Anomalous dispersion calculations near to and on the long-wavelength side of an absorption edge.* By

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Abstract

Recent experimental measurements have revealed systematic differences between measured values of f' and those calculated by the method of Cromer & Liberman [*J. Chem. Phys.* (1970), **53**, 1891–1898] when the incident X-ray is near to and on the long-wavelength side of an edge. The source of the discrepancy has been identified and some previously published values of f' are corrected. These corrections also apply to Table 2.3.1 in *International Tables for X-ray Crystallography*, Vol. IV [(1974), Birmingham: Kynoch Press].

Introduction

About two years ago we learned from Mr D. P. Siddons (1978), who was continuing the X-ray interferometric work begun by Cusatis & Hart (1974, 1977), that there were systematic differences between his experimental measurements of f' for Nb and our theoretical calculations (Cromer & Liberman, 1970a, b, hereafter CLa and CLb). He noted that near to and on the long-wavelength side of the K edge of Nb our calculations of f' were less negative than experimentally observed.

At about the same time, Phillips, Templeton, Templeton & Hodgson (1978), using synchrotron radiation, noted remarkably large values of f' near the L edges of Cs. They used the very straightforward method of making f' and f'' parameters in a crystal-structure refinement of cesium hydrogen (+)-tartrate. We calculated these quantities and found the same systematic differences on the long-wavelength sides of the edges of Cs as had been observed for Nb.

We have investigated the discrepancy and found that the Gaussian integration method was not correctly evaluating the dispersion integral in this energy region. After casting the integral in a different form, we found calculated and observed values of f' in excellent agreement for Zr, Nb and Mo (Siddons, 1979; Hart & Siddons, 1981) and for Cs (Templeton, Templeton, Phillips & Hodgson, 1980).

The experimental values of Cs show some structure on the high-energy side of the absorption edge and are not monotonic. This structure is related to the fine structure of the absorption edge and ought to be a function of the chemical state and surroundings of the absorbing atom. The theoretical model is a free-atom model and has no structure.

It is the purpose of this note to report corrected values for the commonly used X-ray wavelengths previously reported by us (CLa; Cromer, 1976) and now tabulated in *International Tables for X-ray Crystallography* (1974). Fortunately there are very few cases where these wavelengths are close enough to an edge for an appreciable error to have occurred.

Method of calculation

When the energy of an edge is between 1 and 70 keV, which will be true in cases of interest, equation (30a) of CLa is used for the calculation of f'. On the long-wavelength side of an edge, where the cross section for the incident X-ray is zero, this equation has the form

$$ f^{+} = \frac{c\varepsilon_1}{2\pi^2} \int_0^1 \frac{\sigma(-\varepsilon_1/x)\varepsilon_1^2}{x^2[x^2(\hbar\omega)^2 - \varepsilon_1^2]}\,dx, \tag{1} $$

where c = velocity of light, $\sigma(a)$ = photoelectric cross section of energy a, ε_1 is the binding energy of the electron, $\hbar\omega$ is the energy of the X-ray and $x = -\varepsilon_1/(\varepsilon^+ - \varepsilon_1)$ with ε^+ = the energy of a positive energy state.

When the discrepancy between observed and calculated f' was brought to our attention we tested (1), for an appropriate case, with up to 30 points in the Gaussian integration. Very near the edge the function still had not converged.

Equation (1) was modified by adding and subtracting a certain quantity to yield

$$ f^{+} = \frac{c\varepsilon_1}{2\pi^2}\left[\int_0^1 \frac{\sigma(-\varepsilon_1/x)\varepsilon_1^2 - \sigma(\varepsilon_1)\,\varepsilon_1^2\,x^2}{x^2[x^2(\hbar\omega)^2 - \varepsilon_1^2]}\,dx \right. $$
$$ \left. + \int_0^1 \frac{\sigma(\varepsilon_1)\,\varepsilon_1^2\,x^2}{x^2[x^2(\hbar\omega)^2 - \varepsilon_1^2]}\,dx \right]. \tag{2} $$

The second integral of (2) can be evaluated in closed form and is

$$ \frac{\sigma(\varepsilon_1)\varepsilon_1}{2\hbar\omega}\log\left(\frac{-\varepsilon_1 + \hbar\omega}{-\varepsilon_1 - \hbar\omega}\right), $$

similar to (28) of CLa. The first integral is small because the positive and negative parts nearly cancel. The cross section at energy ε_1 is not known but $\sigma(\varepsilon_1)$ in (2) is effectively an arbitrary constant. In practice, the use of $\sigma(1\cdot001\varepsilon_1)$, the cross section at an energy slightly above ε_1, proved effective. Practical convergence of the integral was obtained with five terms. With more than five points, the value of f' oscillated and remained within $\pm 0\cdot05$ of the value with five points.

