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Low temperature XRD study of actinide metals and compounds

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Résumé. — La variation du paramètre de réseau entre 50 et 300 K a été mesurée pour Th, Pa, PaC, UC, PuC, PuN et Pu(C,N). Aucune transformation de phase ou anomalie n'a été observée dans ce domaine de températures. Les coefficients de dilatation linéaire ont été déterminés à partir des courbes $a(T)$. Ils sont proches de zéro pour UC, PuC et PuN entre 50 et 100 K. Le volume de la maille de Pa décroît puis augmente si ce métal est refroidi de 300 à 50 K.

Abstract. — The low temperature lattice parameter variation was measured for Th, Pa, PaC, UC, PuC, PuN, and Pu(C, N). No phase transformation or anomaly was observed in the range 50 to 300 K. The coefficients of thermal linear expansion were deduced from the $a(T)$ curves. For UC, PuC, and PuN, the expansion coefficient is close to zero between 50 and 100 K. The unit cell volume of Pa first decreases then increases on cooling from 300 to 50 K.

1. Introduction. — Some actinide metals and compounds were studied on a low temperature X-ray diffractometer equipped with a closed-cycle helium cooling device. Particular attention was paid to metals and compounds for which anomalies in physical properties such as thermal expansion, electrical resistivity, and magnetic susceptibility had been observed at low temperature.

2. Experimental. — 2.1 MATERIAL. — The materials studied were :

— *thorium* and *protactinium* metal prepared by thermal dissociation of the iodides on a radiofrequency-heated tungsten sphere [1],

— *protactinium monocarbide* obtained by carbothermic reduction of Pa_2O_5 [2], [3] ; this sample still contained a large amount of graphite,

— *uranium monocarbide* prepared from the melt by NUKEM (4.72 % C, 0.04 % O, 0.06 % N),

— *plutonium monocarbide* of composition $\text{PuC}_{0.79}\text{N}_{0.015}\text{O}_{0.025}\square_{0.17}$ ($\square$ = non-metal lattice vacancies) prepared by carbothermic reduction of PuO_2 [4],

— *plutonium mononitride* of composition $\text{PuN}_{0.99}\text{C}_{0.02}\text{O}_{0.01}$ prepared by carbothermic reduction of PuO_2 in the presence of nitrogen [4],

— *plutonium monocarbonitride* prepared by sintering the two preceding products together [4].

2.2 APPARATUS AND METHOD. — The expander tube of a closed-cycle cryogenic system was mounted into an evacuated camera with beryllium windows which fitted onto an X-ray dif-

fractometer [5]. A thin layer of the powdered sample was fixed on the end-plate of the expander tube ; temperature was measured by a Au-0.07 % Fe/chromel thermocouple inserted into a radial bore of this end-plate. Details of the method are given elsewhere [4], [5].

3. Results and discussion. — Figures 1, 2, and 3 show the variation of the lattice parameters between 50 K and temperatures slightly above room temperature. An anomaly indicating phase transformations or other transformations was not detected in this temperature range. In particular, the anomaly in thermal expansion previously reported for PuC between 80 and 100 K on the basis of strain gauge measurements [6] was not confirmed by the present work. Protactinium kept its tetragonal structure

Fig. 1. — Lattice parameter variation for UC, PuC, PuN, and Pu(C, N).

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down to 55 K ; the variation of slope of resistivity observed for this metal at about 100 K [7], [8] is thus not connected to a change in crystallographic structure.

Fig. 2. — Lattice parameter variation for PaC and Th.

Fig. 3. — Variation of lattice parameters and unit cell volume V for Pa.

The thermal linear expansion $\Delta L/L_{293}$ and, wherever possible, the coefficient of thermal linear expansion were calculated from the lattice parameters. Figure 4 shows the alignment of the present data with the recommended curve for thermal linear expansion at $T > 293$ K [9] and the variation of the expansion coefficient between 50 and 350 K for plutonium monocarbide. Similar curves were obtained for PuN, UC, and Pu(C, N), but for Th (Fig. 5),

Fig. 4. — Thermal linear expansion and instantaneous coefficient of thermal linear expansion for PuC.

Fig. 5. — Thermal linear expansion for Th.

the present results indicate an approximately linear variation of $\Delta L/L_{293}$ below 293 K.

The expansion coefficients are the instantaneous coefficients $\alpha_1 = (a_2 - a_1)/[a_{293}(T_2 - T_1)]$, a_2 and a_1 being the lattice parameters at T_2 and T_1 , resp., where $T_2 = T_1 + 20$; they are valid at $T_m = (T_1 + T_2)/2$. a_1 , a_2 , and a_{293} were read from the lattice parameter *versus* temperature curve. For the following materials, only the mean coefficient of thermal linear expansion for the range 60-293 K was determined :

$$\text{PaC}, \alpha_m = 3.9 \times 10^{-6} \text{ K}^{-1};$$

$$\text{Th}, \alpha_m = 11.9 \times 10^{-6} \text{ K}^{-1};$$

$$\text{Pa}/\text{c}, \alpha_m = 3.4 \times 10^{-6} \text{ K}^{-1}.$$

It is noteworthy that for UC, PuC, and PuN, the lattice parameter contraction becomes very small below 100 K. It is of the order of the accuracy of the measurement, and thus makes the $a = f(T)$ curves appear horizontal in the range 50 to 100 K. For the actinide dioxides, Marples [10] observed a similarly small lattice parameter variation for this temperature range. This *leveling off* cannot be due to plutonium self-heating as it is also observed for UC. It is not observed for the f.c.c. metal Th (Figs. 2 and 5) nor for most of the common cubic metals.

We determined the instantaneous expansion coefficients from Marples' lattice parameter curves for the oxides and observed that the $\alpha_1 = f(T)$ curve for PuO_2 is practically congruent with that for PuC shown in figure 4. The thermal expansion behaviour of these two compounds is thus very similar between 50 and 293 K.

For Pa, the c parameter slightly decreases with decreasing temperature. The measured values for the a parameter are best fitted by a second degree function which increases when cooling between 150 and 50 K. The volume of the unit cell calculated from the $a(T)$ and $c(T)$ functions first decreases, then increases on cooling.

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