

On the Use of Anomalous Scattering of X-rays in the Solution of Centrosymmetric Structures

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A method to solve centrosymmetric structures with anomalous scatterers which is analogous to the method given by Hargreaves for centrosymmetric structures with normal scatterers is proposed. It is shown that the difference between the values of a structure factor measured with two different wavelengths ($F_H(\lambda_1)$ and $F_H(\lambda_2)$) is a complex magnitude that has a constant phase. A linear relationship between $F_H(\lambda_1)$ and $F_H(\lambda_2)$ results and by plotting a correlation diagram the signs can be readily assigned to the different reflexions.

The case of centrosymmetric structures has been treated by Mitchell (1957) by the two-wavelength method first outlined by Pepinsky & Okaya (1956).

However, the practical application of this method would be rather troublesome, because the observed structure factors for both wavelengths must be put on an absolute scale and the absorption differences for the two wavelengths used are likely to be of large importance. Error in the scaling tends to be higher when heavy atoms are present and Wilson's method is being used, thus rendering the correct assignment of signs rather difficult.

In the case of centric isomorphous structures with normal dispersion, the signs can be readily assigned by the method given by Hargreaves (1946, 1957).

In this paper a treatment similar to that of Hargreaves is proposed for centric structures with anomalous dispersion.

Absorption corrections must, of course, be performed before the present method is used.

For a crystal with n atoms in its unit cell, m of the atoms being anomalous scatterers (denoted hereafter by $A.S.$), a structure factor can be expressed as

$$F_H = \sum_{j=1}^{n-m} f_j \exp [2\pi i \mathbf{H} \cdot \mathbf{r}_j] + \sum_{k=n-m+1}^n (f_k^0 + f_k' + i f_k'') \exp [2\pi i \mathbf{H} \cdot \mathbf{r}_k], \quad (1)$$

where $\mathbf{H} = (h, k, l)$; $\mathbf{r}_j = (x_j, y_j, z_j)$ and $\mathbf{r}_k = (x_k, y_k, z_k)$ are the coordinates of atom j or k ; subindices j apply to normal scatterers ($N.S.$) and k to $A.S.$; $f_k = f_k^0 + f_k' + i f_k'' =$ atomic scattering factor of an $A.S.$

In Mitchell's notation,

$$F_H = (A_H^{NS} + \Delta A_H' - B_H'') + i(B_H^{NS} + \Delta B_H' + A_H''), \quad (2)$$

where

$$\left. \begin{aligned} A_H^{NS} &= \sum_{j=1}^n f_j^0 \cos 2\pi \mathbf{H} \cdot \mathbf{r}_j, \\ \Delta A_H' &= \sum_{k=n-m+1}^n f_k' \cos 2\pi \mathbf{H} \cdot \mathbf{r}_k, \\ A_H'' &= \sum_{k=n-m+1}^n f_k'' \cos 2\pi \mathbf{H} \cdot \mathbf{r}_k, \\ B_H^{NS} &= \sum_{j=1}^n f_j^0 \sin 2\pi \mathbf{H} \cdot \mathbf{r}_j, \\ \Delta B_H' &= \sum_{k=n-m+1}^n f_k' \sin 2\pi \mathbf{H} \cdot \mathbf{r}_k, \\ B_H'' &= \sum_{k=n-m+1}^n f_k'' \sin 2\pi \mathbf{H} \cdot \mathbf{r}_k. \end{aligned} \right\} \quad (3)$$

(2) is valid in general, i.e. for acentric structures. If the structure is centric:

$$B_H^{NS} = \Delta B_H' = B_H'' = 0.$$

F_H is then

$$F_H = A_H^{NS} + \Delta A_H' + i A_H'' \quad (4)$$

Moreover,

$$A_H^{NS} = A_{\bar{H}}^{NS}, \quad \Delta A_{\bar{H}}' = \Delta A_H', \quad A_H'' = A_{\bar{H}}'';$$

and then

$$F_H = F_{\bar{H}}, \quad (5)$$

i.e., Friedel's law holds again.

Let $F_H(\lambda_1)$ and $F_H(\lambda_2)$ be the observed structure factors when X-rays of wavelengths λ_1 and λ_2 are used. These values must be measured either by using film or counter techniques. In general the sets will be obtained on different scales, and although in the latter case it is not difficult to find the scale factors, it is better to employ a technique which solves the phase problem at the same time. If a_1 and a_2 are the required scale coefficients relating $F_H(\lambda_1)$ and $F_H(\lambda_2)$ to the absolute scale, then

$$a_1 F_H(\lambda_1) = A_H^{NS} + \Delta A'_H(\lambda_1) + i A''_H(\lambda_1),$$

and

$$a_2 F_H(\lambda_2) = A_H^{NS} + \Delta A'_H(\lambda_2) + i A''_H(\lambda_2).$$

A_H^{NS} is the same in both cases, so that, by subtraction,

$$a_1 F_H(\lambda_1) - a_2 F_H(\lambda_2) = [\Delta A'_H(\lambda_1) - \Delta A'_H(\lambda_2)] + i[A''_H(\lambda_1) - A''_H(\lambda_2)]; \quad (6)$$

or

$$\begin{aligned} a_1 F_H(\lambda_1) - a_2 F_H(\lambda_2) &= \sum_{k=n-m+1}^n \{ [f'_k(\lambda_1) - f'_k(\lambda_2)] \\ &+ i[f''_k(\lambda_1) - f''_k(\lambda_2)] \} \cos 2\pi \mathbf{H} \cdot \mathbf{r}_k. \end{aligned} \quad (6')$$

In the case of a structure having only one class of $A.S.$, the imaginary quantity within braces in (6') is a constant. Let us concentrate on this case.

