4.2. X-RAYS

silicon are thought to be the most accurate determinations of the atomic form factor $f(\omega, \boldsymbol{\Delta})$ for that material. From these data, Price, Maslen & Mair (1978) were able to refine values of $f'(\omega, \boldsymbol{\Delta})$ 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 ($\hbar\boldsymbol{\Delta}$). 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* ($\omega/\omega_\kappa \to 0$)

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 $\mathrm{Ag}\,K\alpha_1$, $\mathrm{Mo}\,K\alpha_1$ and $\mathrm{Cu}\,K\alpha_1$. Of the atomic species listed, the first three are approaching the high-energy limit at $\mathrm{Ag}\,K\alpha_1$, whilst for germanium the K-shell absorption edge lies between $\mathrm{Mo}\,K\alpha_1$ and $\mathrm{Ag}\,K\alpha_1$.

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_κ), 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 $0.77366\,\text{Å}$ yielded a value of 0.018 in good agreement with the relativistic multipole value 0.017.

At still smaller values of (ω/ω_κ), the non-relativistic theory yields values considerably at variance with the experimental data, except for the case of LiF using $\mathrm{Cu}\,K\alpha_1$ 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 $Cu K\alpha_1$, $Mo K\alpha_1$ and $Ag K\alpha_1$. 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* $Ag K\alpha_1$, $Mo K\alpha_1$ *and* $Cu K\alpha_1$ *with theoretical predictions; the experimental accuracy claimed for the experiments is shown thus: (10) = 10% error*

Sample	Reference	$f'(\omega, 0)$		
		$Cu K\alpha_1$	$Mo K\alpha_1$	$Ag K\alpha_1$
LiF	Theory			
	This work	0.075	0.017	0.010
	Cromer & Liberman (1981)	0.068	0.014	0.006
	Wagenfield (1975)	0.080	0.023	0.015
	Experiment			
	Creagh (1984)	0.085 (5)	0.020 (10)	0.014 (10)
	Deutsch & Hart (1984*b*)	–	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 *et al*. (1978)	–	0.085 (7)	0.047 (7)
	Gerward *et al*. (1979)	0.244 (7)	0.099 (7)	0.070 (7)
	Creagh (1984)	0.236 (5)	0.091 (5)	0.060 (5)
	Deutsch & Hart (1984*b*)	–	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 *et al*. (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 *et al*. (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

references