

THE MAGNETIC SUSCEPTIBILITY OF ^{244}Cm METAL AND ^{249}Cf METAL*

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INTRODUCTION

Magnetic measurements on the transplutonium metals are of great importance because it is in this region of the actinide series that the metals exhibit localized magnetic behavior characteristic of the lanthanide metals [W.Nellis, 1]. Furthermore, most of the lanthanide metals exhibit complex magnetic behavior as a function of temperature which has generated many detailed theoretical and experimental studies [J.Elliott, 2]. As of this time there have been no definitive magnetic studies on the transplutonium metals.

Some of the transplutonium elements exhibit polymorphic behavior. It should be possible to correlate the chemical valences of the metals with their structural properties as determined from crystallographic studies. Such correlations have been proposed by Zachariasen [3] and been modified by Cunningham and Wallmann [4] for the first half of the actinide series. The basic assumption inherent in this model is that the f electrons in these metals are non-bonding and do not contribute to the formation of chemical bonds between metal atoms. This assumption as applied to the early actinide metals has been questioned [H.Hill,5; A.Freeman,6]. However, the model may be applicable to the transplutonium metals.

Few magnetic measurements have been reported for the transplutonium metals because of the major experimental difficulties encountered in obtaining pure, well characterized samples and the small amounts of materials available. In this paper we report a preliminary measurement on the magnetic susceptibility of ^{244}Cm metal and the first magnetic susceptibility measurements on ^{249}Cf metal.

EXPERIMENTAL

Approximately 10 mg of ^{244}Cm and 2 mg of ^{249}Cf were separated from other actinides and metal ions by conventional ion-exchange techniques. A spectrochemical analysis of the purified ^{244}Cm is shown in Table I. Emission spectrochemical analysis of one of the ^{249}Cf samples after dissolution of the metal showed no gross contamination. However, the sample submitted was on the order of 1 μg so the sensitivity was poor. The only major impurity in the ^{244}Cm sample, Si, was eliminated in the subsequent steps used to produce the metal.

The Cm metal was produced by the reduction of CmF_3 with Ba metal according to the reaction



The hydrated CmF_3 was precipitated from solution and then heated and dehydrated in a flow of anhydrous gaseous HF . The rest of the synthesis was similar to that described by Cunningham and Wallmann [4] except for two modifications. First, the

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TABLE 1. Results of the emission spectrochemical analysis on ~ 40 µg of ²⁴⁴Cm. The units are µg/sample.^a

Ac		Gd	< .05	Ra	
Ag		Ge		Rb	
Al	< 0.1	Hf		Re	
Am	< .1	Hg		Rh	
As		Hb	< .05	Ru	
At		In		S	
Au		Ir		Sb	
B		K	< 1	Sc	
Ba		La	< .01	Se	
Be		Li		Si	1
Bi	< .05	Lu		Sm	< .05
C		Mg	.03	Sr	< .1
Ca	.01	Mn	< .01	Ta	
Cb		Mo		Tb	
Cd		Na	< 1	Tc	
Ce	< .1	Nd		Te	
Cm	~ 40	Ni	< .05	Th	
Co		Np		Ti	< .01
Cr	< .01	Os		Tl	
Cs		P		Tm	
Cu		Pa		U	
Dy		Pb	< .1	V	
Er		Pd		W	
Eu		Po		Yb	< .01
Fe	< .01	Pr		Y	< .01
Fr		Pr		Zn	< .1
Ga		Pu	< 1	Zr	< .01

^aValues reported as less than a certain quantity represent the limit of detection for that element. Elements not reported were not read on the plate and were considered unlikely contaminants.

reaction was ran in an inert atmosphere box so that at no time from the reduction step to the sealing of the sample in a quartz container for magnetic susceptibility measurements was the Cm metal exposed to air. Secondly, a BaF₂ crucible was used as a reaction vessel instead of a W spiral. After the metal was formed the temperature of the Ta container was raised to ~ 1450°C so that both the Cm metal and the BaF₂ crucible were melted. The molten drop of BaF₂ was held in a Ta ring by surface tension and the Cm liquid drop was also held by surface tension in the BaF₂ liquid. In this way no contact was made between the molten metal and a

metallic container. This technique was first used by Cunningham and Dod [R.Dod, 7] in the synthesis of Pa metal.