Let

$$G_H = \sum_{k=n-m+1}^n \cos 2\pi \mathbf{H} \cdot \mathbf{r}_k, \quad (7)$$

and

$$\Delta_\varphi(\lambda_1, \lambda_2) = [f'_k(\lambda_1) - f'_k(\lambda_2)] + i[f''_k(\lambda_1) - f''_k(\lambda_2)]. \quad (8)$$

G_H is a geometric factor depending only on the positions (\mathbf{r}_k) of the $A.S.$ When these positions are known from classical methods, G_H can be calculated for every rational plane $H(hkl)$. $\Delta_\varphi(\lambda_1, \lambda_2)$ is a constant complex quantity for a given kind of atom and a pair of wavelengths. Its phase φ is constant irrespective of H , so that the difference

$$a_1 F_H(\lambda_1) - a_2 F_H(\lambda_2)$$

will also have a constant phase.

$$a_1 F_H(\lambda_1) - a_2 F_H(\lambda_2) = \Delta_\varphi(\lambda_1, \lambda_2) \cdot G_H.$$

Considering real and imaginary parts, one obtains:

$$a_1(A_H(\lambda_1)/G_H) - a_2(A_H(\lambda_2)/G_H) = \Delta \cdot \cos \varphi \quad (9)$$

and

$$a_1(B_H(\lambda_1)/G_H) - a_2(B_H(\lambda_2)/G_H) = \Delta \cdot \sin \varphi, \quad (10)$$

here

$$a A_H(\lambda) = A_H^{NS} + \Delta A'_H(\lambda) = A_H^{NS} + G_H \cdot f'(\lambda),$$

$$a B_H(\lambda) = A''(\lambda) = G_H \cdot f''(\lambda),$$

$$\Delta \cdot \cos \varphi = f'(\lambda_1) - f'(\lambda_2),$$

and

$$\Delta \cdot \sin \varphi = f''(\lambda_1) - f''(\lambda_2).$$

Thus the imaginary part of the structure factor in the case under consideration can be calculated for both wavelengths used.

If we now consider only relatively high structure factors, it is clear that the real part will in general be much greater than the imaginary; we can then make the approximation

$$|A_H| \cong |F_H|;$$

and substituting F_H for A_H in (9),

$$a_1(F_H(\lambda_1)/G_H) - a_2(F_H(\lambda_2)/G_H) = f'(\lambda_1) - f'(\lambda_2). \quad (11)$$

The only unknowns in equation (11) are a_1 and a_2 .

If now we plot a correlation diagram using $F_H(\lambda_1)/G_H$ as ordinates and $F_H(\lambda_2)/G_H$ as abscissae, it is clear that the points should be on a straight line. Reasonable deviations due to: 1) experimental errors in the F 's, 2) errors in the positions of the $A.S.$ and hence in G_H , and 3) the approximation involved ($|A_H| \cong |F_H|$) are to be expected. The analysis proceeds then in the same way as in Hargreaves' method. Intercepts on both axes give estimates of the scale factors a_1 and a_2 .

If $f'(\lambda_1) - f'(\lambda_2)$ is rather small, the straight line will lie near the origin, and it will not be easy to decide whether a given point belongs to the line or to its symmetric. In such a case the method will fail and the correct assignment of signs will not be possible. The distance from the line to the origin needs to be at least several times the order of $\Delta F/G_H$, where ΔF stands for the error in the F 's.

Conclusions

1. λ_1 and λ_2 should be selected in such a way as to make $f'(\lambda_1) - f'(\lambda_2)$ relatively high (of the order of several electrons) for each particular case. Dauben & Templeton (1955) have computed $f'(\lambda)$ and $f''(\lambda)$ for atoms with $Z \geq 20$ using the wavelengths Cr $K\alpha$, Cu $K\alpha$ and Mo $K\alpha$. Templeton (1960) has recently extended these calculations to lighter elements and to different values of $\sin \theta/\lambda$ for the same three wavelengths. His values for $\sin \theta/\lambda = 0$ are those published by Dauben & Templeton with modifications that take into account the effect of N -shell electrons, while those for other values of $\sin \theta/\lambda$ were obtained by multiplying the contribution of each electron group by its orbital transform. As predicted, the dispersion corrections are only slightly sensitive to changes in $\sin \theta/\lambda$. The author was not aware of Templeton's latest figures during the preparation of the present paper, but the conclusions obtained remain unchanged. In order to allow for the mentioned variations of the dispersion corrections with $\sin \theta/\lambda$ one may use their mean value rather than the value for $\sin \theta/\lambda = 0$.

