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Anomalous Scattering of X-Rays by Centro-symmetric Crystals

I. General Theory

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A method is described for solving the phase-problem in the centrosymmetric case by using the anomalous scattering of X-rays. The method which requires the comparison of structure amplitudes measured with two radiations may be applied when the imaginary component, $\Delta f''$, of the anomalous scattering is too large to be neglected. Various techniques for the scaling of the observed data are discussed.

When an atom scatters X-rays of wavelength (λ) close to its own K absorption edge (λ_K) the usual atomic scattering factor f_0 must be replaced by $f = f_0 + \Delta f' + \Delta f''$, where $\Delta f'$ and $\Delta f''$ are the real and imaginary components of the anomalous dispersion correction (James [1]).

Methods have been described [2,3] where the positions of the anomalous scatterers may be determined, the signs of the structure factors relative to the contribution from the anomalous scatterers and hence the signs themselves may be found by comparing structure factors observed with different wavelengths. One of these wavelengths being close to the K-absorption edge of one of the atoms. These methods are valid if $\Delta f''$ can be neglected, which is so if $\lambda/\lambda_K > 1$. The method described here may be used when $\Delta f''$ is of the same order of magnitude as $\Delta f'$, in the limit as $\Delta f'' \rightarrow 0$ the method becomes identical with those previously described.

Black [4] has recently published a general account of the use of nuclear and electronic resonance scattering in crystallography, the methods for sign determination described below are an explicit form of his general solution.

THEORY

The assumptions are made that only one type of atom scatters anomalously with the exciting radiation and that all atoms scatter normally with the second radiation. For the normal case the structure amplitude $F(H)$ is

$$F(H) = \sum_{a} f_a \cos 2\pi \, H \cdot \Theta_a + \sum_{n} f_n \cos 2\pi \, H \cdot \Theta_n \tag{1}$$

where H is (h,k,l), $\Theta_i = (x_i,y_i,z_i)$, the subscript $_a$ refers to an anomalous scatterer, and $_n$ to a normal atom. For the excited case the structure factor $F_a(H)$ is given by

$$F_a(H)^2 = (\sum_{a}(f_a + \Delta f_a')\cos 2\pi H \cdot \Theta_a + \sum_{n} f_n \cos 2\pi H \cdot \Theta_n)^2 + (\sum \Delta f_a'' \cos 2\pi H \cdot \Theta_a)^2 \tag{2}$$

which, putting $\sum_{a} \Delta f_a' \cos 2\pi H \cdot \Theta_a = \Delta F'(H)$ and $\sum_{a} \Delta f_a'' \cos 2\pi H \cdot \Theta_a = \Delta F''(H)$ and rearranging becomes

$$F_a(H)^2 = F(H)^2 + 2F(H) \cdot \Delta F'(H) + (\Delta F'(H))^2 + (\Delta F''(H))^2 \tag{3}$$

further if the ratio $\Delta f''/\Delta f' = k$ is known then

$$F_a(H)^2 = F(H)^2 + 2F(H) \cdot \Delta F'(H) + (1 + k^2)\Delta F'(H)^2 \tag{4}$$

SIGN DETERMINATION

A Patterson function calculated with $|\Delta F'(H)|^2$ as coefficients contains only peaks corresponding to vectors between anomalous scatterers. The first problem then is the recovery of $|\Delta F'(H)|$ from $|F_a(H)|$ and $|F(H)|$.

