Thermal Expansion Coefficients for Uranium Boride and β-Uranium Silicide

THE thermal expansion coefficients for uranium boride (UB_2) and β-uranium silicide (USi_2) have been determined by X-ray powder methods with a high-temperature camera. The mean values for the expansion coefficients between room temperature and 205° C. for different directions in the lattice are summarized in Table 1.

Table 1. THERMAL EXPANSION COEFFICIENT (PER DEG. C.), MEAN VALUE BETWEEN 20° C. AND 205° C.

Compound	Thermal expansion coefficient	Direction in the lattice
UB_2	9×10^{-6}	*a*-axis
	8	*c*-axis
	6	U–B bond direction
β-USi_2	57	*a*-axis
	−26	*c*-axis
	16	U–Si bond direction

These two compounds were selected because of their formally identical crystal structures. They both belong to space group $C\ 6/m\ m\ m$ and are of the AlB_2-type ($C\ 32$)[1–3]. The uranium atoms are situated in the 000 position of the simple hexagonal cell, whereas the non-metal atoms are situated in the $\frac{1}{3}\frac{2}{3}\frac{1}{2}$ and $\frac{2}{3}\frac{1}{3}\frac{1}{2}$ position. The structure may be regarded as formed by plane hexagonal sheets of uranium atoms (*A*) and plane hexagonal networks (*H*) of boron or silicon atoms. The sequence of the sheets in the [001] direction is *AHAHAH* ..... The lattice constants and the interatomic distances for the two compounds are summarized in Table 2. MeB_2-lattices have also been discussed from several aspects by Post *et al.*[4].

Table 2. LATTICE PARAMETERS AND BOND-LENGTHS FOR UB_2 AND β-USi_2 (IN A.)

Compound	Lattice parameters	Distance U–U		Distance U–B (or U–Si)	Distance B–B (or Si–Si, network *H*)
		In sheet (*A*)	Between sheets (*A*)		
UB_2	$a=3\cdot136$ $c=3\cdot988$	3·14	3·99	2·69	1·81
β-USi_2	$a=3\cdot85$ $c=4\cdot06$	3·85	4·06	3·01	2·22

A study of the bond-lengths shows that, although uranium boride and β-uranium silicide are isostructural and formed by the same metal atom, several fundamental differences exist which depend on the difference in radius between the boron and the silicon atoms. If the small boron atom (r_B = 0·86 A.) is taken up between the hexagonal uranium sheets, the distance U–U between the sheets of 3·14 A. is still within the limits for a metallic bond to be formed between the uranium atoms. (In the α-, β-, γ-phases of uranium the distances between nearest neighbours of metal atoms varies within the limits 2·75–3·30 A.) The silicon atom (r_{Si} = 1·17 A.), however, is accommodated between the metal sheets only if the uranium atoms are considerably separated (distance U–U = 3·85 A. in the sheets). There is thus probably no bond-formation between the uranium atoms in the metallic sheets of β-uranium silicide.

In the hexagonal networks (*H*) of non-metal atoms in uranium boride, the boron atoms have a separation of 1·81 A., which is 5 per cent larger than the sum of the atomic radii. In β-uranium silicide, however, the silicon–silicon distance of 2·22 A. is 5 per cent smaller than the sum of the atomic radii.

The U–B distance in uranium boride is 11 per cent bigger than $r_U + r_B$ and the U–Si distance in β-uranium silicide is 10 per cent bigger than $r_U + r_{Si}$, using 1·50 A. as the radius for the uranium atom.

The difference in the nature of the bonds in the isostructural compounds uranium boride and β-uranium silicide is clearly reflected in the thermal expansion coefficients for the two lattices. The lattice of uranium boride, with a radius ratio of $r_B/r_U = 0\cdot57$, expands uniformly. The coefficient of thermal expansion is nearly equal in different bond directions, indicating that the lattice is held together by bonds of the same nature. It is thus conceivable that the atoms in the same uranium sheets (*A*) are held together by metallic bonds, whereas the distance between the uranium atoms in different sheets is too big (3·98 A.) to permit any direct bond formation. The sheets are held together by the boron atoms, forming uranium–boron–uranium bonds in addition to the boron–boron bonds in the networks (*H*). A possible way might be that electrons from the boron atoms are taken up by the unfilled 6*d*-levels of the uranium atoms and the lattice stabilized by electron oscillation in different bond directions.

For β-uranium silicide the radius ratio r_{Si}/r_U is 0·78. The extraordinarily big thermal expansion of the uranium sheets (the direction of the *a*-axis) probably depends on the facts that no direct binding forces exist between the uranium atoms in the sheets and that the hexagonal networks of silicon atoms parallel to the sheets are considerably 'compressed'. The lattice is held together by silicon–silicon and uranium–silicon–uranium bonds. The negative expansion coefficient between the uranium sheets (*c*-axis) is remarkable and shows that the type of bonding in the β-uranium silicide lattice is different from the bonding in the uranium boride lattice.

Other studies of the thermal expansion coefficients for pairs of isostructural compounds are planned. Uranium boride and chromium boride[3] form, for example, a pair of isostructural compounds where the size of the metal atom is varied for the same non-metal atom. The isostructural pair uranium silicide[2] and iron boride[3] might show other aspects of the nature of the bonds within silicides and borides.

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Symbols for Lattice Disorders

MODERN concepts of crystal physics and chemistry have made it necessary that appropriate symbols should be evolved to designate all kinds of disorders occurring in a crystal lattice. Though several sets of symbols are in use, they are not universally accepted and they are not self-explanatory ; indeed, authors often include a glossary of their symbols, which shows that they do not expect the reader to understand or recognize their symbols. It is never