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Authors

Marei, S.A.

Cunningham, B.B.

Publication Date

1971-07-01

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MAGNETIC MEASUREMENTS OF CURIUM METAL, CmF_3 , AND CmOCl *

S. A. Marei[†] and B. B. Cunningham^{††}

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

July 1971

ABSTRACT

Magnetic susceptibility measurements of curium metal in the temperature range 145°K - 550°K followed the Curie-Weiss law with an effective moment of $7.99 \pm 0.15 \mu_B$ and show the metallic valence to be approximately three. Similar measurements on tripositive curium compounds also follow the Curie-Weiss law in the temperature range 77°K - 298°K with an effective moment of $7.65 \pm 0.10 \mu_B$.

INTRODUCTION

Curium metal was first prepared by Wallman, Crane, and Cunningham [1] and the structure of a crystalline phase was later determined by Cunningham and Wallman [2]. They identified the double hexagonal close packed (dhcp) phase isostructural with α La and the dhcp form of americium [3]. From a consideration of the ionic radius of curium metal they proposed the metallic valence to be +3 in contradiction to the empirical correlation of metallic radius vs metallic valence proposed by Zachariasen, which extrapolated to a metallic valence of +3.8 for curium [4]. Subsequently Smith, Hale, and Thompson [5] measured the vapor pressure of curium metal and reported a new high temperature, face centered cubic phase to which they assigned a +4 metallic valence. In this paper we report magnetic susceptibility measurements on curium metal in the temperature range 77°K - 550°K which support the proposed metallic valence of +3. We also include magnetic measurements of the curium compounds $\text{CmF}_3 \cdot 1/2 \text{H}_2\text{O}$, CmOCl , and 5.6 mole % CmF_3 diluted in LaF_3 .

EXPERIMENTAL

A. Sample Preparation

Curium metal was prepared by the method of Cunningham and Wallman [2]. Four samples were used for the magnetic susceptibility measurements. Spectrographic emission analysis showed no impurities at a level that would significantly effect the magnetic moment. Analysis of one sample by ^3He activation analysis showed the presence of ~ 4000 ppm of oxygen. Table 1 lists the physical characteristics of the metal samples. Pieces of metal sealed in quartz tubes weighing 50 to 200 μg were used for the measurements.

Curium trifluoride was prepared as described by Cunningham and Wallman [2]. The material was assumed to be hydrated by analogy with the air dried aqueous precipitates of PuF_3 [6]. Samples from 100 - 600 μg were used for the magnetic measurements.

CmOCl was prepared by heating the hydroxide at 550°C for two hours in a stream of N_2 gas bubbled through a 28% HCl solution. The curium oxychloride was identified by its x-ray diffraction powder pattern. Samples from 100 - 300 μg were used for magnetic measurements.

Lanthanum oxide (10 milligrams) was dissolved in aqueous HCl to which was added 500 μg of curium in 6M HCl . Enough aqueous HF was added to make the solution 2M in HF . The solution was centrifuged, the supernatant drawn off, and the precipitate dried. The precipitate was then heated in vacuo at 200°C . A similar procedure was used for a sample of pure LaF_3 . Magnetic measurements were made on the pure sample and were subsequently used for correcting for the diamagnetism of the LaF_3 matrix in the mixture. A small weighed part of the mixture was dissolved and assayed for curium. The results showed 5.6 mole % CmF_3 in the mixture. Samples from 200 - 600 μg were used for magnetic measurements.

B. Magnetic Susceptibility Apparatus

Susceptibility measurements were made with a modified Faraday apparatus in which the sample is suspended on a quartz fiber and placed in an inhomogeneous magnetic field. Cunningham [7] has previously described the principles of the method. For variable temperature measurements the sample was hung on the fiber inside a quartz tube which was placed inside a dewar. For low temperature measurements

various constant temperature baths were used. For measurements above room temperature the quartz tube was surrounded by a copper block which was wrapped with platinum wire. Current was passed through the wire in order to attain high temperatures. All measurements were made with $\sim 1/3$ atm He in order to attain rapid thermal equilibrium. The apparatus was calibrated using $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ as a standard [8].

