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PREPARATION AND STUDY OF ELEMENTAL CALIFORNIUM-249*

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ABSTRACT

Bulk samples of ^{249}Cf metal have been prepared on the 10 μg scale via the Li metal vapor reduction of $^{249}CfF_3$. Above about 725°C elemental Cf exhibits a face-centered cubic (fcc) structure with an average, room-temperature lattice parameter of 5.75(1)Å. Between about 600°C and 725°C, the stable form of Cf metal is another fcc structure with an average, room-temperature lattice parameter of 4.94(1)Å. Below 600°C metallic Cf exhibits a double hexagonal closest packed (dhcp) structure with average, room-temperature lattice parameters of a_o = 3.39(1)Å and c_o = 11.01(5)Å. By comparison of the metallic radii calculated for these three forms with those of the preceding transuranium elements, it is suggested that the two, lower temperature modifications represent Cf with a metallic valence of three, while the highest temperature form represents a metallic valence of two. Although the data reported here are from the most complete study to date of elemental Cf, the limitations accompanying such microscale research are duly noted.

INTRODUCTION

Crystal structures, lattice parameters, and phase relationships of well-characterized actinide metals have been reported only through berkelium (Bk). The scarcity of ^{249}Cf and the high volatility of californium (Cf) metal have resulted in greatly complicating the preparation of bulk samples of this metal for detailed study.

Attempts to prepare elemental Cf by reduction of Cf_2O_3 with La or Th metal or by reduction of CfF_3 with Li or K metals have been described previously [1-9]. Cunningham and Parsons [2], using the trifluoride reduction scheme, and independently, Asprey [3,5], using the oxide reduction scheme, reported Cf metal to exhibit a face-centered cubic (fcc) structure with a lattice parameter of 5.41Å. Additionally, Asprey [3,5] noted the possibility of a second fcc phase, having a_o = 4.81Å. However, Haire and Baybarz [4,7,8], using the oxide reduction scheme and an electron microscope, examined thin film deposits of condensed Cf vapor and reported a fcc form (a_o = 5.743(6)Å) and a hexagonal closest packed (hcp) form (a_o = 3.988(4)Å and c_o = 6.887(8)Å). These workers were uncertain about the phase relationship with temperature, but concluded that the hcp form, if it were a true metal phase, would most likely be the low-temperature form with respect to the fcc modification. Zachariasen [10] has recently interpreted these data as representing Cf_2O_2S (hcp form) and CfS (fcc form) and not Cf metal at all.

Working with much larger samples also produced by the oxide reduction scheme, Haire and Asprey [9] interpreted their X-ray powder diffraction data to support the existence of two different double hexagonal closest packed (dhcp) modifications of Cf metal. One was characterized by average (N = 7) lattice

parameters(σ) of a_o = 3.398(5)Å and c_o = 11.034(16)Å, and the other, by average (N = 8) lattice parameters(σ) of a_o = 4.002(6)Å and c_o = 12.803(21)Å. Independently, Baybarz [7] reported his observation of still another form of Cf metal, a rhombohedral, α-Sm type structure with lattice parameters of a_o = 3.375Å and c_o = 25.05Å. Stevenson [6], working on the several microgram scale and employing trifluoride reduction, prepared two bulk Cf metal samples, both exhibiting a fcc structure with an average cell edge(2σ) of 4.994(12)Å.

In most of the above work, however, interconversion between the various observed metallic phases and confirmation of their being true metal phases have not been adequately demonstrated. Reported here are the results of a detailed study of the crystal structures, lattice parameters, and phase relationships of ^{249}Cf metal.

EXPERIMENTAL

Materials

The approximately one milligram of ^{249}Cf available for this work was the daughter of ^{249}Bk, synthesized in the Oak Ridge High Flux Isotope Reactor as part of the U.S.E.R.D.A. program of heavy elements production and research. The separation and purification procedures have been described elsewhere [11]. Because the small size of the metal samples prepared in this study precluded accurate analyses for cationic and anionic impurities in the individual samples themselves, three independently purified batches of ^{249}Cf were used. Two batches were purified by R. G. Haire at the TRU facility of the Oak Ridge National Laboratory [12] and one was purified and kindly supplied by T. C. Parsons of the Lawrence Berkeley Laboratory [13].