An x-ray powder diffraction pattern was not obtained on this sample. However, the diameter of the sphere was measured as 0.30 mm with the aid of a microscope and a density of 13.2 was calculated from the empirical mass of the sample which was determined by weighing. The density obtained for the dhcp phase from the reported cell constants is 13.51.

The two ^{249}Cf metal samples were synthesized as reported elsewhere [M.Noé, 8] and characterized by x-ray powder diffraction techniques. Both samples were of the expanded fcc phase with a lattice parameter of $\sim 5.75 \text{ \AA}$. The mass of each of the samples was determined after the magnetic measurements by dissolution of the sample and subsequent alpha assay. These numbers are given in Table 2.

The apparatus used for the magnetic measurements was an improved Faraday balance of the type first suggested by Cunningham [B.Cunningham, 9] which has been described previously [R.Dod, 7]. The dewar system has been modified and the temperature was adjusted between 4.2°K - 300°K by varying the flow of cold N_2 or He gas about the sample chamber, which contained approximately one half atmosphere of He exchange gas. The temperature was monitored by a calibrated GaAs diode installed in the sample chamber less than 1 cm below the sample. The apparatus was calibrated with $\text{HgCo}(\text{SCN})_4$ [B.Figgis, 10].

Experimental Results

The magnetic susceptibility of Cm metal #5 was measured in the temperature range 140°K - 300°K. Corrections of the data for ferromagnetic impurities in the temperature range above 220°K were less than 1%, at temperatures between 140°K - 220°K the corrections were between 1% - 4%. The sample followed the Curie-Weiss equation

$$\chi_M = \frac{C}{T + \Delta}$$

as shown in Fig. 1. The data are tabulated in Table 2.

TABLE 2. Results of the magnetic measurements.

Sample	Phase	Mass (μg)	ν_{eff} (m)	Δ (°K)	T (°K)
^{244}Cm #5	dhcp	186	6.0	-72.2	140 - 300
^{249}Cf (LI-48A)	fcc	8.85	9.84	- 3.24	28 - 298
^{249}Cf (LI-54)	fcc	5.64	9.67	3.00	22 - 298

The magnetic susceptibility of the first Cf sample, LI-48A, was measured in the temperature range 28°K - 298°K. The second Cf sample, LI-54, was studied in the temperature range 22°K - 298°K. In both samples corrections for ferromagnetic impurities were negligible. A graph of the reciprocal deflections of the sample and container at various field strengths vs. temperature is shown in Fig. 2 for one of the samples. Both samples followed the Curie-Weiss equation and the results for LI-48A are shown in Fig. 3. The results for the two samples are tabulated in Table 2.

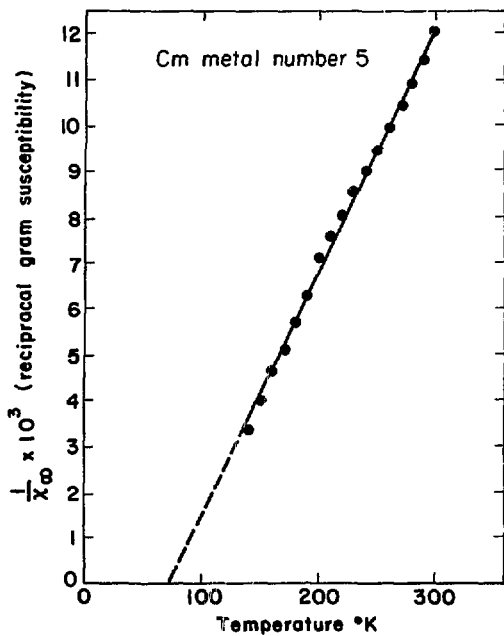


Fig. 1. Reciprocal gram susceptibility vs temperature for ^{244}Cm metal.

