

## 4. PRODUCTION AND PROPERTIES OF RADIATIONS

Table 4.2.6.6. Comparison of  $f'(\omega_A, 0)$  for copper, nickel, zirconium, and niobium for theoretical and experimental data sets; in this table: BR  $\equiv$  Bragg reflection; IN  $\equiv$  interferometer; KK  $\equiv$  Kramers–Kronig; CA = critical angle; and REF = reflectivity; measurements have been made for the K-absorption edges of copper and nickel and near the K-absorption edges of zirconium and niobium; claimed experimental errors are not worse than 5%

Reference	Method	$f'(\omega_A, 0)$			
		Cu	Ni	Nb	Zr
Experiment					
Freund (1975)	BR	−8.2			
Begum, Hart, Lea & Siddons (1986)	IN	−7.84	−7.66		
Bonse & Materlik (1972)	IN		−8.1		
Bonse, Hartmann-Lotsch & Lotsch (1983a)	IN	−8.3			
Hart & Siddons (1981)	IN	−9.3	−9.2	−4.396	−6.670
Kawamura & Fukimachi (1978; cited in Bonse & Hartmann-Lotsch, 1984)	KK		−7.9		
Dreier <i>et al.</i> (1984)	KK	−8.2	−7.8		−7.83
	IN	−8.3	−8.1		
Bonse & Hartmann-Lotsch (1984)	KK	−8.3	−7.7		
Fukamachi <i>et al.</i> (1978; cited in Bonse & Hartmann-Lotsch, 1984)	KK	−8.8			
	CA	−10.0			
Bonse & Henning (1986)	IN			−7.37; −7.73	
	KK			−7.21; −7.62	
Stanglmeier, Lengeler, Weber, Gobel & Schuster (1992)	REF	−8.5	−8.1		
Creagh (1990, 1993)	REF	−8.2	−7.7		−6.8
Theory					
Cromer & Liberman (1981)		−13.50	−9.45	−4.20; −7.39	−6.207
This work		−9.5	−9.40	−4.04; −7.23	−6.056
Averaged values (5 eV) window		−9.0	−7.53	−8.18	−6.04

This is the zeroth-order approximation to a solution, but it is in fact the only way crystal structures are solved *ab initio*.

The existence of chemical bonding imposes additional restrictions on the symmetry of lattices, and, if the associated influence this has on the complexity of energy levels is taken into account, significant changes in the scattering factors may occur in the neighbourhood of the absorption edges of the atoms comprising the crystal structure. The magnitudes of the dispersion corrections are sensitive to the chemical state, particularly oxidation state, and phenomena similar to those observed in the XAFS case (Section 4.2.4) are observed.

The XAFS interaction arising from the presence of neighbouring atoms is proportional to  $f''(\omega, 0)$  and therefore is related to  $f'(\omega, 0)$  through the Kramers–Kronig integral. It is not surprising that these modulations are observed in diffracted intensities in those X-ray diffraction experiments where the photon energy is scanned through the absorption edge of an atomic species in the crystal lattice. Studies of this type are referred to as diffraction absorption fine structure (DAFS) experiments. A recent review of work performed using counter techniques has been given by Sorenson (1994). Creagh & Cookson (1995) have described the use of imaging-plate techniques to study the structure and site symmetry using the DAFS technique. This technique has the ability to discriminate between different lattice sites in the unit cell occupied by an atomic species. XAFS cannot make this discrimination. The DAFS modulations are small perturbations to the diffracted intensities. They are, however, significantly larger than the tensor effects described in the following paragraphs.

In the case where the excited state lacks high symmetry and is oriented by crystal bonding, the scattering can no longer be

Table 4.2.6.7. List of wavelengths, energies, and linewidths used in compiling the table of dispersion corrections (a) Agarwal (1979); (b) Deutsch & Hart (1982)

Radiation	Wavelength (Å)	Energy (keV)	Linewidth (eV)
<sup>79</sup> Au $K\alpha_1$	0.180195	68.803	46 (a)
<sup>74</sup> W $K\alpha_1$	0.209010	59.318	43 (a)
<sup>73</sup> Ta $K\alpha_1$	0.215947	57.412	42 (a)
<sup>47</sup> Ag $K\alpha_1$	0.559360	22.165	7 (a)
<sup>42</sup> Mo $K\alpha_1$	0.709260	17.480	4 (a)
<sup>29</sup> Cu $K\alpha_1$	1.540520	8.04792	2.61 (b)
<sup>27</sup> Co $K\alpha_1$	1.788965	6.9302	1.8
<sup>26</sup> Fe $K\alpha_1$	1.93597	6.4040	1.6
<sup>24</sup> Cr $K\alpha_1$	2.289620	5.4149	1.5
<sup>22</sup> Ti $K\alpha_1$	2.748510	4.5108	1.4

described by a scalar scattering factor but must be described by a symmetric second-rank tensor. The consequences of this have been described by Templeton (1994). It follows therefore that material media can be optically active in the X-ray region. Hart (1994) has used his unique polarizing X-ray optical devices to study, for example, Faraday rotation in such materials as iron, in the region of the iron  $K$ -absorption edge, and cobalt(III) bromide monohydrate in the region of the cobalt  $K$ -absorption edge.

The theory of anisotropy in anomalous scattering has been treated extensively by Kirfel (1994), and Morgenroth, Kirfel