

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

4.2. X-RAYS

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