

High Temperature X-Ray Study of the Thermal Expansion of IrAs₃ and IrSb₃

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IrAs₃ and IrSb₃ with the CoAs₃-type structure, have been studied by the X-ray powder method at temperatures in the range from 20 to 998°C. The average linear thermal expansion coefficient, β_a , is equal to $6.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (20–473°C), $5.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (600–998°C), $8.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (20–432°C), and $6.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (737–988°C). The volume expansion coefficient, α , is $20.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (20–473°C), $17.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (600–998°C), $24.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (20–432°C), and $20.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (737–988°C).

In recent high temperature X-ray studies^{1,2} of thermal expansion the author found a departure from linearity in both linear and volume expansion at higher temperatures. The reasons for the different types of expansion found are not fully explained by the existing theories for the perfect lattice. Since a quantitative explanation might be possible when sufficient data are available to test a proposed theory, further expansion experiments are to be carried out.

The present paper is concerned with the thermal expansion of IrAs₃ and IrSb₃ which have structures of the CoAs₃-type³. A drawing of one unit cell of the CoAs₃-type structure is shown in Fig. 1. The atomic arrangement in terms of the space group $Im\bar{3} (T_h^6)$ is as follows:

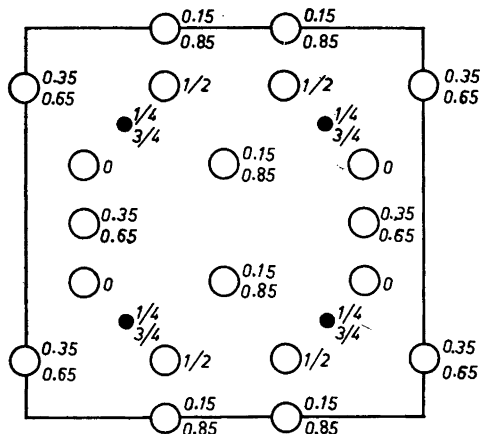
8 Co in (e) $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ etc.

24 As in (g) 0 y z etc.

The two parameters y, z are 0.350 ± 0.002 , 0.146 ± 0.002 , and 0.343 ± 0.001 , 0.157 ± 0.001 for IrAs₃ and IrSb₃, respectively, according to Kjekshus and Pedersen³.

As IrAs₃ and IrSb₃ were formed peritectically^{3,4}, these compounds were also chosen to study the expansion below a decomposition point. A relationship of thermal expansion to transition-, decomposition- or melting-point is suggested to have important practical as well as theoretical significance^{5,6}.

Fig. 1. Projection of one unit cell of the CoAs₃-type structure, with $y = 0.35$ and $z = 0.15$. Filled circles represent metal atoms and open circles represent metalloid atoms. Figures give the x -parameters of the atoms.



EXPERIMENTAL

The iridium metal used in this study was kindly placed at the disposal of Kjemisk Institutt by Falconbridge Nikkelverk A/S, Kristiansand S. A spectrographic analysis showed the presence of the following impurities: 0.1 % Ni, 0.01 % Rh, 0.01 % Pt, 0.001 % Ag, and 0.001 % Si.

The metallic arsenic was obtained from American Smelting and Refining Co. and reported to contain 99.999 % arsenic. The only reported impurities were a very faint trace of Cu and Pb. The high purity antimony from Brodley Mining Co., San Francisco, contained 0.001 % As, 0.0003 % Cu, 0.0003 % Fe, and 0.0002 % Pb.

According to Kjekshus and Pedersen³ the IrAs₃ and IrSb₃ samples were made by heating stoichiometric quantities of iridium and arsenic or antimony, respectively, at about 850°C in pure alumina crucibles, placed inside silica tubes which were evacuated and sealed. The samples were heated at this temperature for one month and finally slowly cooled to room temperature.

X-Ray powder photographs of the compounds were taken in a 190 mm Unicam high-temperature camera, with the samples sealed in thin-walled quartz capillaries. The samples were studied at temperatures between 20 and 998°C.

By means of a voltage regulator, the registered temperature of the furnace surrounding the specimen was kept constant to within $\pm 5^\circ\text{C}$. The Pt/Pt-Rh thermocouples of the furnace had been calibrated with a standard couple located at the position of the specimen.

