to the structures, in complete agreement with the above model.

It should be noted that structure transformation by periodic slip processes from a hexagonal structure will always result in polytypes of even periodicity. As all polytypes identified in this laboratory (more than 60; Steinberger & Mardix, 1967) were of even periodicity, it is safe to assume that all these were derived from the 2H hexagonal phase. This assumption is in full accord with the high ($\sim 1250\,^\circ$C) growth temperature.

Two further observations have to be quoted here because of their relevance to the model. First, in a given crystal specimen all the polytypes are closely related (Mardix et al., 1967); this fact is in full accord with the assumption that the polytypes have been created by periodic slip from the same parent structure. The second observation deals with the transformation process itself; it has been shown (Mardix & Steinberger, 1966; Steinberger & Mardix, 1967) that by applying moderate pressure by a knife edge polytypes can be transformed even at room temperature. Simultaneously, macroscopic tilt angles are induced.

This work dealt only with the essentially geometrical description of polytype formation. Discussion of the underlying physical processes seems to be still too speculative, though little doubt can exist about the fundamental role of dislocations. It should be noted in this connexion that the transformation $2H \rightarrow$ cubic was directly observed (d'Aragona, 1966) to be due to the expansion of partials.

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Determination of Thermal Expansion of Germanium, Rhodium, and Iridium by X-rays

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The lattice parameters of germanium, rhodium, and iridium were measured with a Unicam 19 cm high-temperature powder camera; the following equations represent the results:

Ge: $a_t = 5\cdot6569 + 34\cdot22 \times 10^{-6}t + 10\cdot17 \times 10^{-9}t^2 - 0\cdot66 \times 10^{-12}t^3$
Rh: $a_t = 3\cdot8026 + 29\cdot27 \times 10^{-6}t + 10\cdot49 \times 10^{-9}t^2 + 0\cdot54 \times 10^{-12}t^3$
Ir: $a_t = 3\cdot8383 + 23\cdot52 \times 10^{-6}t + 4\cdot92 \times 10^{-9}t^2 + 0\cdot89 \times 10^{-12}t^3$

Thermal expansion coefficients and Grüneisen parameters were also calculated.

Introduction

Experimental data on the thermal expansion of germanium, rhodium, and iridium at high temperatures are very scarce. The available data either refer to low temperatures or give the mean value at high temperatures measured over large intervals. In the case of germanium macroscopic measurements have been made by Dennis (1928) in the range 20 to 400°C. Straumanis & Aka (1952) made X-ray measurements for a very short range between 10 to 50°C. Nitka (1937) has determined the thermal expansion of 99·9% pure germanium by measuring the lattice parameters only at four temperatures from 20 to 840°C. His room-temperature lattice parameter value differs from that of Straumanis & Aka (1952) by about 0·002 Å.

The macroscopic thermal expansion coefficients of rhodium at high temperatures have been determined by Ebert (1938) and those of iridium by Holborn & Valentiner (1907). No X-ray measurements are available for either of these metals. Owing to this lack of data, it was thought desirable to measure the lattice parameters of these three metals in detail at high temperatures. Results of measurements are reported in this paper.

Experimental

Germanium, rhodium, and iridium were 'Specpure' powder which were filled in quartz capillaries of inner diameter 0·5 mm and annealed. Photographs were taken with a Unicam 19 cm diameter high-temperature powder camera in more than two sets. The camera was

calibrated by finding out the lattice parameters of 'Spec-pure' silver at different temperatures and comparing them with the results of Hume-Rothery & Reynolds (1938) and Spreadborough & Christian (1959). Specimen temperature was maintained accurately within $\pm 2\,°C$ by using an input voltage stabilizer. The lattice parameters at different temperatures were calculated by Cohen's (1936) analytical method using Nelson & Riley's (1945) extrapolation function and they were expressed in an analytical form

$$a_t = a_0 + bt + ct^2 + dt^3$$

where a_t is the lattice parameter in Å at $t\,°C$. The thermal expansion coefficients were calculated by differentiating the parabolic equation and finding

$$\alpha_t = \frac{1}{a_0}\left(\frac{da_t}{dt}\right)_t$$

Results and discussion

Determination of the lattice parameters and the thermal expansion coefficients

(i) *Germanium*

The lattice parameters of germanium from 20 to 812 °C are listed in Table 1. They can be expressed in an analytical expression of the form

$$a_t = 5{\cdot}6569 + 34{\cdot}22 \times 10^{-6}t$$
$$+ 10{\cdot}17 \times 10^{-9}t^2 - 0{\cdot}66 \times 10^{-12}t^3\,.$$

The lattice parameters calculated by the above expression are also given in Table 1 for the sake of comparison with observed values. The thermal expansion coefficients are given by the expression

$$\alpha_t = 6{\cdot}05 \times 10^{-6} + 3{\cdot}60 \times 10^{-9}t - 0{\cdot}35 \times 10^{-12}t^2$$

and are listed in the last column of Table 1.

Table 1. *Lattice parameters (a) and thermal expansion coefficients (α) for germanium*

Temperature (°C)	a observed (Å)	a calculated (Å)	α × 10⁶ (°C⁻¹)
20	5·6575	5·6575	6·12
124	5·6614	5·6613	6·49
223	5·6648	5·6650	6·83
322	5·6691	5·6690	7·17
419	5·6728	5·6730	7·49
517	5·6772	5·6772	7·81
616	5·6814	5·6816	8·13
714	5·6866	5·6863	8·44
812	5·6909	5·6910	8·74

The lattice parameter of 99·9% pure germanium at 20 °C measured by Nitka (1937) is $5{\cdot}659 \pm 4$ Å and that of 99·99% pure germanium determined by Straumanis & Aka (1952) is 5·65748 Å at 20 °C. Our value at this temperature is 5·6575 Å which is in good agreement with that of the latter authors.

