those of Truter* & Carpenter in Table 2. The agreement between the three sets is quite good. As might be expected, the principal differences occur for nitrogen. The standard deviations for the neutron analysis are considerably lower than the X-ray values. The improved accuracy is perhaps overstated, however, since scattering length errors were not considered.

Table 2. *Comparison of atomic coordinates*

	Truter	Carpenter	Kay & Frazer
y_{Na}	0·5852	0·5862	0·5853
$\sigma(y_{Na})$	0·002	0·002	0·001
y_N	0·1217	0·1188	0·1200
$\sigma(y_N)$	0·005	0·004	0·0007
z_O	0·1946	0·1944	0·1941
$\sigma(z_O)$	0·003	0·002	0·0006

The distances and bond angles found are as follows:

$$\text{Na–O} = 2{\cdot}471 \pm 0{\cdot}004,\ \text{Na–N} = 2{\cdot}589 \pm 0{\cdot}009,$$
$$\text{N–O} = 1{\cdot}240 \pm 0{\cdot}003\text{Å};$$
$$\sphericalangle\ \text{O–N–O} = 114{\cdot}9 \pm 0{\cdot}5^\circ.$$

The errors were calculated assuming no error in cell dimensions, so that they are too small by perhaps as much as a factor of two. Even so, the accuracy for the bond angle is substantially better than that of Truter (1954) and Carpenter (1955). Their standard deviations were 4° and 1·73°, respectively.

Table 3. *Root mean square displacements in Ångströms from anisotropic temperature factors**

Atom	u_M	$\sigma(u_M)$	u_m	$\sigma(u_m)$	d†
Na	0·128	0·015	0·118	0·017	0°
N	0·125	0·007	0·114	0·005	90°
O	0·160	0·007	0·112	0·007	5·5 ± 3°

* Subscripts M and m refer to the major and minor vibration axes, respectively.

† Angle between the major axis, and the crystallographic b axis. In the case of oxygen, the inclination is away from N, so as to approach being transverse to the N–O bond.

The thermal vibration results are given in Table 3 as root mean square displacements. Oxygen is the only atom that shows a definitely measurable degree of anisotropy. Since the phase transition is marked by the gain of a mirror plane perpendicular to b, implying a rotating or disordered structure above θc, thermal anisotropy along $\bar{b}$ may become significant for nitrogen and sodium at higher temperatures. Investigation of the effects of temperature on the structure are now under way in collaboration with Dr R. Ueda of Waseda University, Tokyo, Japan.

The spontaneous polarization calculated on the basis of simple Na^+, N^{+3}, and O^{-2} ions is 74 μ coulombs/cm^2, which is off by an order of magnitude from the observed value of 7 μ coulombs/cm.^{2} (Sawada *et al.*, 1958). This poor agreement is of course a result of the highly covalent nature of the nitrite group. It is of interest to see what effective ionic charges n_N and n_O would have to be placed at the N and O positions in order to obtain agreement with the observed polarization. These can be determined from the two equations

$$P_s = 1{\cdot}6 \times 10^{-19} \times V^{-1} \Sigma n_j Y_j = 7\ \mu\ \text{coulombs/cm.}^2,$$

and

$$n_N + 2n_O = -1\ ,$$

where V is the cell volume in cm.^{3}, the Y_j are the atomic coordinates in cm., and Σ extends over all atoms in the cell. For sodium $n = +1$. The calculation yields $n_N = -0{\cdot}36$ and $n_O = -0{\cdot}32$. While this result is only a rough approximation, it is of qualitative significance. The fact that n_N comes out to be as strongly negative as n_O suggests that the Na^+ ion exerts a strong counter polarizing influence on the NO_2^- group. The net electric moment for NO_2^- is still in the same direction as one would expect, however.

The authors would like to thank Dr W. C. Hamilton for assistance with the extinction calculations, and to acknowledge helpful discussions with Dr S. C. Abrahams and Dr T. Mitsui.

