

## 4.2. X-RAYS

Table 4.2.6.5. Comparison of measurements of  $f'(\omega, 0)$  for C, Si and Cu for characteristic wavelengths  $AgK\alpha_1$ ,  $MoK\alpha_1$  and  $CuK\alpha_1$  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 $K\alpha_1$
<sup>6</sup> 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
<sup>14</sup> 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
<sup>29</sup> 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)]·8H<sub>2</sub>O for the characteristic emission lines  $CuK\alpha_1$ ,  $CuK\alpha_2$ ,  $CuK\beta$ , and  $MoK\alpha_1$  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  $CuK\alpha_1$  experiment gives  $-(16.0 \pm 0.2)$  whereas the relative multipole approach yields  $-15.0$ . For  $CuK\alpha_2$ , 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  $\pm 0.25(E_{\text{tot}}/mc^2)$ . 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.