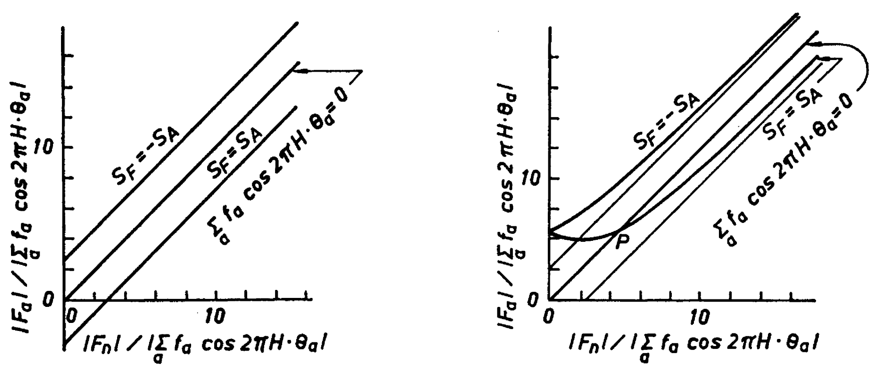

Fig. 1. Plot of $|F_a|/|\sum_{a} f_a \cos 2\pi H \cdot \Theta_a|$ *versus* $|F_n|/|\sum_{a} f_a \cos 2\pi H \cdot \Theta_a|$. The curves are calculated for one anomalous scatterer per asymmetric unit: a) $\Delta f_a' = -2.6$, $\Delta f_a'' = 0$. b) $\Delta f_a' = -2.6$, $\Delta f_a'' = 3.9$. The intercept on the ordinate is $\sqrt{(\sum_{a}(\Delta f_a')^2 + \sum_{a}(\Delta f_a'')^2)}$.

Consider the following cases:

i) The sign, S_F, of $F(H)$ is the same as the sign, S_A, of $\sum_a f_a \cos 2\pi H \cdot \Theta_a$

ii) $S_F = -S_A$

iii) $\sum_a f_a \cos 2\pi H \cdot \Theta_a = 0$ when $F_a(H) = F(H)$

when $\Delta f_a'' \sim 0$ these cases may be represented,[3] Fig. 1a, by plotting $|F_a(H)|/|\sum_a \cos 2\pi H \cdot \Theta_a|$ against $|F(H)|/|\sum_a \cos 2\pi H \cdot \Theta_a|$ which gives three straight lines for the three cases, and $|\Delta F'(H)| = ||F_a(H)| - |F(H)||$. If $|\Delta F''(H)|$ is small compared with $|F(H)|$ this is still a reasonable approximation, but as $|\Delta F''(H)|/|F(H)|$ becomes larger this gives an increasingly worse estimate of $|\Delta F'(H)|$, underestimating $|\Delta F'(H)|$ if $S_F = S_A$ (Fig. 2a) and overestimating

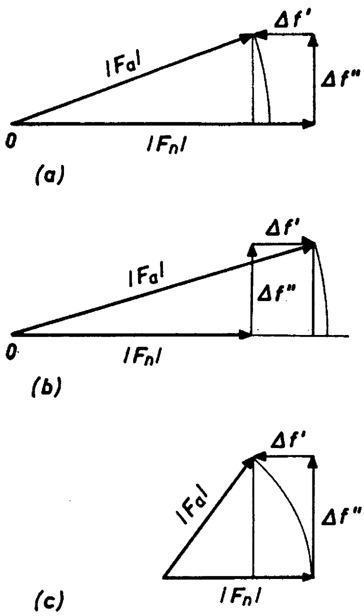

Fig. 2. Vector representation of the following cases:

a) $S_F = S_A$ and $|F_a| < |F_n|$,

b) $S_F = -S_A$ and $|F_a| > |F_n|$,

c) $S_F = S_A$ and $|F_a| = |F_n|$, this corresponds to the situation at point P in Fig. 1b. An arc is drawn through the origin 0 with radius $|F_a|$ to facilitate the comparison of $||F_a| - |F_n||$ with $|\Delta F_a'|$.

if $S_F = -S_A$ (Fig. 2b). In Fig. 1b $|F_a(H)|/|\sum_a \cos 2\pi H \cdot \Theta_a|$ is plotted against $|F(H)|/|\sum_a \cos 2\pi H \cdot \Theta_a|$ for $\Delta f_a' = -2.6$ and $\Delta f_a'' = 3.9$. As may be seen the lower branch actually crosses the line through the origin corresponding to $\sum_a \cos 2\pi H \cdot \Theta_a = 0$ when $|F_a(H)| = |(1 + k^2)\ \Delta F'(H)|/2$. This situation is represented in Fig. 2c.