---

* Truter's coordinates have been taken from Carpenter (1955), where they appeared as a privately communicated improved set.

References

Busing, W. R. & Levy, H. (1959). *A Crystallographic Least Squares Refinement Program for the I.B.M.* 704. Oak Ridge National Laboratory Report 59-4-37.

Carpenter, G. B. (1952). *Acta Cryst.* **5**, 132.

Carpenter, G. B. (1955). *Acta Cryst.* **8**, 852.

Frazer, B. C. (1958). Unpublished notes.

Sawada, S., Nomura, S., Fujii, S. & Yoshida, I. (1958). *Phys. Rev. Letters*, **1**, 320.

Strijk, B. & MacGillavry, C. H. (1943). *Rec. Trav. Chim. Pays-Bas*, **62**, 705.

Shull, C. G. & Wollan, E. O. (1956). *Solid State Physics*, Vol. 2. New York: Academic Press.

Truter, M. R. (1954). *Acta Cryst.* **7**, 73.

Ziegler, G. E. (1931). *Phys. Rev.* **38**, 1040.

Acta Cryst. (1961). **14**, 57

The structure of Hf_5Sn_3.*

By D. M. Bailey and J. F. Smith, *Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.*

(*Received* 31 *May* 1960)

Compounds with the formula M_5N_3 often occur between transition elements, M, and Group IV B elements, N. An appreciable number of these compounds crystallize in the $D8_8$ structure if interstitial impurities, particularly carbon, are present (Nowotny, Lux & Kudielka, 1956). In the case of silicides and germanides, reduction in content or absence of interstitial impurities results in

---

* Contribution No. 898. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

instability of the $D8_8$ structure (Parthé & Norton, 1958; Nowotny, Searcy & Orr, 1956). The availability of relatively pure hafnium and tin prompted an investigation to determine whether Hf_5Sn_3 would form in the $D8_8$ structure and, if so, to obtain some measure of the interstitial impurity content.

The hafnium metal which was used to prepare the samples was obtained from Dr H. A. Wilhelm and had previously been purified by the iodide process (Carlson, Schmidt & Wilhelm, 1957). The tin metal was 'Baker Analyzed' reagent grade which had been further purified by a drossing process. Analytical data for the interstitial impurity content of the hafnium and tin are shown in Table 1.

Table 1. *Analyses of alloying components for interstitial impurities*

Element	Hafnium (wt.%)	Tin (wt.%)
Carbon	0·03*	0·0027*
Oxygen	0·02†	0·0005†
Nitrogen	0·009§	not detected†
Hydrogen	0·001†	not detected†
Boron	not detected‡	not detected‡

* Combustion–conductometric analysis.
† Vacuum fusion analysis.
‡ Spectrographic analysis.
§ Kjeldahl analysis.

An alloy on the tin-rich side of the stoichiometric ratio was prepared by arc melting under a helium atmosphere. The excess tin was dissolved in dilute HNO_3. Debye–Scherrer patterns taken on the residue were indexed on the basis of a hexagonal structure with $a = 8{\cdot}39_1$ and $c = 5{\cdot}82_3$ Å. These patterns showed qualitative agreement in both line position and intensity with the $D8_8$ structure.

Single crystals were separated from the dissolution residue and mounted so that the axis of rotation was the c-axis. The symmetry of the layer line patterns obtained with Weissenberg and precession cameras indicated space group symmetry $P6_3/mcm$, $P6_3cm$, or $P\bar{6}c2$. Since the $D8_8$ structure has the symmetry $P6_3/mcm$, intensities were calculated on the basis of the $D8_8$ structure:

6 Hf_1 in $6(g)$: $x, 0, \frac{1}{4}$ with $x = 0{\cdot}23$;
4 Hf_2 in $4(d)$: $\frac{1}{3}, \frac{2}{3}, 0$ parameterless;
6 Sn in $6(g)$: $x, 0, \frac{1}{4}$ with $x = 0{\cdot}60$.

