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THE MAGNETIC SUSCEPTIBILITIES OF SOME COMPOUNDS OF AMERICIUM AND CURIUM

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ABSTRACT

The molar magnetic susceptibility of CmF_3 has been found to be -22,500 ± 4000 c.g.s. units in an environment at 295°K. and -58,000 ± 6000 in an environment at 77°K. The temperatures of the samples were probably significantly higher because of the self-heating caused by radioactivity of the isotope Cm^{242}.

The susceptibility of CmF_3 is in agreement within experimental error of that expected theoretically for a $5f^7$ configuration.

The susceptibility of AmF_3, corrected for diamagnetic contributions, was found to be 1040 ± 300, 1290 ± 300 and 1740 ± 300 at temperatures of 295, 199 and 77°K., respectively.

The susceptibility of AmF_3, and its temperature dependence, is in agreement with a $5f^6$ configuration for Am^{+3} and a multiplet splitting between the $^7F_0$ and $^7F_1$ states comparable to kT, but smaller than in the case of europium (III).

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The magnetic susceptibilities of the aqueous ions of Np(VI), Np(V), Np(IV), Pu(IV), Pu(III), and Am(III) have been measured by Howland and Calvin,[1] who suggest possible low energy states to account for the experimental susceptibilities. The measurements of Howland and Calvin were made at room temperature only.

In the present investigation, the magnetic susceptibilities of some solid compounds of americium and curium[2] have been measured at room temperature and at lower temperatures down to 77°K. In the case of curium compounds, a novel complication existed because of the intense radioactivity of the isotope[2] Cm^{242}. An energy release of 1.2×10^{-4} watts per microgram is converted mainly to heat within the samples which are thus maintained at temperatures substantially higher than that of the surroundings.

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(1) Howland and Calvin, J. Phys. Chem., in press.

(2) The curium used in this work consisted mainly of the isotope Cm^{242}. The production, separation and purification of this isotope is described by Werner and Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 22.5 (McGraw-Hill Book Co., Inc., New York, 1949).

EXPERIMENTAL

Apparatus

The susceptibility measurements were made by a modification of the Faraday method, using mainly the apparatus shown in Fig. 1.

The sample, mounted in a thin quartz tube of about 1 mm. I.D. and 6 mm. in length, was suspended by a thin quartz fiber attached to the free end of the beam of the balance.[3] Sample and balance were surrounded by protecting tubes of pyrex

(3) The construction and operation of balances of this kind have been described by Cunningham, Nucleonics, 5, No. 5, 62 (1949).

glass as shown in the figure. The front end of the horizontal 4 cm. diameter tube was provided with an aluminum disk closure, with a central opening covered with a thin mica window through which the pointer attached to the free end of the balance could be observed with a microscope. The end closure was sealed to the tube with Gelva wax.

A stopcock ("A" of Fig. 1) attached to the back permitted evacuation and the assembled apparatus was vacuum tight.

Temperature control was achieved by surrounding the vertical tube in which the sample was suspended by a small dewar filled with a suitable refrigerant.

The microscope provided a magnification of about 200 diameters, and by the use of a filar micrometer it was possible to read the position of the pointer to about $\pm 0.3\ \mu$. Since the sensitivity of the balance was about 1 cm./mg., this corresponded to a sensibility, or limit of precision of reading, of about $\pm 0.03\ \mu g$.

The microscope was attached to the arm of a simple rack-and-pinion manipulator for convenience in focusing and adjustment.

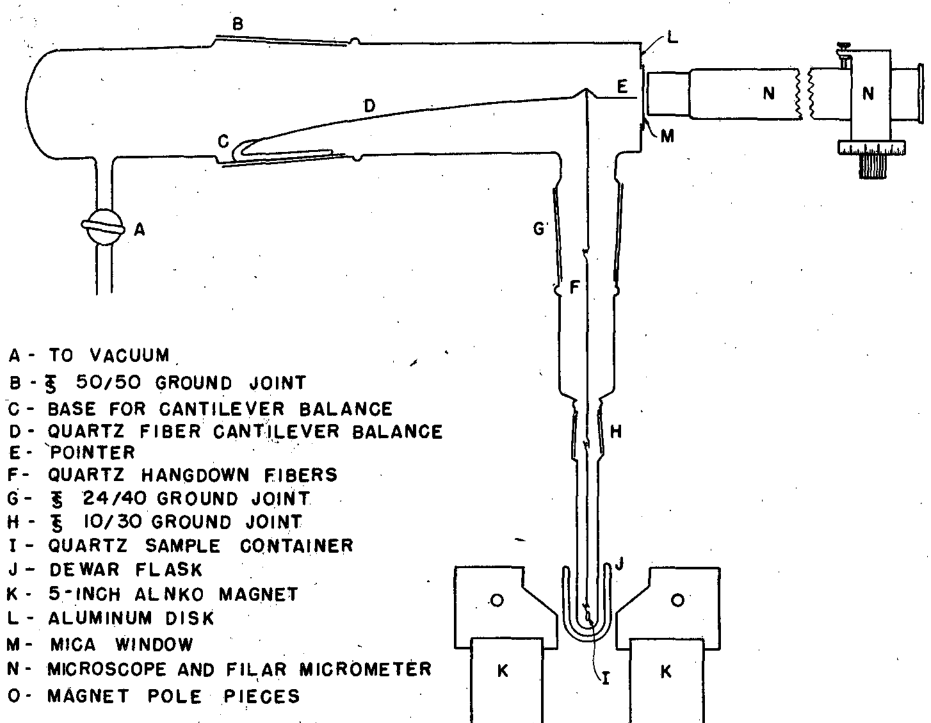

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FIG. I

MAGNETIC SUSCEPTIBILITY APPARATUS

The susceptibility apparatus and microscope were mounted on a single heavy wooden frame, beneath which a 5-inch "alnico No. 5" permanent magnet could be slid in and out along a heavy brass track. The entire apparatus was placed in a box, provided with windows and glove ports, in which the experimental measurements could be made without undue risk of radioactive contamination.