Table 1. *Corrected values of f' for certain elements and X-ray wavelengths*

Atom	X-ray $(K\alpha_1)$	Edge	λ/λ_{edge}	$f'_{(present)}$	$f'_{(CLa)}$
V	Cr	1s 1/2	1·009	−4·51	−3·84
Mn	Fe	1s 1/2	1·021	−3·61	−3·37
Fe	Co	1s 1/2	1·026	−3·38	−3·20
Ni	Cu	1s 1/2	1·035	−3·06	−2·96
Zr	Mo	1s 1/2	1·030	−3·09	−2·97
Rh	Ag	1s 1/2	1·048	−2·70	−2·65
Xe	Cr	2s 1/2	1·007	−8·58	−8·13
Cs	Cr	2s 1/2	1·055	−10·77	−10·74
Ba	Cr	2p 1/2	1·039	−11·56	−11·46
La	Cr	2p 3/2	1·013	−13·13	−12·14
Ce	Fe	2p 1/2	1·023	−8·52	−8·39
Pr	Fe	2p 1/2	1·006	−11·40	−10·37
Nd	Co	2s 1/2	1·028	−8·64	−8·49
Nd	Fe	2p 1/2	1·050	−11·07	−11·02
Pm	Fe	2p 3/2	1·009	−13·55	−12·12
Sm	Fe	2p 3/2	1·049	−9·72	−9·62
Eu	Cu	2s 1/2	1·001	−9·36	−7·72
Eu	Co	2p 3/2	1·007	−13·93	−12·17
Gd	Cu	2s 1/2	1·041	−9·29	−9·24
Gd	Co	2p 3/2	1·045	−9·79	−9·66
Tb	Cu	2p 1/2	1·025	−9·69	−9·50
Ho	Cu	2p 3/2	1·003	−15·40	−12·26
Er	Cu	2p 3/2	1·039	−9·90	−9·73
At	Mo	2s 1/2	1·001	−8·73	−7·44
Rn	Mo	2s 1/2	1·033	−8·93	−8·86
Fr	Mo	2p 1/2	1·024	−8·09	−7·91
Ra	Mo	2p 1/2	1·058	−7·65	−7·62
U	Cr	3d 3/2	1·025	−10·98	−10·93
Np	Ag	2s 1/2	1·012	−8·06	−7·84
Np	Mo	2p 3/2	1·008	−12·50	−11·16
Np	Cr	3d 3/2	1·057	−12·17	−12·15
Pu	Ag	2s 1/2	1·042		
		2p 1/2	1·005	−12·50	−8·47
Pu	Mo	2p 3/2	1·033	−10·46	−9·73
Pu	Cr	3d 3/2	1·023	−12·50	−12·28

Results

Values of f' were recomputed whenever $1\cdot0 < \lambda/\lambda_{edge} < 1\cdot06$ for the wavelengths used by CL*a* and Cromer (1976), namely $K\alpha_1$ for Cr, Fe, Co, Cu, Mo and Ag. For wavelengths longer than $1\cdot06\lambda_{edge}$ the correction is less than

0·05 electrons, the estimated numerical accuracy of the calculations. The results are shown in Table 1 along with the previous values for comparison.

Errata

A few errors in CL*a* and CL*b* have come to light. In Table V the calculated values of f' for the 1s 1/2 orbital of Ge with Mo and Ag radiation have the wrong sign. These values should be +0·082 and +0·142. Agreement with experiment is considerably improved.

In equation 30*b*, $\sigma(-\varepsilon_1 x^{1/2})$ should be $\sigma(-\varepsilon_1/x^{1/2})$.

All values of f' and f'' for Pr are incorrect because a book-keeping error had interchanged two wavefunctions. Corrected values are given below:

Radiation	Cr	Fe	Co	Cu	Mo	Ag
f'	−8·31	−11·40	−6·46	−2·73	−0·55	−0·87
f''	4·13	9·32	12·96	10·29	2·82	1·86

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