Experimental values for the diffraction intensities were obtained by the multiple film technique with a Weissenberg camera and Cu $K\alpha$ radiation. A comparison of observed and calculated values for $(hk0)$ reflections is shown in Table 2. The discrepancy index,

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| ,$$

for these data is 0·146 which is adequate to verify the structure. The tabulated intensity values include corrections for Lorentz and polarization effects plus an artificial temperature factor ($B/\lambda^2 = 1{\cdot}22$) which was obtained from the slope of a semi-log plot of the ratio of observed intensity to uncorrected calculated intensity versus $\sin^2\theta$ (Lipson & Cochran, 1953). No additional corrections were made.

Cursory attempts to vary the parameters in either direction resulted in an increase in the discrepancy index. However, extensive effort on parameter refinement was not warranted since the primary interest was in the nature of the structure and not in a precise determination of interatomic distances.

In their study of the stabilization of Mo_5Si_3 in the $D8_8$ structure by carbon, Nowotny *et al.* (1954) report the structure to be unstable with less than 0·9 carbon atom per unit cell. A reasonable estimate of the impurity content of the compound Hf_5Sn_3 can be made from the analyses of the hafnium and tin. On this basis Hf_5Sn_3 contains less than one carbon atom per twenty unit cells and a total of only one impurity atom of any of the analyzed species per ten unit cells. The interstitial impurity content is thus an order of magnitude less than that necessary to stabilize Mo_5Si_3 in the $D8_8$ structure. The implication of these data is that tin is more tolerant of the $D8_8$ structure than either silicon or germanium, and it is at least possible that the presence of interstitials is not necessary for the stability of Hf_5Sn_3 in the $D8_8$ structure.

The authors wish to thank Dr H. A. Wilhelm for providing the hafnium metal and Dr O. N. Carlson for discussions concerning the impurity content. The authors are also indebted to Dr C. V. Banks and his group for the carbon and nitrogen analyses, to Dr V. A. Fassel and his group for the spectrographic analyses, and to Miss V. Horrigan for the vacuum fusion analyses.

References

Carlson, O. N., Schmidt, F. A. & Wilhelm, H. A. (1957). *J. Electrochem. Soc.* **104**, 51.

Lipson, H. & Cochran, W. (1953). *The Crystalline State*, Vol. III, *The Determination of Crystal Structures*, p. 61. London: Bell.

Nowotny, H., Lux, B. & Kudielka, H. (1956). *Mh. Chem.* **87**, 447.

Nowotny, H., Parthé, E., Kieffer, R. & Benesovsky, F. (1954). *Mh. Chem.* **85**, 255.

Nowotny, H., Searcy, A. W. & Orr, J. E. (1956). *J. Phys. Chem.* **60**, 677.

Parthé, E. & Norton, J. T. (1958). *Acta Cryst.* **11**, 14.

Table 2. *Observed structure factors compared with calculated structure factors based on the $D8_8$ structure for* Hf_5Sn_3

$hk0$	$\lvert F_o\rvert$	F_c	$hk0$	$\lvert F_o\rvert$	F_c	$hk0$	$\lvert F_o\rvert$	F_c
120	49·5	−49·6	240	29·6	−38·4	400	25·7	23·4
130	25·5	−23·0	250	17·4	22·9	440	35·9	36·6
140	51·4	68·5	260	21·4	−22·7	450	<4	5·4
150	15·0	−19·6	270	21·2	−15·9	460	<4	−6·2
160	38·7	−36·7	300	64·4	62·1	500	54·4	47·5
170	19·5	16·5	330	<4	4·9	550	30·4	35·2
180	<4	−1·2	340	8·5	−11·2	600	11·9	15·8
200	21·4	−18·9	350	<4	6·4	700	<4	−3·7
220	15·7	15·5	360	<4	5·1	800	24·4	17·9
230	<4	−10·6	370	<4	−5·3	900	32·6	30·0