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A note on the absolute scaling of intensities by Kartha's method.

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It is useful to be able to place observed X-ray intensities on an absolute scale as a routine procedure. With the increasing availability of electronic computers this ideal is capable of attainment. Using an I.B.M. 1620 computer all intensities observed in this laboratory are being so scaled.

The scale factor used is that given by Kartha (1953) as

$$c = \frac{(V/2\pi^2)\sum_{k=1}^{N}\int_0^{\xi_m}\xi^2 f_k^2(\xi)d\xi - F^2(\mathbf{O})}{\sum_{\mathbf{H}} F_o^2(\mathbf{H})} \tag{1}$$

where

V = volume of the unit cell,

$F_o(\mathbf{H})$ = observed magnitude of the structure factor on a relative scale,

$f_k(\xi)$ = atomic scattering factor of the kth atom, corrected for thermal motion,

and

$\xi = (4\pi \sin \theta)/\lambda$.

The integration limit ξ_m corresponds to the maximum observed value of ξ.

The use of this method requires at least an approximate knowledge of the thermal parameters of the atoms. In our procedure such an approximate value of the mean temperature factor is obtained by Wilson's method (1942). This value appears to be good enough in most cases but it has not been completely checked out with compounds containing atoms of widely different atomic numbers.

The major problem in programming the Kartha procedure is evaluation of the integral (1). Numerical integration is of course always possible but the time required to carry out the integration with the precision desired is comparatively long. Eiland *et al.* (1957) have suggested an expression for the scattering factor which gives a rather good fit with the tabulated curves (except at rather high angles, which region is less important in the present context). This expression is,

$$f_0(\sin\theta) = A\exp(-a\sin^2\theta) + B\exp(-b\sin^2\theta)$$

where A, a, B, b are constants depending on the atom involved, or

$$f_0(\xi) = A\exp(-a'\xi^2) + B\exp(-b'\xi^2) \tag{2}$$

where

$$a' = a\lambda^2/16\pi^2,$$
$$b' = b\lambda^2/16\pi^2,$$

and

λ = wavelength of X-rays.

Taking anomalous scattering into account the scattering factor becomes:

$$f(\xi) = f_0(\xi) + \Delta f' + i\Delta f''$$

and

$$\begin{aligned} f^2(\xi) &= [f_0(\xi)+\Delta f']^2 + \Delta f''^2 \\ &= f_0^2(\xi) + 2f_0(\xi)\Delta f' + \Delta f'^2 + \Delta f''^2. \end{aligned} \tag{3}$$

The correction to be applied to $f^2(\xi)$ for thermal vibration is $\exp(-M\sin^2\theta/\lambda^2)$ where M is the mean temperature factor obtained by the Wilson method. Expressed in terms of ξ this becomes $\exp[-M\xi^2/16\pi^2]$. On multiplying (3) by the temperature correction and substituting (2) for $f(\xi)$ we obtain:

$$f_M^2(\xi) = \sum_{j=1}^{6}\alpha_j'\exp(-\beta_j'\xi^2)$$

where

$f_M^2(\xi)$ = square of complete scattering factor corrected for temperature,

and the α_j' and β_j' are constants for a given atom and temperature factor. The integral in equation (1) then becomes:

$$\int_0^{\xi_m}\sum_{j=1}^{6}\xi^2\alpha_j'\exp(-\beta_j'\xi^2)d\xi = \sum_{j=1}^{6}\alpha_j'\int_0^{\xi_m}\xi^2\exp(-\beta_j'\xi^2)d\xi\,. \tag{4}$$

To integrate these integrals it is convenient to change the variable from ξ to $y_j = \xi\sqrt{\beta_j}$. On making the appropriate substitutions and carrying out the integration the result involves the error integral,

$$\frac{\sqrt{\pi}}{2}\Phi(y_j) = \int_0^{y_{m,j}}\exp(-y_j^2)dy_j\,.$$

This integral may be evaluated using a polynomial approximation given by Hastings (1955). This approximation is good to 1 in 10^5, which is adequate for scale factor calculation. On making these substitutions the integral in (1) takes the form:

$$\sum_{j=1}^{6}[\alpha_j\Phi(y_{m,j}) - \beta_j\exp(-y_{m,j}^2)]\,, \tag{4}$$

where

$$\begin{aligned}
\alpha_1 &= VA^2[2\pi/(M/2+a\lambda^2)]^{3/2} \\
\alpha_2 &= 16VAB[\pi/[M+(a+b)\lambda^2]]^{3/2} \\
\alpha_3 &= VB^2[2\pi/(M/2+b\lambda^2)]^{3/2} \\
\alpha_4 &= 16VA(\Delta f')[\pi/(M+a\lambda^2)]^{3/2} \\
\alpha_5 &= 16VB(\Delta f')[\pi/(M+b\lambda^2)]^{3/2} \\
\alpha_6 &= 8V[(\Delta f')^2+(\Delta f'')^2](\pi/M)^{3/2}
\end{aligned}$$

