CONF-8606149--2

MASTER

[For publication (Physica B+C) in the Proceedings of the Second Workshop "Actinides Under Pressure", Karlsruhe, Federal Republic of Germany, June 2-3, 1986.]

CONF-8606149--2

DE86 013550

A NEW LOOK AT THE ATOMIC VOLUMES OF THE β-FORM OF THE TRANSPLUTONIUM METALS

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Running headline: Atomic volumes of transplutonium metals

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Key words: Atomic volumes/Transplutonium Metals/Am, Cm, Bk, Cf

*Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy under contracts DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc., DE-AS05-76ER04447 with the University of Tennessee, Knoxville, and by the Commission of the European Communities, Joint Research Centre, Karlsruhe Establishment.

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Contents

Abstract

The atomic volumes of the beta-form of the first four transplutonium metals were evaluated using data for samples prepared by thermal and by pressure treatment. The volumes derived for curium, berkelium, and californium metals quenched from elevated temperatures were found to be consistently larger than those for "pressure-quenched" samples, whose volumes were in good agreement with values for the alpha-forms. The cubic lattice parameters from "pressure-quenched" samples also provided a more consistent trend than those obtained from thermally-quenched samples when compared to the parameters for the mononitrides of the metals.

1. Introduction

The electronic configuration and bonding in actinide metals are important topics in actinide solid state science. Studies of the actinide metals under pressure have contributed to an understanding of their electronic behavior as a function of their position in the series, as well as determining their physical properties under pressure. The crystallographic properties of the first five transplutonium metals under normal pressure [1-7] and the behavior of the first four transplutonium metals under pressure [8-20] have been reported. From studies at normal pressure, americium, curium, berkelium, and californium metals are known to have a dhcp (α)form and a high temperature fcc (β)form. The next metal in the series, einsteinium, is a divalent metal and has an atomic volume significantly larger than those for the other transplutonium metals [21]. A notable difference in crystal behavior between the first four transplutonium metals (5f metals) and the lighter lanthanide metals (Pr-Pm, 4f metals) under normal pressure is that these latter metals exhibit a bcc instead of a fcc high temperature phase.

Under pressure, the first four transplutonium metals tend to follow the same structural sequence that has been reported for some of the lanthanide metals [22]. Starting with the normal pressure, room temperature dhcp structure, the sequence is dhcp → fcc → fcc' → orthorhombic, except that curium and berkelium metals do not exhibit the distorted cubic structure. Details about these transitions with increasing pressure, and discussions about the pressures required for delocalization of the 5f electrons in these metals, are given in the

references cited. Of interest here are the atomic volumes of the transplutonium metals following pressure treatment and the comparison of these volumes with those obtained from thermally-treated samples.

2. Experimental

The experimental techniques and equipment employed in the work described here are adequately covered in the references cited above [11-13, 17,18]. They are summarized here for completeness. Diamond anvil pressure cells of the Syassen-Holzapfel type were used in conjunction with energy dispersive x-ray diffraction analysis. Silicon oil was used as the pressure transmitting medium in the cells. Pressures in the cells were determined from a measurement of the shift in the laser-excited fluorescnece of ruby chips located in the sample cavity of inconel gaskets.

3. Results and Discussion

Each of the first four transplutonium metals exhibits the dhcp structure as its normal pressure-room temperature α-form. Like the lanthanide metals, praseodymium and neodymium [22], under pressure these actinide metals first change to a cubic (fcc) structure and eventually form the α-uranium, orthorhombic structure [8,11,17] In addition, americium [20] and californium [11] metals, like the above mentioned lanthanide metals, form a distorted cubic phase prior to the appearance of the α-uranium orthorhombic structure.

Upon the release of pressure, we have observed that the α-uranium orthorhombic structure of these actinide metals rapidly converts to the cubic, or the distorted cubic and then the cubic phase, showing little if any hysteresis. In contrast, the cubic to dhcp transformation in these samples was essentially irreversible. The kinetics of this latter transformation at room temperature were so slow that, after release of all pressure on these transplutonium metals, the cubic phase was either the primary or the only phase observed in the samples. When evidence for the dhcp phase was observed after releasing the pressure on these samples, it was limited to detecting the presence of the strongest line (hkl = 102) of the dhcp phase. In the case of curium metal, the pressure-induced cubic phase was the only phase detected in three samples after several months of storage at normal pressure. Structural transformations in the lanthanide metals have also been shown to be slow at room temperature [23], and it is reasonable to assume that the transplutonium metals may exhibit similar characteristics. A recent study on the kinetics of the dhcp/fcc transitions in lanthanium metal has also shown that the hysteresis of the transition increases with lower temperatures [24]. Thus, the fcc phase of lanthanium metal can be readily quenched from high pressure and retained at normal pressure if the temperature is kept low.