Lattice constants are given in Ångström units ($\lambda\text{CuK}\alpha_1 = 1.54050 \text{ \AA}$). The lattice constants were calculated by the extrapolation method of Nelson and Riley⁷ using the

Table 1. Lattice constants and unit cell volumes of IrAs₃ at different temperatures.

t (°C)	a (Å)	V (Å ³)
20	8.4691	607.45
243	8.4818	610.19
306	8.4854	610.97
473	8.4947	612.98
600	8.5012	614.39
766	8.5096	616.21
903	8.5156	617.51
998	8.5208	618.64

Table 2. Lattice constants and unit cell volumes of IrSb₃ at different temperatures.

t (°C)	a (Å)	V (Å ³)
20	9.2495	791.33
179	9.2617	794.46
304	9.2703	796.68
432	9.2792	798.97
588	9.2878	801.20
737	9.2949	803.03
890	9.3042	805.45
988	9.3104	807.06

high angle reflection lines only. The probable error in the lattice constant determinations at temperatures above room temperature is estimated to be less than 0.01 %. Errors due to specimen contamination can be neglected, since the lattice constants at room temperature before and after the high temperature treatment were equal within the limit of the experimental error.

RESULTS

The lattice constant results and unit cell volumes are listed in Tables 1 and 2. The ratios $\frac{a_t - a_{20}}{a_{20}} = \frac{\Delta a}{a_{20}}$ and $\frac{V_t - V_{20}}{V_{20}} = \frac{\Delta V}{V_{20}}$ are calculated and plotted as $\frac{\Delta a}{a_{20}}$ versus t and $\frac{\Delta V}{V_{20}}$ versus t , respectively. The calculations of the expansion coefficients were based upon these data.

As shown in Fig. 2 the change in the length of the a -axis is similar. The a -axis increases linearly with increasing temperature for both compounds below 432 and above 737°C. The expansion coefficient, β_a , is equal to $6.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (20—473°C), $5.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (600—998°C), $8.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (20—432°C), and $6.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (737—988°C). At temperatures between 432 and 737°C the a -axis increases nonlinearly; this is most significant on the expansion-curve for IrSb₃.

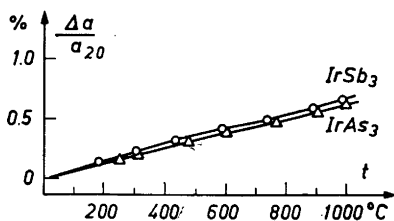


Fig. 2. Relative lattice constant variation as function of temperature.

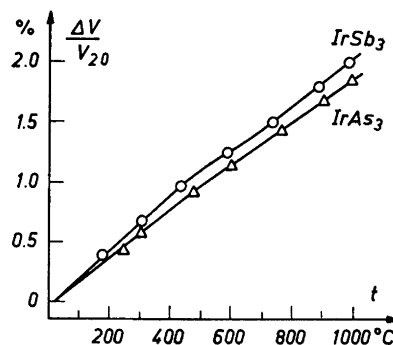


Fig. 3. Relative changes in volume with temperature.

The volume expansion is plotted as a function of temperature in Fig. 3. For both compounds the volume expansion has a similar temperature dependence as the a -axis. Since β_a is of the order of 10^{-6} , the average thermal volume expansion coefficient α is approximately $3\beta_a$. The numerical values for α are $20.2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (20—473°C), $17.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrAs₃ (600—998°C), $24.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (20—432°C), and $20.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for IrSb₃ (737—988°C).

The intensities of the reflections on X-ray photographs taken at higher temperatures are almost equal to those of the corresponding photographs taken at room temperature. The parameters y and z must thus be nearly the same. The shortest interatomic distances between metal and metalloid atoms are

$$\begin{aligned} a \cdot 0.2887 \pm 0.0012 \text{ \AA} & \quad (\text{IrAs}_3) \\ a \cdot 0.2825 \pm 0.0006 \text{ \AA} & \quad (\text{IrSb}_3) \end{aligned}$$

and between the metalloid atoms

$$\begin{aligned} a \cdot 0.292 \pm 0.034 \text{ \AA} & \quad (\text{IrAs}_3) \\ a \cdot 0.300 \pm 0.034 \text{ \AA} & \quad (\text{IrAs}_3) \\ a \cdot 0.314 \pm 0.018 \text{ \AA} & \quad (\text{IrSb}_3). \end{aligned}$$

The thermal expansion is approximately equal to the expansion of the cell edge, *cf.* Fig. 2.

As the a -axis and the volume of IrAs₃ increase more slowly above 473°C than at lower temperatures the relative expansion is still on the upper part of the sigmoidal curve. The a -axis and the volume of IrSb₃ increase more slowly between 432 and 737°C than above 737°C and the relative expansion of this compound above 737°C is thus not on the sigmoidal part of the expansion curve. No large increase in the coefficient of thermal expansion for IrAs₃ and IrSb₃ is observed in the examined temperature range. A more rapid increase might well take place at higher temperatures.

The expected peritectical decomposition^{3,4} of IrAs₃ and IrSb₃ is not observed at temperatures between 20 and approximately 1 000°C. Decomposition must accordingly take place in the range between approximately 1 000 and 1 200°C. For IrSb₃ this is higher than the range 800 to 950°C reported by Kuzmin *et al.*⁴

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