$$\begin{aligned}
\beta_1 &= 2VA^2\xi_m/(M/2+a\lambda^2) \\
\beta_2 &= 8VAB\xi_m/[M+(a+b)\lambda^2] \\
\beta_3 &= 2VB^2\xi_m/(M/2+b\lambda^2) \\
\beta_4 &= 8VA(\Delta f')\xi_m/(M+a\lambda^2) \\
\beta_5 &= 8VB(\Delta f')\xi_m/(M+b\lambda^2) \\
\beta_6 &= 4V[(\Delta f')^2+(\Delta f'')^2]\xi_m/M
\end{aligned}$$

On substituting (4) in (1) the scale factor is seen to be:

$$c = \frac{\sum_{k=1}^{N}\left[\sum_{j=1}^{6}[\alpha_j\Phi(y_{m,j}) - \beta_j\exp(-y_{m,j}^2)]\right]_k - F^2(\mathbf{O})}{\sum_{\mathbf{H}}F_o^2(\mathbf{H})}\,.$$

Although the expressions for the α_j and β_j seem rather forbidding in appearance, in fact the 1620 can evaluate c in a very few seconds once the sum of the intensities is known. Furthermore if anomalous scattering is not important then α_4, α_5, α_6, β_4, β_5, β_6 are all zero.

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The crystal structure of β-K_3Bi[*].

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K_3Bi undergoes a phase change at 280 °C. The low temperature form, α-K_3Bi, has the Na_3As, DO_{18}, type structure (Brauer & Zintl, 1937). The structure of the high temperature modification, β-K_3Bi, determined from powder patterns taken at 400 °C., is of the BiF_3, DO_3 type.

Samples of K_3Bi were crushed in a dry box and loaded into 0·3 mm. quartz capillaries. Powder photographs were taken at about 400 °C. in a Central Research Laboratories high temperature powder camera using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). These patterns were indexed as face-centered cubic with $a = 8{\cdot}805 \pm 0{\cdot}005$ Å. The density calculated on the basis of four K_3Bi formula units per unit cell is 3·17 g.cm.$^{-3}$.

The symmetry and composition of this phase suggest a structure of the DO_3 type of BiF_3 and this structure was ultimately confirmed. Among other compounds, Li_3Bi (Zintl & Brauer, 1935) and β-Li_3Sb (Brauer & Zintl, 1937) also have this same structure. The atoms occupy the following positions of space group O_h^5–$Fm3m$ (*International Tables for X-ray Crystallography*, 1952):

4 Bi in $4a$: $(0, 0, 0)$ + face centering,
4 K_I in $4b$: $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ + face centering,
8 K_{II} in $8c$: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4};\ \frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ + face centering.

The intensities of the first 14 lines of a typical powder pattern were estimated by visual comparison with a standard scale. After correction of the intensities by the Lorentz-polarization and multiplicity factors, structure factors were obtained for each of the 16 contributing forms. These data were used in a least squares refinement to obtain isotropic temperature factors for each species of atom and a scale factor. The atomic form factors of James & Brindley (1931) for neutral atoms were used in the calculated structure factors. The reliability coefficient, $R = \Sigma|F_o - F_c|/\Sigma|F_o|$, was 0·10 after these computations. The isotropic temperature factors which resulted are 2·2 Å^2 for Bi, 13·9 Å^2 for K_I, and 9·5 Å^2 for K_{II}. The powder pattern is listed in Table 1; the the intensities have been normalized so that the maximum I_0 is 100.

Table 1. *Powder pattern of* β-K_3Bi

hkl	d_o	d_c	I_o	I_c
111	5·07 Å	5·08 Å	75	66
200	4·36	4·40	62	40
220	3·10	3·11	100	160
311	2·647	2·655	89	77
222	2·540	2·539	27	22
400	2·195	2·200	45	34
331	2·013	2·020	48	46
420	1·964	1·969	30	39
422	1·795	1·797	55	71
511 333	1·693	1·695	40	40
440	1·556	1·557	25	21
531	1·489	1·488	37	41
442 600	1·468	1·468	19	22
620	1·396	1·392	27	26

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