The mean thermal expansion coefficient calculated by Nitka (1937) from 20 to 840°C is $7{\cdot}13 \times 10^{-6}\,°C^{-1}$, which is in fair agreement with our value from 20 to 812°C, namely, $7{\cdot}45 \times 10^{-6}\,°C^{-1}$. Straumanis & Aka (1952) determined the mean thermal expansion of 99·999% germanium from 10 to 50°C and found it to be $5{\cdot}92 \times 10^{-6}\,°C^{-1}$, which is in fair agreement with our value $6{\cdot}18 \times 10^{-6}\,°C^{-1}$ in the same temperature range.

(ii) *Rhodium*

The lattice constants of rhodium at different temperatures are tabulated in Table 2 and variations of the lattice parameters and the thermal expansion coefficients with temperature are expressed by the parabolic equations

$$a_t = 3{\cdot}8026 + 29{\cdot}27 \times 10^{-6}t$$
$$+ 10{\cdot}49 \times 10^{-9}t^2 + 0{\cdot}54 \times 10^{-12}t^3$$

and

$$\alpha_t = 7{\cdot}70 \times 10^{-6} + 5{\cdot}52 \times 10^{-9}t + 0{\cdot}43 \times 10^{-12}t^2$$

respectively.

The lattice parameter determined by us at 30°C is $a = 3{\cdot}8034$ Å, which is in fair agreement with those of Owen & Yates (1933), $a = 3{\cdot}8034$ Å (converted from kX) at 18°C and Goldschmidt & Land (1947), $a = 3{\cdot}8046$ Å (temperature not given).

The thermal expansion coefficients of rhodium determined by various authors are summarized in Table 3.

Table 2. *Lattice parameters and thermal expansion coefficients of rhodium*

Temperature (°C)	a observed (Å)	a calculated (Å)	α × 10⁶ (°C⁻¹)
30	3·8034	3·8035	7·89
133	3·8066	3·8067	8·44
235	3·8103	3·8101	9·02
338	3·8136	3·8137	9·62
440	3·8176	3·8176	10·21
552	3·8222	3·8220	10·88
655	3·8265	3·8264	11·50
767	3·8313	3·8314	12·19
865	3·8360	3·8361	12·80

Table 3. *Coefficients of thermal expansion of rhodium*

Authors	Mean temperature or temperature range (°C)	α × 10⁶ (°C⁻¹)
Erfling (1939)	0–40	8·41
Fizeau (1869)	40	8·5
Swanger (1929)	25	9·6
Holzmann (1931)	20–812	10·2
Ebert (1938)	0–800	9·6
Present work	30–865	10·27

(iii) *Iridium*

The lattice constants and the thermal expansion coefficients are given in Table 4 and their variations with temperature are expressed by the equation

$$a_t = 3{\cdot}8383 + 23{\cdot}52 \times 10^{-6}t$$
$$+ 4{\cdot}92 \times 10^{-9}t^2 + 0{\cdot}89 \times 10^{-12}t^3$$

and

$$\alpha_t = 6\cdot13 \times 10^{-6} + 2\cdot56 \times 10^{-9}t + 0\cdot70 \times 10^{-12}t^2$$

respectively.

The room-temperature lattice parameter determined by Owen & Yates (1933) is 3·8391 Å (converted from kX) which is in good agreement with our value 3·8390 Å at 30°C.

Table 4. *Lattice parameters and thermal expansion coefficients of iridium*

Temperature (°C)	a observed (Å)	a calculated (Å)	$\alpha \times 10^6$ (°C⁻¹)
30	3·8390	3·8390	6·21
133	3·8414	3·8415	6·48
235	3·8443	3·8441	6·77
338	3·8466	3·8468	7·08
440	3·8499	3·8497	7·39
552	3·8531	3·8529	7·76
655	3·8561	3·8561	8·11
767	3·8594	3·8596	8·51
865	3·8629	3·8629	8·87

The mean thermal expansion value from 0 to 800°C calculated from the analytical formula given by Holborn & Valentiner (1907) is $7\cdot62 \times 10^{-6}$ °C⁻¹. Our value from 30 to 865°C is $7\cdot33 \times 10^{-6}$ °C⁻¹.

Calculation of Grüneisen parameter

Grüneisen constants at different temperatures were calculated by the relation $\gamma = 3\alpha V/C_v \psi$ from the present thermal expansion data, and are given in Table 5. The room temperature values of volume V and compressibility ψ were used in calculations. The specific heats C_p were taken from the American Institute of Physics Handbook (second edition 1963) and C_v were estimated by means of the Nernst–Lindemann equation

$$C_p - C_v = 0\cdot0214 C_p^2 T/T_s$$

where T_s is the melting temperature in °K.

It is observed that γ increases with temperature as found earlier by Sharma (1951), Deshpande & Sirdeshmukh (1961) and others.

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Table 5. *Values of the Grüneisen constant at different temperatures*

Temperature (°C)	Germanium $V = 13\cdot6$ cm³.mol⁻¹ $\psi = 12\cdot82 \times 10^{-13}$ cm².dyne⁻¹ γ	Rhodium $V = 8\cdot3$ cm³.mol⁻¹ $\psi = 3\cdot67 \times 10^{-13}$ cm².dyne⁻¹ γ	Iridium $V = 8\cdot6$ cm³.mol⁻¹ $\psi = 2\cdot76 \times 10^{-13}$ cm².dyne⁻¹ γ
25	0·86	2·12	2·35
127	0·87	2·21	2·40
227	0·89	2·30	2·46
327	0·93	2·39	2·53
427	0·96	2·49	2·60
527	1·00	2·58	2·67
627	1·04	2·67	2·75
727	1·08	2·76	2·83