Specially cleaned and selected cation-exchange resin beads (Dowex AG 50W) of about 0.3 mm diameter (air dry) were loaded to saturation with Cf^{3+} ions and ignited in oxygen up to 1200°C, according to a technique devised by Cunningham [14]. Our ignition apparatus using induction heating is similar to the one described by Baybarz [15]. The resulting oxide samples were treated with anhydrous HF gas at 600°C in a monel furnace heated by induction. The light green colored, spherical shaped samples obtained were shown by X-ray diffraction analysis to correspond to CfF_3 [16]. The anhydrous HF gas was obtained by fluorination of Matheson tank HF in accord with the procedure used by Asprey [17] and its dryness verified by testing with K_3NiF_7. The Li metal reductant was purified by distillation in Ar and contained less than 100 ppm oxygen [18].

Metal Preparation

Samples of californium metal ($\leq$10 μg each) were prepared by reduction of californium trifluoride with lithium metal vapor. The low total heat capacity crucible reduction system has been described elsewhere [19]. The glass vacuum enclosure was changed for this and future work to an O-ring system (from the standard taper joint) to prevent any grease contamination.

The trifluoride reductions were carried out at temperatures ranging from 600 to 1000°C under a vacuum of approximately 10^{-5} torr. Typical heating times were 12 to 15 sec for the high-temperature cycles and 30 to 50 sec for the low-temperature cycles. These short heating times, coupled with the rapid attainment of thermal equilibrium upon heating and cooling, enabled reasonable product metal yields to be obtained, despite the high volatility of Cf metal.

All the metal preparations were carried out in an inert atmosphere enclosure under a circulation of helium. The He was continually purified

from oxygen and water contamination by cycling through molecular sieves and from nitrogen contamination by passing through a trap containing metallic lithium. A more detailed description of the inert atmosphere gloved box facility has been given elsewhere [20].

The metal samples were handled only within the inert atmosphere enclosure and were sealed in 3/4 atmosphere of pure helium in quartz capillaries suitable for analysis by X rays.

X-Ray Diffraction Analysis and Data Reduction

All metal samples were examined at room temperature by standard X-ray powder diffraction techniques. The X-ray generator was a G.E. Model XRD-6. CuK radiations were obtained from a CA-8S "Small Focal Spot" tube. The camera was a 57.3 mm diameter Philips Debye-Scherrer type, using Straumanis film mounting, and modified to receive a beryllium cup [21] to protect the fragile capillary during loading and unloading of the film. Exposure times of 1 to 2 hours were found to be adequate, using Ilford Industrial G X-ray film and operating the generator at 50 kV - 20 mA.

Line positions were read on a Philips-Norelco reader provided with a 0.05 mm precision vernier. The observed line intensities were compared to values calculated by program POWD [22]. The lattice parameters were refined using the program LCR-2 [23] including the Nelson-Riley extrapolation function. Our lattice parameters are reported only to the nearest hundreth angstrom because of the absence of sufficient analytical data regarding the purity of the Cf metal samples studied. The error limits given in parentheses on the average lattice parameters represent the 95 per cent confidence interval calculated using the standard statistical method for the average of a number of independent determinations and rounded up to the nearest hundreth angstrom.

The number in parentheses following the lattice parameter of an individual metal sample is the standard deviation rounded up to the nearest hundreth angstrom.

RESULTS AND DISCUSSION

Crystal Structures, Lattice Parameters, and Metallic Radii and Valence

Twenty-two samples of californium metal have been prepared from three independently purified batches of ^{249}Cf, designated by batch numbers TRU-1, TRU-2, and LBL-3. The results described below are based on the sixteen samples prepared from the material of batches TRU-2 and LBL-3. The ^{249}Cf metal produced from these sources has behaved similarly in all treatments. On the other hand, the results obtained from Cf metal samples prepared from batch TRU-1 (the same used in Stevenson's work [6]) were inconsistent with those obtained on metal samples stemming from the other two batches and were, therefore, disregarded as being representative of only a particular batch of Cf and not of Cf itself.

All the metal samples prepared at reduction temperatures ranging from about 725°C up to the melting point exhibited a single face-centered cubic (fcc) structure characterized by an average lattice parameter of 5.75(1)Å. This phase shall be referred to as the expanded fcc form throughout this paper. A typical line list from an X-ray diffraction pattern of this form is given in Table I with the observed and calculated line intensities. These data are included here to make note of the satisfactory agreement between the observed and calculated line intensities, considering that the calculated intensities become progressively greater than the actual intensities as the diffraction angle increases because of the absence of a correction for X-ray absorption by the sample. The crystallinity of all these Cf samples was excellent, and their X-ray diffraction powder patterns often showed spotty lines due to the large crystallite size.