RESULTS

A. Curium Metal

In figure 1 the inverse susceptibility vs T is plotted for four metal samples. One sample showed a field dependence attributed to ferromagnetic impurities and the measured susceptibility was corrected for these effects. For the temperature range 145°K - 550°K the Curie-Weiss law

$$\chi_g = \frac{C}{(T + \Delta)} \quad ,$$

is followed where χ_g is the gram susceptibility, T is the absolute temperature and Δ is Weiss constant measured in °K. However there are two noticeable features on this graph; 1) the slopes of the lines are parallel to within experimental error but there are different vertical displacements corresponding to very different Weiss constants; 2) the points at 77°K for all four samples are low.

Table 2 lists the effective moments and Δ values. If we assume the valence of curium metal is tripositive the open shell configuration would be $5f^7$, $g_J = 1.93$ and $\mu_{\text{eff}} = 7.67 \mu_B$ [9]. The measured value appears $\sim 5\%$ too high but nevertheless confirms the metallic valence as approximately 3. We are

unable to explain the large differences in Δ values from sample to sample. The high value for the susceptibility at 77°K appears real since it occurred in all four samples.

B. Curium Compounds

The measured susceptibility of all the trivalent curium compounds followed the Curie-Weiss law in the temperature range 77°K - 298°K. Table 3 lists the effective moments and calculated Landé g factors assuming the crystal field splittings are small compared to kT and the ground state is $J = 7/2$ [10,11]. The measured g value agrees with that found from electron paramagnetic resonance experiments (1.925) and its deviation from 2.00 shows the effects of strong spin-orbit coupling [9,10]. The Δ values provide a measure of the exchange interactions between curium ions and decrease with increasing magnetic dilution.

DISCUSSION

Magnetic measurements on curium metal (dhcp) have shown the metallic valence is about 3. The slightly higher measured susceptibility might be due to a conduction electron contribution. Further measurements are needed in the temperature range below 77°K in order to determine the cause of the deviation from Curie-Weiss behavior at that temperature. Measurements on the high temperature fcc phase are needed to corroborate the suggested +4 metallic valence [5].

The model of a $5f^7$ configuration with a relatively small crystal field splitting fits the measured data on the curium compounds adequately. Further measurements at lower temperatures should show deviations due to the higher crystal field levels becoming depopulated. Estimates of crystal field splittings from measurements of this kind could be obtained and compared with the lanthanide analog, Gd^{3+} . Previous work has shown that $5f^7$ splittings are at least an order of magnitude greater than in $4f^7$ compounds [10,12].

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[†] Present Address: Faculty of Science, University of Libya, P. O. Box 656, Tripoli, Libya.

^{††} Deceased.

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Table 1. PHYSICAL PROPERTIES OF CURIUM METAL SAMPLES

Sample No.	Reductant	Metal Support	X-Ray	Comments
2	Ba	Parallel W wires	No lines	Product looked good. Metal wet wires
4	Ba	Parallel W wires	No lines	Product looked dark and poor, surface not smooth, malleable
5	Ba	Parallel W wires	Good dhcp pattern	Product looked extremely shiny. Surface smooth but not melted
7	Ba	Parallel W wires	Some lines dhcp	Product looked good. Had not wet wires

Table 2. EFFECTIVE MOMENTS OF Cm METAL 145°K - 550°K

Sample	$\mu_{\text{eff}}(\mu_B)$	$\Delta(^{\circ}\text{K})$
2	8.15 ± 0.15	135
4	7.85 ± 0.1	224
5	7.96 ± 0.1	348
7	8.01 ± 0.1	286
Ave.	7.99 ± 0.15	

Table 3. EFFECTIVE MOMENTS OF Cm^{3+} COMPOUNDS $T = 77^\circ\text{K} - 298^\circ\text{K}$

Compound	Sample No.	$\mu_{\text{eff}}(\mu_B)$	$\Delta(^{\circ}\text{K})$	g_J
$\text{CmF}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$	1	7.62 ± 0.1	7	1.92 ± 0.02
	2	7.87 ± 0.1	5	1.98 ± 0.02
	3	7.63 ± 0.1	4	1.92 ± 0.02
CmOCl	1	7.53 ± 0.1	21	1.90 ± 0.02
	2	7.62 ± 0.1	24	1.92 ± 0.02
5.6 mole % CmF_3 diluted in LaF_3	1	7.66 ± 0.15	7.5	1.93 ± 0.04
	2	7.78 ± 0.15	4	1.96 ± 0.04

FIGURE CAPTION

Fig. 1. Inverse susceptibility vs T.

XBL717-3885

Fig. 1

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