stimmung mit der pyknometrisch ermittelten Dichte 1,50 g.cm.$^{-3}$.

Da der Beitrag leichter Atome zum Strukturfaktor infolge ungleich stärkeren Abfalls des Atomformfaktors mit steigendem $\sin \theta/\lambda$ neben dem der schweren Atome vernachlässigt werden kann, liess sich aus dem visuell geschätzten Gang der Intensitäten bei hohen Beugungswinkeln die Punktlage der schweren Atome (Ce, Th, U) angenähert bestimmen.

Vierzählige spezielle Punktlage (*c*) in der Raumgruppe *Pccn*:

$$\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{8}\pm\Delta z;\quad \tfrac{3}{4}, \tfrac{3}{4}, -\tfrac{1}{8}\pm\Delta z;\quad \tfrac{1}{4}, \tfrac{1}{4}, \tfrac{5}{8}\pm\Delta z;\quad \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{3}{8}\pm\Delta z\,,$$

mit $\Delta z = 0{,}015 \pm 0{,}002$ für Thorium und $\Delta z = 0{,}018 \pm 0{,}002$ für Cer und Uran.

Um die weitere Aufklärung der Struktur sind wir bemüht.

Literatur

ALBERS, H., DEUTSCH, M., KRASTINAT, W. & OSTEN, H. VON (1952). *Chem. Ber.* **85**, 267.

SACCONI, L. & ERCOLI, R. (1949). *Gazz. chim. ital.* **79**, 731.

WOLF, L. & JAHN, H.-J. (1955). *J. Prakt. Chem.* **1**, 257.

Acta Cryst. (1957). **10**, 606

Structure factor algebra. II.

By E. F. BERTAUT, *Laboratoire d'Électrostatique et de Physique du Métal, Institut Fourier, Grenoble, France,* and J. WASER, *Department of Chemistry, The Rice Institute, Houston, Texas, U.S.A.*

(*Received* 30 *April* 1957)

The simple rules for finding symmetry relations between structure factors and for the linearization of structure factors stated in the paper entitled 'Algèbre des facteurs de structure' (Bertaut, 1956, henceforth referred to as I) do not always apply without modification.

Symmetry relations

Consider two equivalent vectors $\mathbf{r}$ and $\mathbf{r}'$, related by the symmetry operation C: $\mathbf{r}' = C\mathbf{r}$. The operation C contains in general a translational component $\mathbf{t}$ and a dyadic part A (proper or improper rotation):

$$\mathbf{r}' = C\mathbf{r} = A\mathbf{r}+\mathbf{t}\,.$$

Now, as was stated by Waser (1955), the relationship between $\mathbf{r}$ and $\mathbf{r}'$ in direct space engenders the relationship

$$F(\mathbf{h}) = F(\mathbf{h}') \exp\,(2\pi i\mathbf{h}.\mathbf{t}) \tag{1}$$

between structure factors $F(\mathbf{h}')$, and $F(\mathbf{h})$, where $\mathbf{h}' = \mathbf{h}A = A^{-1}\mathbf{h}$.

In general A^{-1} is not identical with A, as was implied by the simple rule of paper I. However, $A^{-1} = A$ whenever A is of order $2(m, \bar{1}, 2)$, and then the rule given in I is correct.

The index triple (h', k', l') symbolized by $\mathbf{h}' = A^{-1}\mathbf{h} = \mathbf{h}A$ may be obtained by post-multiplication of the row matrix (h, k, l) with the 3×3 matrix representing A (cf. MacGillavry, 1950), or by the following method of inspection.

Consider, for example, the equivalent points $\mathbf{r} = x, y, z$, and $\mathbf{r}' = C\mathbf{r} = \tfrac{1}{2}-y, x, z$ (space group $Pn3n$, cf. Waser, 1955). The latter contributes to the structure factor the term $(-1)^h \exp 2\pi i(-hy+kx+lz)$. Rearrange so as to bring the parameters x, y, z into their usual sequence again. This regrouping of the parenthesis casts $\mathbf{h}.\mathbf{r}'$ into the equivalent form $(\mathbf{h}A)\mathbf{r}+\mathbf{h}.\mathbf{t}$ and here results in $(-1)^h \exp 2\pi i(kx+\bar{h}y+lz)$. From this the symmetry relation

$$F(hkl) = (-1)^h F(k\bar{h}l)$$

may be read off directly.