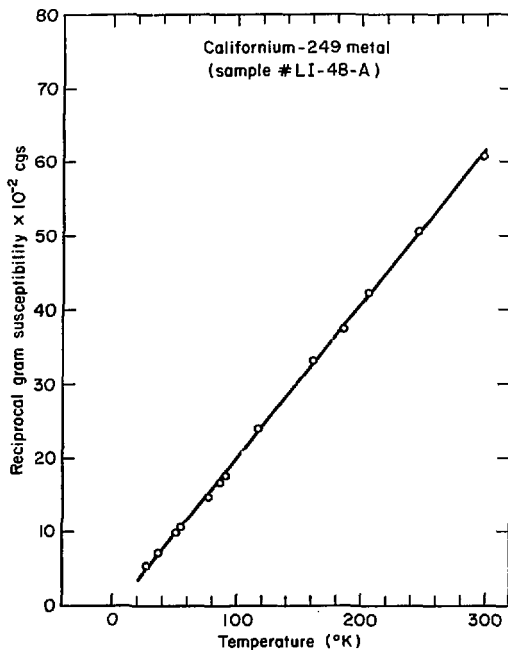


Fig. 3. Reciprocal gram susceptibility vs temperature for ^{249}Cf metal.

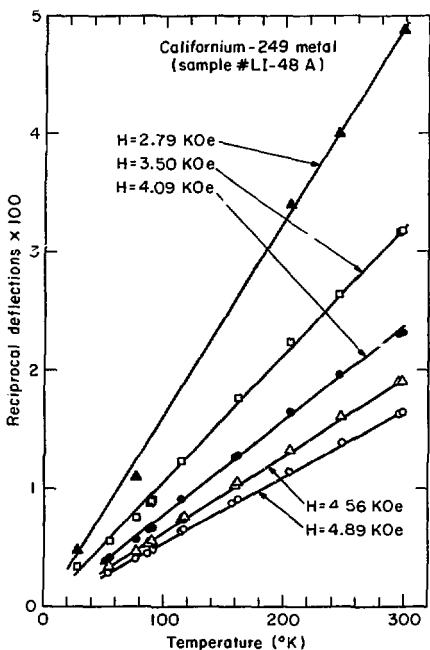


Fig. 2. Reciprocal deflections vs temperature for ^{249}Cf metal.

DISCUSSION

The expected valence state for Cm metal is Cm^{3+} , $5f^7$. The ion has the *free configuration*, $5f^7$ and has been extensively studied when diluted in various ionic crystals. The Landé g value for the ground $J=7/2$ state was measured to be 1.95 [N.Edelstein,11]. We may then calculate a $\mu_{eff} = 7.66$ BM. This calculated value is approximately 25% greater than the measured value given in Table 2. An earlier paper reported much better agreement with the calculated value [S.Marei, 12]. Another possibility, Cm^{2+} , would have the $J=0$ state lowest and be expected to show a temperature independent susceptibility. The high value for L , the Weiss constant, indicates the possibility of magnetic ordering at lower temperatures. Such magnetic ordering has been reported for one sample of Cm metal [J.Fournier,15]. More experiments are necessary to check our low value of the effective moment and to investigate further the magnetic ordering.

The two likely valence states for Cf metal are $5f^{10}$, Cf^{+2} , or $5f^9$, Cf^{3+} . We may estimate the free ion Landé g values for the ground term, including the effects of spin orbit coupling, and then calculate the effective free ion moments for Cf^{2+} , $J=8$, $\mu_{eff} = 10.22$ BM; and Cf^{3+} , $J=15/2$, $\mu_{eff} = 10.18$ BM. The experimental values agree within the experimental error which we estimate as less than 5%. The calculated μ_{eff} is about 4% higher than the experimental value for which we have no explanation. It is unfortunate that for this particular case the magnetic susceptibility measurements do not differentiate between the dipositive and tripositive ions. Nevertheless, it is of great interest to determine if the other phases of Cf metal exhibit the same type of behavior.

CONCLUSION

We have reported here the first magnetic susceptibility measurements on the expanded fcc phase of ^{248}Cf metal. Further measurements are needed on other Cf metal phases. Another measurement of the magnetic susceptibility of ^{248}Cm metal in a limited temperature range has been reported. The result does not agree with previously reported values. Further work is continuing on the synthesis of ^{248}Cm metal and ^{248}Cm metal and magnetic measurements on these samples.

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