

References

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Thermal expansion coefficients of α -monoclinic selenium. By CLARENCE J. NEWTON and MALCOLM Y. COLBY, *Department of Physics, University of Texas, Austin, Texas, U.S.A.*

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Selenium crystals with particle size ranging from that of a fine powder to specimens approximately 1 mm. in their greatest dimension were obtained from a saturated solution of carbon disulfide. The samples examined showed no characteristics either to optical or X-ray examination to differentiate them into more than one class, Se_α .

The camera used was an adaptation of Buerger's (1937) precision back-reflection Weissenberg camera, diameter 7.993 cm., $K = 2^\circ$ per mm., oscillation amplitude about 50° . The temperature was controlled by means of an electrically powered furnace designed by the author as a modification of the Buerger (1943) high-temperature powder camera. The single selenium crystal was mounted on the end of a short glass capillary and aligned on a goniometer head by means of Laue, rotation and Weissenberg photographs. It was then coated with fine filings of very pure aluminum, and the two desired Weissenberg patterns, one at tap-water temperature and the other at approximately 1 W. power input ($\Delta t \doteq 55^\circ \text{C.}$) were taken together on the same film.

The patterns were measured on a Cenco 10 cm. comparator. The aluminum powder lines, with the aid of the data of Nix & MacNair (1941), served, with known data on the aluminum thermal expansion and the measured tap-water temperature, to calibrate the film as to angle per millimeter and to give the value of the elevated temperature. Radiation used was unfiltered Cr for the 0.0.10 order and Co for all other cases. Exposure time was usually 5 hr. for each temperature run.

The breadth of the Se lines was less than $8'$, the aluminum about $5'$. Precision in the spacing values was about one part in ten thousand. The results are summarized in Tables 1 and 2.

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Spherical Patterson sections. By A. L. MACKAY, *Birkbeck College Research Laboratory, 21 Torrington Square, London W.C. 1, England*

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Introduction

The lengths of certain interatomic, and particularly intratomic, vectors in an inorganic structure can often be predicted quite accurately from tables of atomic radii. In

Table 1. *Observations at particular temperatures*

| Unit | t_1 ($^\circ \text{C.}$) | t_2 ($^\circ \text{C.}$) | Order indices |
|------------------|---------------------------------|---------------------------------|-------------------------|
| $a_0 \sin \beta$ | 20.0 | 9.0440 kX. 77.3 | 9.0427 kX. 860 and 680 |
| b_0 | 20.0 | 9.0545 | 77.3 9.1003 860 and 680 |
| | 20.5 | 9.0546 | 75.2 9.0954 0.10.0 |
| $c_0 \sin \beta$ | 21.0 | 11.573 | 80.2 11.615 0.0.10 |
| β | 24.2 | 90.882° | 79.9 90.904° 709 |
| | 24.2 | 90.831 | 79.9 90.876 5.0.11 |

Table 2. *Summary at 20°C.*

| Unit | Coefficient of expansion (per $^\circ \text{C.}$) | Author's values | Burbank's (1951) values | Klug's (1934) values |
|---------|---|------------------------|-------------------------|----------------------|
| a_0 | -1.5×10^{-6} | 9.046 kX. | 9.05 kX. | 8.992 kX. |
| b_0 | $+84.7 \times 10^{-6}$ | 9.054 | 9.07 | 8.973 |
| c_0 | $+63.3 \times 10^{-6}$ | 11.573 | 11.61 | 11.52 |
| β | $+5.5 \times 10^{-6}$ | 90° 52' | 90° 46' | 91° 34' |
| V | $+145 \times 10^{-6}$ | 947.7 kX. ³ | | |

Author's values of a_0 , b_0 and c_0 are ± 0.001 kX. units; β is about $\pm 3'$.

In addition to the planes actually used to obtain the above, corroborative readings were made on the following neighboring planes, hot and cold: 1.10.0; 10.1.0 (not resolved since $\Delta\theta = 3'$ only); and 0.1.10.

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three-dimensional Patterson space peaks due to intratomic vectors can be identified at once if there is only one kind of complex ion; in a sulphate all the S-O peaks will be found on a sphere of radius 1.6 Å. round the origin.

Hence, the orientation of an ionic group may be found by examining only a spherical surface of appropriate radius about the origin in Patterson space. Such a spherical section can be calculated by hand without prohibitive labour, especially if the reciprocal lattice has a plane of symmetry.

General principle of the graphical calculation

Following the conventional notation, $\mathbf{r} = (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})$ is a vector representing a point in real space and $\mathbf{r}^* = (h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*)$ a point in reciprocal space. S , the scalar product of the two vectors, is equal to $hx + ky + lz$. Calculations of

$$P(x, y, z) = \sum_{hkl} F^2(h, k, l) \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} 2\pi(hx + ky + lz)$$

$$\text{or } F(h, k, l) = \sum_n f(h, k, l, n) \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} 2\pi(hx_n + ky_n + lz_n)$$

or of other functions of S , can be carried out by forming the scalar product S graphically, as was done in the particular case described below.