Linearization

The correct linearization relation for a structure-factor product (cf. Bertaut, 1955, equation III–12) is shown below to be

$$\xi(\mathbf{h}_1)\xi(\mathbf{h}_2) = \sum_{s=1}^{n} \exp\,(2\pi i\mathbf{h}_2\mathbf{t}_s)\xi(\mathbf{H}_s)\,, \tag{2}$$

where

$$\xi(\mathbf{h}) \sum_{s=1}^{n} = \exp 2\pi i\mathbf{h}C_s\mathbf{r} \tag{3}$$

is the trigonometric part of the structure factor, and where

$$\mathbf{H}_s = \mathbf{h}_1+\mathbf{h}_2A_s\,.$$

This follows from the expansion

$$\begin{aligned}\xi(\mathbf{h}_1)\xi(\mathbf{h}_2) &= \sum_p \sum_q \exp\,(2\pi i\mathbf{h}_1C_p\mathbf{r}) \exp 2\pi i\mathbf{h}_2C_q\mathbf{r})\\ &= \sum_p \sum_s \exp 2\pi i(\mathbf{h}_1+\mathbf{h}_2C_s)C_p\mathbf{r} \end{aligned} \tag{5}$$

with $C_s = C_qC_p^{-1}$. As q runs from 1 to n with p fixed, s varies from 1 to n also, only in different order. Furthermore, $\mathbf{h}_2C_s(C_p\mathbf{r}) = \mathbf{h}_2A_s(C_p\mathbf{r})+\mathbf{h}_2\mathbf{t}_s$. Thus rearrangement of the last double sum in (3) yields

$$\sum_s (\sum_p \exp 2\pi i(\mathbf{h}_1+\mathbf{h}_2A_s)C_p\mathbf{r}) \exp 2\pi i\mathbf{h}_2\mathbf{t}\,,$$

which can be rewritten in the form (2).

The rule for linearization may also be stated as follows: Find all symmetry relations (1) for the structure factor $F(\mathbf{h}_2)$ and list all the reciprocal vectors $\mathbf{h}_2A_s$ as well as the phase factors $\exp 2\pi i\mathbf{h}_2\mathbf{t}_s$, $s = 1, \ldots, n$. Add $\mathbf{h}_1$ to all $\mathbf{h}_2A_s$ to give $\mathbf{H}_s$. Multiply each $\xi(\mathbf{H}_s)$ with the corresponding phase factor and sum.

The simpler rule given in I applies to all space groups containing symmetry elements of order 2 only. It also applies to space groups in which those symmetry operations that interrelate coordinate axes have no translational components. Fortunately, the correct rules were used in the derivation of the *Tables de Linéarisation des Produits et Puissances des Facteurs de Structure* (Bertaut

& Dulac, 1955) mentioned in I. All other parts of I are correct.

References

Bertaut, E. F. (1955). *Acta Cryst.* **8**, 823.
Bertaut, E. F. (1956). *Acta Cryst.* **9**, 769.
Bertaut, E. F. & Dulac, J. (1955). *Tables de Linéarisation des Produits et Puissances des Facteurs de Structure.* *Grenoble: Laboratoire d'Électrostatique et de Physique du Métal.
MacGillavry, C. H. (1950). *Acta Cryst.* **3**, 214.
Waser, J. (1955). *Acta Cryst.* **8**, 595.

---

* About 40 copies are available.

Acta Cryst. (1957). **10**, 607

Crystallographic data for tin monophosphide.

