

## 4. PRODUCTION AND PROPERTIES OF RADIATIONS

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.* (1985*a,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 (1973*a,b*) for