Spherical section calculated graphically

A spherical Patterson section to determine the orientation of PO_4^{3-} groups in $\beta\text{-Ca}_3(\text{PO}_4)_2$ has been calculated. The rhombohedral lattice (space group $R3c$) can be referred, with some simplification, to co-ordinates (x, y, z) chosen so that $y = 0$ is a plane of symmetry. The Patterson function P then reduces to

$$\begin{aligned} P &= \sum_3 F^2 \cos 2\pi ky \cos 2\pi(hx + lz) \\ &= \sum_3 F^2 \cos 2\pi ky \cos 2\pi(\boldsymbol{\rho} \cdot \boldsymbol{\rho}^*), \end{aligned}$$

where $\boldsymbol{\rho}$ and $\boldsymbol{\rho}^*$ are the projections of \mathbf{r} and \mathbf{r}^* on to any plane parallel to $y = 0$. S , the scalar product of $\boldsymbol{\rho}$ and $\boldsymbol{\rho}^*$, is the product of $|\boldsymbol{\rho}|$ and the projection of $\boldsymbol{\rho}^*$ on to $\boldsymbol{\rho}$. The vector \mathbf{r} in real space scans the surface of a sphere of radius r about the origin and has components $r \cos \theta$ parallel to \mathbf{b} and $r \sin \theta$ in a plane parallel to $y = 0$. ϕ is the azimuth angle of the vector \mathbf{r} measured in the plane $y = 0$ from \mathbf{a} . Thus, restricting the summation to give the value of P only at a distance r from the origin, we get

$$P_r = \sum_3 F^2 \cos 2\pi\{kb^*(r/\lambda) \cos \theta\} \cos 2\pi\{\boldsymbol{\rho} \cdot \boldsymbol{\rho}^*\}.$$

Method of calculating the section

For each point (r, θ, ϕ) in the section in real space, the expression for P is separable into two parts, one depending on k and the other on h and l . The summation $\sum_{h,l} F_{hkl}^2 \cos 2\pi(\boldsymbol{\rho} \cdot \boldsymbol{\rho}^*)$ is performed for each of the k layers in turn; the totals are multiplied by the appropriate values of $\cos 2\pi\{kb^*(r/\lambda) \cos \theta\}$, and these products are added to give $P_r(\theta, \phi)$.

Practical details

Layers of the reciprocal lattice parallel to $y = 0$ were reproduced photographically from a drawing and the intensity of each reflexion was written beside it. A table of

$$\chi(\theta, k) = \cos 2\pi\{(r/\lambda) b^* k \cos \theta\}$$

was drawn up, χ being calculated for each value of k and 10° intervals of θ from 0 to 90° . A similar table of the function $\Phi = \cos 2\pi\{(r/\lambda) s \sin \theta\}$ was calculated for the same intervals of θ and 0.1 intervals of s between 0 and 2.0 . To evaluate P at the point (θ_1, ϕ_1) a scale inscribed with $\Phi(\theta_1, s)$ was laid at an angle ϕ_1 across each layer of the reciprocal lattice in turn, and a set-square sliding along it enabled Φ to be read off for each reflexion and multiplied by F^2 on an electric calculating machine which accumulated the total of the products. The subtotals for the k layers were each multiplied by the appropriate $\chi(\theta_1, k)$ and added together to give $P(\theta_1, \phi_1)$.

The section, of radius 1.56 \AA , calculated for $\beta\text{-Ca}_3(\text{PO}_4)_2$, showed a density distribution which agreed well with that found from a number of ordinary plane sections.

As this is an analogue method of computation it is subject to experimental error occurring in the reading and preparation of the scales, estimated at 0.2% of $\sum_{hkl} F^2$.

It should be noted, especially if sharpened intensities are used, that the heavy diffraction ripples round the origin peak may cause displacement of peaks close to the origin, and due allowance must be made when deciding on the radius at which to calculate a section.

Proposed further mechanization

It is proposed that weighted reciprocal nets should be prepared, having each point represented by a transparent disk (in a photographic plate) of area proportional to the observed intensity of the reflexion. Each layer in turn is to be overlaid with a Bragg-Huggins mask of the Woolfson (1951) half-tone type of such a size as to multiply the intensities by Φ . The light transmission of the combination will be measured by a photoelectric cell and

$$\sum_{h,l} F_{hkl}^2 \cos 2\pi\{(r/\lambda) (\boldsymbol{\rho} \cdot \boldsymbol{\rho}^*) \sin \theta\}$$

will be read off directly for all values of ϕ by rotating the mask. The remaining summations over k will be done by hand as before.

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