By G. Katz, J. A. Kohn and J. D. Broder, *U. S. Army Signal Engineering Laboratories, Fort Monmouth, N. J., U.S.A.*

(*Received* 14 *May* 1957)

According to Hansen (1936, pp. 973–4), the phosphides of tin, SnP_3, Sn_4P_3, and Sn_3P_4, may be formed in the binary system Sn–P. An attempt to prepare SnP_3 was made by the high-temperature reaction of a 1:3 mixture of tin and red phosphorus. The constituent elements were heated to 700° C. in an evacuated (10^{-6} mm. of Hg) vycor tube; afterwards slow-cooled at 40° $C.hr.^{-1}$ to 380° C. and then allowed to reach room temperature. The reaction product was a solidified mass with a silicon-like dull metallic luster. The presence of unreacted phosphorus indicated a deviation from the stoichiometry SnP_3. The product was graphitic in character, i.e., quite soft with an easy cleavage parallel to (00.l). The entire product appeared to be one large single crystal. It was found to be insoluble in concentrated HNO_3 at 300° C. For chemical analysis*, it was fused with K_2CO_3 and sulphur in a platinum crucible and then acidified. The excess sulphur was oxidized and the phosphorus was determined as phosphomolybdate. For the tin determination, the sample was acidified with HCl, reduced with aluminum foil and titrated iodometrically. The results, which are averaged from two analyses, checked closely with the stoichiometry of tin monophosphide, SnP:

	Analysis (wt. %)	Calculated (wt. %)
Sn	78·86	79·30
P	20·47	20·70

This formulation is not in agreement with Hansen (1936, p. 974), who indicated that a monophosphide of tin appeared unlikely.

Rotation and precession patterns were obtained, using a thin cleaved section of the crystal with unfiltered Mo radiation ($\lambda = 0{\cdot}7107$ Å). A hexagonal unit cell was established with the dimensions:

$$a_0 = 8{\cdot}78 \pm 0{\cdot}01 \text{ Å}, \quad c_0 = 5{\cdot}98 \pm 0{\cdot}01 \text{ Å}, \quad c/a = 0{\cdot}682 \, .$$

The unit-cell dimensions were determined from the spacings of high-order reflections: a_0 from the fourteenth order of (h0.0) and c_0 from the twelfth order of (00.l) on zero-level precession photographs. The density of a 77 mg. sample was measured pycnometrically in methanol and found to be 5·01 $g.cm.^{-3}$ as compared to a calculated density of 4·98 $g.cm.^{-3}$ for $Z = 8$.

Table 1. *Principal lines of the powder pattern of* SnP

hk.l	d_c (Å)	d_o (Å)	*I*
00.1	5·98	5·97	*vvw*
20.0	3·80	3·77	*m*
20.1	3·21	3·19	*vs*
00.2	2·99	2·99	*m*−
21.0	2·87	2·91	*vvw*
10.2	2·78	2·82	*m*−
20.2	2·35	2·35	*s*
30.1	2·33		
22.0	2·20	2·18	*s*
31.0	2·11	2·09	*w*
00.3	1·993	2·001	*w*
31.1	1·989	1·973	*vw*
40.0	1·901	1·890	*w*
40.1	1·812	1·804	*m*+
22.2	1·769	1·768	*m*
41.1	1·599	1·598	*w*
22.3	1·476	1·477	*m*−
42.0	1·437	1·433	*vw*
42.1	1·397	1·394	*m*+
20.4	1·391		
42.2	1·295	1·296	*w*
60.0	1·267	1·269	*vvw*
40.4	1·175	1·177	*w*
42.3	1·166	1·166	*w*

In Table 1 the observed d spacings of the powder pattern are compared with those calculated from the lattice constants obtained using single crystal data. The powder pattern was obtained with Ni-filtered Cu radiation ($\lambda = 1{\cdot}5418$ Å); relative intensities were estimated visually. Owing to the soft, graphitic nature of SnP, the diffraction lines for $2\theta > 90°$ were broad and diffuse and not usable for a more accurate determination of the unit-cell dimensions. No systematic absences were observed. The reciprocal-lattice-level symmetry for c axis rotation was characterized by C_{6l} for the zero level and C_{3l} for the upper levels. The diffraction symmetry is D_{3d}–$\bar{3}m$ with the following possible space groups: D_3^2–$P321$; C_{3v}^1–$P3m1$; D_{3d}^3–$P\bar{3}m1$, the last being centrosymmetric. A structure analysis is planned.

The authors are grateful to Mr R. Lefker, of these Laboratories, for the IBM calculation of d spacings.

Reference

Hansen, M. (1936). *Der Aufbau der Zweistofflegierungen.* Berlin: Springer.

---

* Schwarzkopf Microanalytical Laboratory, Woodside 77, New York, N.Y., U.S.A.