When the trifluoride reduction was carried out at lower temperatures, the samples exhibited a fcc structure with an average lattice parameter of

4.94(1)Å. This phase shall be referred to as the collapsed fcc form throughout this paper. With two samples, the low temperature reduction (∿600°C) was followed by a 20 min annealing in situ at ∿550°C in one atmosphere of pure helium. The diffraction data obtained from these samples showed a mixture of the collapsed fcc form and a double hexagonal closest packed (dhcp) structure with average lattice parameters of a_o = 3.39(1)Å and c_o = 11.01(5)Å.

From the lattice parameters of the various forms, metallic radii can be calculated. The results of such calculations for Cf and the two preceding actinide metals are given in Table II. The metallic radii of Cf in its dhcp and collapsed fcc forms are in accord with a smooth decrease in the atomic size with increasing Z, as expected from the actinide contraction for metals exhibiting the same structure and metallic valence. On the basis of an extrapolation of Cunningham and Wallmann's [24] relationship between the radius and valence of actinide metals, these phases correspond to trivalent metals. Our average value of the metallic radius of trivalent californium agrees reasonably well with the value of 1.733Å calculated by Sarkisov [25], assuming twelve-fold coordination and three valence electrons per atom. The metallic radius derived from the dhcp form is somewhat smaller than that calculated from the collapsed fcc form. This observation is in agreement with the corresponding radii of curium [24,26] and berkelium [27] metals.

On the other hand, the expanded fcc form of californium metal yields a metallic radius of 2.03Å, probably corresponding to californium metal with two valence electrons per atom, or divalent Cf, based on the extrapolation [24] mentioned above. Indeed, the conclusion of Nugent et al. [28], based on series correlations of thermodynamic and spectroscopic properties, was that californium metal at room temperature was close to the trivalent-to-divalent transition point but was still trivalent. The divalency of californium metal in its

high-temperature, fcc modification is in agreement with the observed high volatility and low melting point of this metal [27,8].

As a result of the apparent stability of divalent californium metal over a wide range of temperature, the higher valency forms of the metal could only be produced under low-temperature preparative conditions. In particular, the dhcp modification was only observed in mixture with the collapsed fcc form. This behavior contrasts with that of Bk [27] and Cm [26] metals, where the dhcp structure is stable over a wide range of temperature, and the fcc form is only obtained through quenching from elevated temperature. However, with Bk and Cm metals, both these metallic forms are considered to be trivalent [24].

Temperature Relationship of the Metallic Phases

To study in greater detail the phase relationship and relative stabilities, Cf metal samples were subjected to various annealing treatments. Baybarz has shown that storage in liquid nitrogen for several days of ^{244}Cm [26,29] and ^{241}Am [29] metals exhibiting their fcc forms results in their transformation into their lower temperature dhcp forms. Samples of Cf metal exhibiting the collapsed or the expanded fcc forms were stored in liquid nitrogen for a month, but no transformations were detected by subsequent X-ray analyses at room temperature.

When a Cf metal sample exhibiting the high-temperature, expanded fcc form was annealed in its preparation crucible for a few minutes at 600°C and then cooled down slowly to room temperature, it was found to have partially transformed into a contracted fcc form with a lattice parameter of 4.98(1)Å. Another metal sample exhibiting the expanded fcc form was annealed in the preparation crucible at approximately 500°C for three days. The subsequent X-ray analysis at room temperature showed no evidence for the original, expanded fcc phase but instead showed a mixture of a fcc form with a lattice parameter

of 5.00(1)Å and the collapsed fcc form (a_o = 4.94Å). On the other hand, when a Cf sample exhibiting the collapsed fcc form was put back into the reduction coil apparatus and subjected to a high-temperature (1000°C) reduction cycle followed by rapid quenching, the Cf sample was then found to exhibit the expanded fcc form (a_o = 5.75Å) together with the contracted fcc form (a_o = 4.98(1)Å) mentioned above. These experiments indicate that by annealing at moderate temperatures, the high-temperature, expanded fcc form of Cf metal transforms to an intermediate "4.98 - 5.00Å" phase and that the collapsed fcc form (a_o = 4.94Å) of Cf metal only appears after complete disappearance of the expanded form. In fact, the collapsed fcc form of Cf metal has never been observed in coexistence with the expanded fcc form. As soon as the expanded fcc form appears in a sample of the pure collapsed fcc form (quenching experiment), the "4.98 - 5.00Å" phase is also present. These observations suggest the possibility that Cf metal forms a defect structure or exhibits a mixed valence state under these conditions.

