7.2310	4.8944	0.9441	0.8907	0.6827
Os	f'	-4.4183	-3.9016	-4.0478	-4.2711	-4.9801	-1.2165	-0.5280	-1.6170	-1.7107	-2.4688
	f''	15.1553	11.5251	8.9067	7.8753	6.2216	7.6030	5.1558	1.0001	0.9437	0.7238
Ir	f'	-4.5860	-3.9049	-3.9606	-4.1463	-4.7710	-1.4442	-0.5977	-1.5648	-1.6486	-2.2499
	f''	15.9558	12.1453	9.3923	8.3074	6.5667	7.9887	5.4269	1.0589	0.9993	0.7669
Pt	f'	-4.8057	-3.9435	-3.8977	-4.0461	-4.5932	-1.7033	-0.6812	-1.5228	-1.5998	-2.1036
	f''	16.7870	12.7910	9.8985	8.7578	6.9264	8.3905	5.7081	1.1193	1.0565	0.8116
Au	f'	-5.0625	-3.9908	-3.8356	-3.9461	-4.4197	-2.0133	-0.7638	-1.4693	-1.5404	-1.9775
	f''	17.6400	13.4551	10.4202	9.2222	7.2980	8.8022	5.9978	1.1833	1.1171	0.8589
Hg	f'	-5.4327	-4.1029	-3.8228	-3.8921	-4.2923	-2.3894	-0.8801	-1.4389	-1.5055	-1.8958
	f''	18.5241	14.1473	10.9650	9.7076	7.6849	9.2266	6.2989	1.2483	1.1796	0.9080
Tl	f'	-5.8163	-4.2233	-3.8103	-3.8340	-4.1627	-2.8358	-1.0117	-1.4111	-1.4740	-1.8288
	f''	19.4378	14.8643	11.5300	10.2108	8.0900	9.6688	6.6090	1.3189	1.2456	0.9594
Pb	f'	-6.4779	-4.4167	-3.8519	-3.8236	-4.0753	-3.3944	-1.1676	-1.3897	-1.4497	-1.7773
	f''	20.3336	15.5987	12.1106	10.7292	8.5060	10.1111	6.9287	1.3909	1.3137	1.0127
Bi	f'	-7.0419	-4.6533	-3.9228	-3.8408	-4.0111	-4.1077	-1.3494	-1.3721	-1.4290	-1.7346
	f''	21.2196	16.3448	12.7017	11.2575	8.9310	10.2566	7.2566	1.4661	1.3851	1.0685
Po	f'	-7.7195	-4.9604	-4.0267	-3.8855	-3.9670	-5.1210	-1.5613	-1.3584	-1.4133	-1.7005
	f''	22.1974	17.1410	13.3329	11.8209	9.3834	11.0496	7.5986	1.5443	1.4592	1.1266
At	f'	-8.5994	-5.3399	-4.1781	-3.9706	-3.9588	-7.9122	-1.8039	-1.3540	-1.4066	-1.6784
	f''	23.2213	17.9390	13.9709	12.3915	9.8433	9.9777	7.9509	1.6260	1.5367	1.1876
Rn	f'	-10.2749	-5.7275	-4.3331	-4.0549	-3.9487	-8.0659	-2.0847	-1.3475	-1.3982	-1.6571
	f''	24.2613	18.7720	14.6313	12.9815	10.3181	10.4580	8.3112	1.7103	1.6167	1.2504
Fr	f'	-10.8938	-6.2180	-4.5387	-4.1818	-3.9689	-7.2224	-2.4129	-1.3404	-1.3892	-1.6367
	f''	24.3041	19.6009	15.3016	13.5825	10.8038	7.7847	8.6839	1.7986	1.7004	1.3162
Ra	f'	-12.3462	-6.7502	-4.7764	-4.3309	-4.0088	-6.7704	-2.8081	-1.3462	-1.3931	-1.6299
	f''	25.5374	20.4389	15.9778	14.1902	11.2969	8.1435	9.0614	1.8891	1.7863	1.3840
Ac	f'	-12.3496	-7.4161	-5.0617	-4.5270	-4.0794	-6.8494	-3.2784	-1.3473	-1.3922	-1.6190
	f''	25.1363	21.3053	16.6687	14.8096	11.7994	8.5178	9.4502	1.9845	1.8770	1.4553
Th	f'	-13.6049	-8.2118	-5.3692	-4.7310	-4.1491	-7.2400	-3.8533	-1.3524	-1.3955	-1.6136
	f''	26.2511	22.2248	17.4018	15.4642	12.3296	8.8979	9.8403	2.0819	1.9695	1.5284
Pa	f'	-14.4639	-9.4459	-5.7337	-4.9639	-4.2473	-8.0334	-4.6067	-1.3672	-1.4083	-1.6170
	f''	27.4475	23.1548	18.1406	16.1295	12.8681	9.2807	10.2413	2.1835	2.0661	1.6047
U	f'	-12.3528	-9.9362	-6.1485	-5.2392	-4.3638	-9.6767	-5.7225	-1.3792	-1.4184	-1.6188
	f''	30.1725	23.1239	18.8728	16.7952	13.4090	9.6646	10.6428	2.2876	1.1650	1.6831
Np	f'	-17.4143	-11.1080	-6.6136	-5.5633	-4.5053	-11.4937	-6.9995	-1.3941	-1.4312	-1.6231
	f''	31.7405	24.1168	19.6379	17.4837	13.9666	4.1493	9.5876	2.3958	2.2679	1.7648
Pu	f'	-18.0862	-11.4073	-6.9721	-5.8130	-4.6563	-9.4100	-13.5905	-1.4180	-1.4527	-1.6351
	f''	33.8963	23.2960	20.1548	17.9579	14.3729	4.3056	6.9468	2.4979	2.3652	1.8430
Am	f'	-19.7042	-11.7097	-7.7881	-6.2920	-4.8483	-7.8986	-6.7022	-1.4359	-1.4684	-1.6424
	f''	37.3716	24.5715	21.1738	18.8618	15.0877	4.5125	7.3108	2.6218	2.4829	1.9358
Cm	f'	-24.9307	-10.4100	-8.6102	-6.7506	-5.0611	-7.3248	-6.2891	-1.4655	-1.4952	-1.6592
	f''	41.4852	25.8115	21.8880	19.5119	15.6355	4.6980	7.6044	2.7421	2.5974	2.0271
Bk	f'	-32.8492	-9.2185	-9.3381	-7.4293	-5.3481	-6.8498	-6.3438	-1.4932	-1.5203	-1.6746
	f''	32.5421	29.3028	21.9514	20.3581	16.3190	4.9086	7.9477	2.8653	2.7147	2.1208
Cf	f'	-23.6520	-23.5202	-9.7799	-7.8616	-5.5545	-6.6561	-6.4144	-1.5323	-1.5562	-1.6984
	f''	21.9334	31.2999	22.4858	20.8536	16.7428	5.0785	8.1930	2.9807	2.8250	2.2102