For $S_F = S_A$

$$|F_a(H)|^2 = |F(H)|^2 - 2|\Delta F'(H)| \cdot |F(H)| + (1 + k^2) \cdot \Delta F'(H)^2 \tag{5}$$

and for $S_F = -S_A$

$$|F_a(H)|^2 = |F(H)|^2 + 2|\Delta F'(H)| \cdot |F(H)| + (1+k^2) \cdot \Delta F'(H)^2 \quad (6)$$

both of which give

$$|\Delta F'(H)| = \left| \frac{1}{1+k^2} \left\{ |F(H)| - \sqrt{(F(H)^2 - (1+k^2)(F(H)^2 - F_a(H)^2))} \right\} \right| \quad (7)$$

where $\sqrt{}$ implies the positive root.

Then provided that $|F(H)| > |\{(1+k^2)\,\Delta F')\}/2|$ eqn. (7) can be used to give $|\Delta F'(H)|^2$ and the Patterson function calculated. If $\Delta f_a'' = 0$ then $k = 0$ and eqn. (7) reduces to

$$|\Delta F'(H)| = ||F(H)| - |F_a(H)|| \quad (8)$$

Having found the positions of the anomalous scatterers $\sum_a \cos 2\pi H \cdot \Theta_a$ may be calculated and $|Fa(H)|/|\sum \cos 2\pi H \cdot \Theta_a|$ plotted against $|F|/|\sum \cos 2\pi H \cdot \Theta_a|$ and the relative signs, *i.e.* whether $S_F \pm S_A$ and hence the signs may be determined by inspection.

SCALING OF DATA

The knowledge of scale and overall temperature factor needed to place the data on absolute scale and to correct for thermal effects can often be obtained with sufficient accuracy from Wilson [5] plots. The scale factor between the sets of data may however be in error, especially if the Wilson plot does not give a particularly good straight line. A plot of ln $(F_a^2(H)/F(H)^2)$ against $\sin^2\Theta/\lambda^2$ will frequently give a good straight line when the Wilson plot itself does not, and so one can determine the relative scale and temperature factor (this latter is not always zero) between the sets of data. The Wilson plot itself is then used to give approximate scale and temperature factors for one set of data.

The use of the $|F_a(H)|/|\sum_a \cos 2\pi H \cdot \Theta_a|$ *versus* $|F(H)|/|\sum_a \cos 2\pi H \cdot \Theta_a|$ plot can be used to improve the scale factor if the position of the anomalous scatterers are known.[3,6] If, as in a study of the anomalous scattering by $(NH_4)_2Co(SO_4)_2,6H_2O$ [7] there exists a class of reflections for which $\sum_a f_a \cos 2\pi H \cdot \Theta_a = 0$ then plotting $|F_a(H)|$ against $|F(H)|$ gives an extremely good relative scale factor, which compensates partly for the fact that no information can be obtained concerning the signs of those reflections.

If the ratio of the intensities of the primary beams of the two radiations were known the scaling problem could be eliminated. In some cases this can be achieved by using α and β radiations and recording the intensities simultaneously by a photographic method. The ratio $I\alpha/I\beta$ can either be calculated from the ratio *in vacuo* or by measuring α and β reflections obtained with another substance which contains no anomalous scatterers. One example of the use of this method is the study of Cs_2CuCl_4 [8] with Cu$K\alpha$ and Cu$K\beta$ radiations.

CONCLUSION

The purpose of this paper has been to present an account of methods for the phase determination in the case of centrosymmetric structures. Examples of the use of these methods in the solution or partial solution of structures, *e.g.* $(NH_4)_2Co(SO_4)_2,6H_2O$ and Cs_2CuCl_4, are to be given in later papers.

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