Metallic Cf samples exhibiting the expanded or collapsed fcc forms and contained in quartz capillaries were subjected to long-term annealing treatments at 350°C or 500°C. In all cases, these samples transformed after several days into a fcc form with a lattice parameter of 5.58(1)Å. Neither quenching a sample exhibiting this phase from 1000°C in the reduction system (no contact with quartz) nor annealing a similar sample for significantly longer periods of time at 500°C was successful in causing transformation into a known form of Cf metal. Therefore, it was concluded that the "5.58Å" phase was not true metal but a product of reaction of Cf metal with quartz, e.g.,

CfO_x. In fact, as mentioned before, this "5.58Å" phase was not observed following the annealing for three days at 500°C in the absence of quartz of a Cf metal sample which initially exhibited only the expanded fcc structure.

This study has shown that the higher temperature form of Cf metal, stable above approximately 725°C, is an expanded fcc form, probably corresponding to divalent metal. A collapsed fcc form is stable between about 725°C and 600°C and probably corresponds to trivalent Cf metal. At still lower temperatures, californium metal exhibits a dhcp structure in which the metallic valence is also three.

Final Comments

As a result of the existence, and possible coexistence in the same bulk sample, of two metallic valences, the californium metal system is much more complicated than the americium, curium and berkelium metal systems. It is interesting to note that cerium metal, the only lanthanide metal to exhibit more than one metallic valence, also exhibits a collapsed, fcc, low-temperature form and an expanded, fcc, higher temperature form [30]. In both Ce and Cf metals we note a decrease in the average number of conduction electrons per atom with an increase in temperature.

The interconversion of the two fcc forms of Cf metal, the good agreement between the observed and calculated X-ray diffraction intensities, and the reproducibility of our results with metal samples derived from two independently purified batches of ^{249}Cf support the validity of these phases as true Cf metal phases. Although our studies of elemental Cf are the most complete to date, and we have overcome many of the experimental difficulties

encountered by other researchers, our results still suffer from the lack of sufficient analytical data regarding both cationic and anionic impurities in our Cf metal samples. This latter problem, inherent in such microscale work, will be attacked in future studies on larger sample sizes of Cf metal. Larger samples will also allow physical property measurements such as heat of solution and magnetic susceptibility to be made. Results of the latter study would be of particular interest to elucidate the unusual, perhaps unique, metallic valence behavior of elemental Cf.

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TABLE I. Line List and Indexing for Expanded Fcc Californium Metal

hkl	2θ (deg)		Line Intensity	
	Observed[a]	Calculated[b]	Observed[a]	Calculated[c]
111	27.03	27.09	S	10.0
200	31.25	31.34	M	5.2
220	44.69	44.78	M	4.0
311	53.02	53.00	M^+	4.9
222	55.47	55.54	W	1.4
400	65.16	65.03	T	0.7
331	71.68	71.68	M^-	2.1
420	73.79	73.83	W	1.9
422	82.22	82.24	W	1.5
511	88.34	88.43	W	1.7
531	105.10	105.02	M^-	2.2
442	106.80	107.16	W	1.4
620	116.53	115.99	W^-	1.1
533	123.36	123.06	W^-	1.2
622	125.97	125.55	T	1.3
711	146.03	146.29	W	4.0
640	149.95	150.18	T	2.3

[a] A single reading (2θ values are $\pm$ 0.10°) of the powder pattern film LB 131(1) from sample LI-54. Observed intensities decrease in the order S, M^+, M, M^-, W, W^-, T.

[b] Based on a_o = 5.7534Å and λ = 1.54178Å with a Nelson-Riley extrapolation correction.

[c] Calculated using the intensity program POWD [22] with all temperature coefficients taken as zero, no absorption correction, and scaled such that the most intense line has I = 10.0.

TABLE II. Calculated Metallic Radii in Å of Curium, Berkelium, and Californium

Metal	Crystal Form		Reference
	dhcp[a]	fcc[b]	
Cm	1.74_4	1.78_2	[24],[26]
Bk	1.70_4	1.76_7	[27]
Cf	1.69	1.75 (collapsed) 2.03 (expanded)	This work

[a] Radius = $1/4\ a_o + 1/4\ [a_o^2/3 + c_o^2/16]^{1/2}$.

[b] Radius = $a_o/2.828$.

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[13] Emission spectrographic analysis (performed in the Nuclear Chemistry Division, LBL) of 8 μg of the ^{249}Cf showed the presence of 0.03 μg Mg, $\leq$0.01 μg Ca, <0.01 μg Al, and <0.01 μg Fe.

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