& Fischer (1994) have extended this to the description of kinematic diffraction intensities in lattices containing anisotropic anomalous scatterers. Their treatment was developed for space groups up to orthorhombic symmetry.

All the preceding treatments apply to scattering in the neighbourhood of an absorption edge, and to a fairly restricted class of crystals for which the local site symmetry of the electron density of states in the excited state is very different from the apparent crystal symmetry.

These approaches seek to treat the scattering from the crystal as though the scattering from each atomic position can be described by a symmetric second-rank tensor whose properties are determined by the point-group symmetries of those sites. Clearly, this procedure cannot be followed unless the structure has been solved by the usual method. The tensor approach can then be used to explain apparent deficiencies in that model such as the existence of 'forbidden' reflections, birefringence, and circular dichroism.

4. PRODUCTION AND PROPERTIES OF RADIATIONS

Scattering of X-rays from the electron spins in anti-ferromagnetically ordered materials can also be described by imposing a tensor description on the form factor (Blume, 1994). The tensor in this case is a fourth-rank tensor, and the strength of the interaction, even for the favourable case of resonance scattering, is several orders of magnitude lower in intensity than the polarization effects. Nevertheless, studies have been made on holmium and uranium arsenide, and significant magnetic Bragg scattering has been observed.

All the cases cited above represent exciting, state-of-the-art, scientific studies. However, none of the work will assist in the solution of crystal structures directly. Researchers should avoid the temptation, in the first instance, to ascribe anything but a scalar value to the form factor.

4.2.6.3.3.5. Summary

For the imaginary part of the dispersion correction $f''(\omega, \Delta)$, the following observations can be made.

(i) Measurements of the linear absorption coefficient μ_l from which $f'(\omega, 0)$ is deduced should follow the recommendations set out in Subsection 4.2.3.2.

(ii) There is no rational basis for preferring one set of relativistic calculations of atomic scattering cross sections over another, as Creagh & Hubbell (1987, 1990) and Kissel *et al.* (1980) have shown.

(iii) The total scattering cross section for an ensemble of atoms is not simply the sum of the individual scattering cross sections in the neighbourhood of an absorption edge and therefore $f'(\omega, 0)$ will fluctuate as $\omega \rightarrow \omega_\kappa$.

(iv) There is no dependence of $f''(\omega, \Delta)$ and Δ .

For the real part of the dispersion correction $f'(\omega, \Delta)$, the following observations can be made.

(i) The relativistic multipole values listed here tend to accord better with experiment than the non-relativistic and relativistic dipole values.

(ii) There is no dependence of $f'(\omega, \Delta)$ on Δ .

(iii) The theoretical tables are calculated for averaged polarizations.

(iv) Experimentalists wishing to compare their data with theoretical predictions should take account of the energy bandpass of their system when determining the appropriate theoretical value. They should also be aware of the fact that the position of the absorption edge depends on the oxidation state of the scattering atom, and that there is an inaccuracy in the tables of $f'(\omega, 0)$ of either $+0.20(E_{\text{tot}}/mc^2)$ or $-0.10(E_{\text{tot}}/mc^2)$.

4.2.6.4. Table of wavelengths, energies, and linewidths used in compiling the tables of the dispersion corrections

Table 4.2.6.7 lists the characteristic emission wavelengths that are commonly used by crystallographers in their experiments. Also included are the emission energies (since many systems use energy rather than wavelength discrimination) and the line widths (full width at half-maximum) of these lines (Agarwal, 1979; Stearns, 1984; Deutsch & Hart, 1984*a,b*).

4.2.6.5. Tables of the dispersion corrections for forward scattering, averaged polarization using the relativistic multipole approach

See Subsection 4.2.6.3 for comments on the accuracy of these tables. Note also that in the neighbourhood of absorption edges the values for condensed matter may be significantly different from the values in the tables due to XAFS and XANES effects. The values in Table 4.2.6.8 are for scattering by isolated atoms.