Pepinsky has obtained extrapolated values of f'_i for $K\alpha$ radiation from Mn, Fe, Ce and Ni targets. Values for f'_i are desirable if the present method is to be used, although in this case extrapolated values will not probably be accurate enough. It seems to be worth while to extend the calculations to many other wavelengths. One could probably find pairs of values of λ suitable for use in given regions of the periodic table. For instance the pair Cu $K\alpha$ and Mo $K\alpha$ looks quite adequate to deal with elements from $Z = 62$ (Sm) to $Z = 74$ (W), their differences in $f'(\lambda)$ ranging from 5.0 to 12.6 electrons; while Cr $K\alpha$ and Mo $K\alpha$ could

probably be used from $Z=53$ (I) till about $Z=66$ (Dy). Calculations have been undertaken in this laboratory and will be reported in due course.

2. Only planes with a high value of G_H should be plotted. Probably values larger than unity will be needed, but this point cannot be decided without further study.

3. Experimental errors in F_H should be kept as low as possible, for the reasons explained in the text. Visual estimates of intensities would probably be of little use when utilizing this technique.

4. As $f'(\lambda_1) - f'(\lambda_2)$ is nearly independent of $\sin \theta$, only one graph is necessary, except perhaps for crystals with rather high temperature factors.

5. The arguments can easily be extended to include the case where more than one kind of $A.S.$ is present in the structure.

Resumen

En este trabajo se propone un método para resolver estructuras centrosimétricas con dispersores anómalos

en forma análoga a la usada por Hargreaves en estructuras centrosimétricas a dispersión normal.

Se muestra que la diferencia entre los valores de un factor de estructura medidos con dos longitudes de onda diferentes ($F_H(\lambda_1)$ y $F_H(\lambda_2)$) es una magnitud compleja cuya fase es constante. Se obtiene así una relación lineal entre $F_H(\lambda_1)$ y $F_H(\lambda_2)$ y trazando un diagrama de correlación se puede fácilmente asignar los signos de las distintas reflexiones.

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The Crystal Structure of Bi and of Solid Solutions of Pb, Sn, Sb and Te in Bi

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Lattice constants, atomic positional parameters and Debye-Waller temperature factors were measured for Bi and Bi-rich binary solid solutions containing atomic percentages 0 to 30 Sb, 0-39 Pb, 0-125 Sn, 0-15 Te, and 0-22 Te at 4·2, 78, and 298 °K. The alloys were made by zone levelling and were based on very pure, zone refined Bi. The lattice constants of the Bi-Sb alloys vary linearly in the composition range $x=0$ to 30 atomic percent Sb. The variation can be described by the equations:

$$\begin{aligned} a &= 4\cdot546 - 23\cdot84 \cdot 10^{-4}x, & c &= 11\cdot863 - 51\cdot66 \cdot 10^{-4}x, & \text{at } 298 \pm 3 \text{ }^\circ\text{K.}; \\ a &= 4\cdot534 - 21\cdot92 \cdot 10^{-4}x, & c &= 11\cdot814 - 48\cdot75 \cdot 10^{-4}x, & \text{at } 78 \text{ }^\circ\text{K.}; \\ c &= 11\cdot803 - 40\cdot75 \cdot 10^{-4}x & & \text{at } 4\cdot2 \text{ }^\circ\text{K.} \quad (a, c \text{ in } \text{Å}); \end{aligned}$$

the average error is estimated to be 1 part in 2000. The atomic positional parameter z in the Bi-Sb alloys remains approximately constant up to about 12% Sb, and then rises from 0·23407 to 0·23420 at 4·2 °K., 0·23400 to 0·23413 at 78 °K., as the Sb content increases from 0 to 30 atomic percent Sb; the standard deviations of the z 's are estimated as 25×10^{-6} . At room temperature $z = 0\cdot23389$. At 78 °K. the z for the other alloys is not significantly different from the value for pure Bi. The temperature factors B , for vibrations parallel to the c axis, are approximately 0·10, 0·32 and 1·14 at 4·2, 78 and 298 °K., respectively, for pure Bi, and increase slightly with increasing Sb content in the Bi-Sb alloys.

Introduction

Precision structure data on bismuth of extreme purity and its alloys are needed to guide the development of theories on the influence of band structure on crystal structure in these materials, such as the one proposed by Blount & Cohen (unpublished) referred to by Jain (1959) and Barrett (1960), in which it was postulated

that the distribution of electrons in conduction and valence bands directly controls the magnitude of the atomic parameter z , and that consequently z should be altered by changes in electron concentration and temperature. The determinations of the bismuth atomic parameter by James (1921), Hassel & Mark (1924), and Goetz & Hergenrother (1932) are inadequate for present needs; a determination was made