The magnet was provided with pole pieces ("O" of Fig. 1), specially cut to produce a region of pronounced but relatively constant field gradient. The product of field by field gradient in our experimental region was about 3×10^5 $(\text{oersteds})^2/\text{cm}$.

Measurements

Our measurements are relative and depend upon previous calibration with samples of known susceptibility. We have used reagent grade $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ for which we take χ to be 29.45×10^{-6} c.g.s. units at 298°K. as our primary standard. A sample of spectroscopically pure gadolinium fluoride was used as a secondary standard. The gram susceptibility of this material was found to be 115×10^{-6} c.g.s. units, by comparison with ferrous ammonium sulfate.

Since the force exerted on a sample in an inhomogeneous magnetic field varies as the product $H \frac{dH}{dX}$, a portion of the field in the experimental region was explored in preliminary measurements with gadolinium fluoride. It was found that the pull on the sample varied by less than 7% per mm. of vertical displacement. In all subsequent measurements the position of the sample in the field was reproduced to within a few tenths of a millimeter as shown by observation with a cathetometer.

Ore samples, except those of curium, were weighed to within a few tenths of a percent on a torsion microgram balance similar to that described by Kirk, Craig, Gullberg, and Boyer.[4] The samples of curium were assayed radiometrically

(4) Kirk, Craig, Gullberg, and Boyer, Anal. Chem., 19, 427 (1947).

to within ±5% both by alpha-counting and by x-ray counting. Corrections for the diamagnetism of the quartz sample tubes were usually determined directly, but in a few cases were computed from the known weights of the tubes.

A summary of our experimental data is given in Table I.

Table I

Magnetic Susceptibilities of the Trifluorides of Gadolinium, Americium, and Curium

Sample	Wt. of sample (μg)	T (^{o}K.)	M (c.g.s. units x 10^6)	$\chi_M T$
GdF_3	95.8	295[a]	24,800 ± 1000 (R if standard)	7.31
GdF_3	95.8	77[a]	98,600 ± 2000	7.60
CmF_3	24	295	19,000 ± 6000	5.60
CmF_3	31	295	26,000 ± 5000	7.67
CmF_3	31	77	58,000 ± 6000	4.46
AmF_3	910	295	1040 ± 300[b]	0.27
AmF_3	910	199	1290 ± 300[b]	0.23
AmF_3	910	77	1740 ± 300[b]	0.12

[a] Temperature of the environment. The temperature of the sample may have been appreciably different. See discussion.
[b] Corrected for the diamagnetism of the fluoride and an estimated diamagnetism of -0.5 for Am^{+3}.

The values of $\chi_M T$ for GdF_3 at 295° and 77°K. agree within the error of the measurements and are consistent with previous observations[5] that the

(5) Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N.Y., 1943.

Δ value for solid compounds of gadolinium is very small.

Because of the smaller quantities of curium used and its smaller gram susceptibility, the deflections measured were much less than in the case of gadolinium; the error of measurement is proportionally larger.

Our mean value of χ_M (298°K.) = 22,500 ± 4000 x 10^{-6} c.g.s. units for CmF_3 is in reasonable agreement with the value 26,000 calculated from the theoretical relation:

$$\chi_M = \frac{Ng^2\beta^2J(J+1)}{3kT} + N\alpha$$

if we adopt the configuration $5f^7$ for Cm^{+3}, in agreement with the actinide concept, and assume that Russel-Saunders coupling provides a satisfactory description of the electron interactions. The term $N\alpha$ then has the value zero, and the susceptibility would be expected to have no temperature-independent component other than that due to the Heisenberg exchange interaction.

The apparently large temperature independent component observed for CmF_3 probably is quite unrelated to its magnetic properties, but is due to the self-heating of the samples produced by their radioactive disintegration. In order to avoid the creation of thermal air currents which disturbed the measurements at low temperatures, all measurements were made at low pressure. Under these conditions the thermal exchange between the sample and its surroundings was poor, and the steady state temperature differences might be expected to be appreciable. Unfortunately, it was not possible to determine the temperatures of the samples directly.

The magnetic susceptibility measurements on AmF_3 are in agreement with the actinide concept,[6] if we assume that the multiplet splitting of the low lying

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(6) Seaborg, Nucleonics 5, no. 5, 16 (1949).

terms $^7F_0$ and $^7F_1$ is comparable to kT. The situation is analogous to that which exists for Eu^{+3} except that the lower susceptibility indicates a greater splitting as might be expected because of the higher effective charge of Am^{+3}.

Qualitatively, the temperature function of the susceptibility would be expected to show a resemblance to that of Eu^{+3}. The temperature independent component should be smaller however, and the total susceptibility less than that of Eu^{+3} at all temperatures. A consequence to be expected from a smaller $N\alpha$ term is an increased slope in the χ_M-T relationship. By comparison with the data given in Selwood[5] we find that our experimental data are entirely in agreement with these expectations, and in agreement with the configuration $5f^6$ for Am^{+3}.

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