

## 4. PRODUCTION AND PROPERTIES OF RADIATIONS

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  $E_{\text{tot}}/mc^2$ . The Cromer & Liberman (1970) relativistic dipole value is  $+\frac{2}{3}(E_{\text{tot}}/mc^2)$ , 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  $^{62}\text{Sm}$  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*,  $\mu_1$ . The refractive index depends on the dielectric susceptibility  $\chi$  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,  $\Delta$ , 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

## 4.2. X-RAYS

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		
<sup>13</sup> 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
<sup>14</sup> 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
<sup>30</sup> 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
<sup>32</sup> 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
<sup>47</sup> Ag	Cu $K\alpha_1$	47.075	46.940	46.936		47.131
<sup>62</sup> Sm	Ag $K\alpha_1$	58.307	56.304	56.299		56.676
<sup>73</sup> Ta	Ag $K\alpha_1$	72.625	72.063	71.994		72.617
<sup>82</sup> 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
<sup>13</sup> 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
<sup>14</sup> 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
<sup>30</sup> 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
<sup>32</sup> 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
<sup>47</sup> Ag	Cu $K\alpha_1$	4.242	4.282		4.282
<sup>62</sup> Sm	Cu $K\alpha_1$	12.16	12.218		12.218
<sup>73</sup> Ta	Ag $K\alpha_1$	4.403	4.399		4.399
<sup>82</sup> 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  $\mu_l$  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  $\Delta$  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  $\Delta$ , 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