

## 4. PRODUCTION AND PROPERTIES OF RADIATIONS

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

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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  $\Delta$ .

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  $\Delta$  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.