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X-RAY DISPERSION EFFECTS IN CRYSTAL STRUCTURE DETERMINATIONS

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Author

Templeton, David H.

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David H. Templeton

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David H. Templeton

Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

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Much attention is now devoted toward obtaining more accurate diffraction data and more precise structures of crystals. It seems appropriate to call attention to effects, which have frequently been neglected, caused by the tight bonding of the inner electrons in medium and heavy elements.

The atomic scattering factor f is a complex function:

$$f = f_0 + \Delta f' + i\Delta f'' \quad (1)$$

where f_0 is a real function of $\sin \theta/\lambda$ which has been tabulated for many atoms (International Tables, 1935). The real and imaginary dispersion corrections $\Delta f'$ and $\Delta f''$ are nearly independent of θ but are functions of λ . Recent independent calculations by Eisenlohr and Müller (1954) and Parratt and Hempstead (1954) have shown that for the wave lengths used in diffraction these corrections are not negligible for most elements because of contributions from K, L, and in some cases, M electrons. The effects are not limited to regions "very near" to absorption edges, although that is where they are greatest. A table of $\Delta f'$ and $\Delta f''$ for Cr, Cu, and Mo K_α radiation has been prepared by Dauben and Templeton (1955).

For centrosymmetric crystals the structure factor is:

$$F = \Sigma Q(f_0 + \Delta f') \cos 2\pi(hx + ky + lz) \\ + i \Sigma Q \Delta f'' \cos 2\pi(hx + ky + lz) \quad (2)$$

$$= F_r + iF_i \quad (3)$$

Q is a temperature factor. The magnitude of F , which is to be compared with the experimental value, is:

$$|F| = \sqrt{F_r^2 + F_i^2} \quad (4)$$

When the corrections are neglected, the large structure factors are brought more or less into agreement with the observed ones by adjustment of the normalization factor and by use of incorrect temperature factors. Then the small structure factors are of two kinds. If the contribution of each kind of atom separately is small, the agreement is good. If the contributions of two kinds of atoms are large and of opposite sign, substantial errors result. For the real correction the errors may be positive or negative. For the imaginary correction the error always tends to make the correct amplitude larger than the one in which $\Delta f''$ is omitted. The use of individual incorrect temperature factors can diminish the discrepancy caused by neglect of $\Delta f'$, but it cannot absorb the effect of $\Delta f''$.

The observed structure factors are not the correct coefficients for the electron-density function. The correct coefficients can be approximated, for example, by:

$$F'_0 = F'_c |F_0| / |F_c| \quad (5)$$

where F'_c is a structure factor calculated for the trial structure with f_0 in place of f .

Fortunately, for centric crystals most of the reflections are not much affected by these corrections. Atomic positions derived from all the data probably are not in great error, but the electron-density function and the temperature factors may have systematic errors. The criterion of large opposite contributions from two kinds of atoms is the signal that care must be taken.

For noncentrosymmetric crystals equation (2) has four terms, and $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ have different magnitudes and nonconjugate phases. Some examples have been discussed by Bijvoet (1951,1952). Equation (5) can be used in this case also, with F' a complex number. Because of experimental errors the magnitudes of $F'_0(hkl)$ and $F'_0(\bar{h}\bar{k}\bar{l})$ may be different, and the average value should be taken for each.

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