Retention of this cubic phase in the transplutonium metals after release of pressure ("pressure-quenched" forms) provided an opportunity to compare the atomic volumes of the β-form of these metals with the volumes of the same form of the metals that had been generated by thermal treatment ("treatment-quenched" forms). In the latter case, the metal samples were quenched from elevated temperatures in order to

retain their β-form at room temperature. In Table I the atomic volumes for the α- and β- forms of the transplutonium metals are given, having been calculated from published lattice parameters and the parameters obtained from pressure-treated samples. It is apparent from Table I that, except for americium metal, the volumes of the β-forms of the metals from thermal treatment are all considerably larger than for their α-forms. In contrast, the volumes of the β-forms obtained from pressure studies on the metals are in good agreement with the volumes reported for their α-forms. With americium metal the lattice parameters published for the α- and β-forms [1] obtained from thermal treatment yield essentially the same atomic volume. The lattice parameter of the β-form obtained from vapor deposition [25] is also very similar to the earlier published parameter for the β-form (see Table I). However, data obtained from americium metal quenched from the molten state gave a larger lattice parameter for the β-form [25]. With curium metal, quenching from the molten state produced a parameter for the β-form of this metal nearly identical to the first published value for ths form [3] but smaller than a more recent value [5] obtained with the less radioactive Cm-248 isotope (see Table I). Thus, the larger atomic volumes for the β-form of the three transamericium metals obtained from thermal treatment suggest that these materials may have retained an expanded lattice as a result of the preparative technique. The difference in behavior for americium and the next three transplutonium metals may be due in part to their transition temperatures. That is, the α-β transition temperature for americium metal is ∿500°C below the metal's melting point, whereas with the other three metals this difference is ≤120°C [26]. Experimentally it is difficult to obtain the

β-form of curium, berkelium, and californium metals by quenching from elevated temperatures.

The close structural similarity of the dhcp and fcc forms, the similar atomic volumes that have been obtained for the two forms of americium metal, together with the similar atomic volumes for the α- and β-forms of lanthanide metals, all suggest that the two crystal forms of each of the three transcurium metals should also have similar atomic volumes. In addition to these rationale, there is another reason to prefer the smaller atomic volumes for the β-form of the transamericium metals. In Table II are given the lattice parameters for the first four transplutonium monopnictides and the β-forms of these metals. It can be seen that the lattice parameter of americium nitride is larger than that of the β-form of the americium metal, that parameters for curium and berkelium nitrdes are smaller than those for the literature values of the β-forms of the metals, while the extrapolated value for californium nitride is the same as the reported value for the β-form of the metal. In contrast, the lattice parameters for the β-form of curium, berkelium, and californium metals obtained from pressure experiments and the reported value for β-americium, are all smaller than the respective nitride parameters. Thus, the data obtained from the pressure experiments provide a consistent trend in behavior for these transplutonium materials.

The conclusion reached in this work is that the lattice parameters obtained from pressure treatment of the transamericium metals provide lattice parameters for the β-forms of these metals that are preferable to those obtained by quenching samples from elevated temperatures. The parameters obtained from samples following pressure treatment generate

atomic volumes for the β-forms of the metals that are very similar to those established for the α-forms of these metals, and provide a consistent trend when the lattice parameters of the β-form of the metals are compared to the lattice parameters of the transplutonium monopnictides.

5. Acknowledgement

This work was sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under contracts DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. and DE-AS05-76ER04447 with The University of Tennessee, and by the Commission of the European Communities, Joint Research Center, European Institute for Elements, Karlsruhe, FRG. The authors are indebted to the Office of Basic Energy Sciences, U.S. Department of Energy through the transplutonium element production facilities at Oak Ridge National Laboratory for the use of the curium-248, the berkelium-249, and the californium-249 isotopes.

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Table I. Atomic Volumes of the α- and β-Forms of the First Four Transplutonium Metals

Metal	dhcp, α-form			fcc, β-Form (thermal-quench, at 25°C)			fcc, β-Form (formed by pressure)		
	L.P.*	Volume*	Ref	L.P.*	Volume*	Ref	L.P.*	Volume*	Ref
Am	a_o = 0.34681	29.27	1, 25	a_o = 0.4894	29.30	1	-	-	-
	c_o = 1.1241			a_o = 0.48868	29.18	25			
Cm	a_o = 0.3496	29.98	2	a_o = 0.5065	32.48	5	a_o = 0.493	30.0	This work
	c_o = 1.1331			a_o = 0.5039	31.99	3			
Bk	a_o = 0.3416	27.96	4	a_o = 0.4997	31.19	4	a_o = 0.482	28.0	This work
	c_o = 1.1069								
Cf	a_o = 0.3384	27.37	6	a_o = 0.494	30.1	7	a_o = 0.478	27.3	This work
	c_o = 1.1040								

*L.P. = lattice parameter(s) in nm: Volume = atomic volume in $nm^3 \times 10^3$

Table II. Cubic Lattice Parameters for Selected Transplutonium Metals and Monopnictides

Material	Lattice Parameter, nm	Reference
β-Am	0.4894	1
β-Am†	0.5004	25
AmN	0.4995-0.5002	28,29
β-Cm	0.5065	5
β-Cm	0.5039	3
β-Cm*	0.493	This Work
CmN	0.5027	5
β-Bk	0.4997	4
β-Bk*	0.482	This Work
BkN	0.4951	27
β-Cf	0.494	7
β-Cf*	0.478	This Work
CfN (extrapolated)	(0.494)	This Work

*Material formed by pressure at room temperature, parameters obtained from material at normal pressure and room temperature.

†Metal quenched from melt; see text.