Magnetic susceptibility of californium fluorides

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Results of magnetic measurements are presented for polycrystalline samples of CfF_3 (both the hexagonal-LaF_3-type and orthorhombic-YF_3-type crystal structures) and CfF_4 (monoclinic-UF_4-type). Measurements were performed at temperatures between 4.2 and 340 K and in magnetic fields of up to 50 kG. The effective paramagnetic moments, μ_{eff}, and the Weiss constants, Θ_P, have been determined in the Curie-Weiss temperature region (150–340 K). In the trifluorides no significant differences in μ_{eff} and Θ_P were observed as a function of crystal structure or sample age (radiation damage). For the tetrafluoride, two distinct sets of values for μ_{eff} and Θ_P were obtained depending on the sample age. Antiferromagnetic ordering was observed in both Cf compounds at temperatures below 12 K. Crystal-field effects were evident in the temperature range between about 12 and 150 K. The calculated susceptibilities for these compounds are presented and discussed.

I. INTRODUCTION

Magnetic measurements have been made previously on several californium oxide[1] and trichloride compounds.[23] As part of a program to investigate the magnetic properties of ionic compounds of heavy actinides and to determine the sensitivity of these properties to crystal fields, we have extended these measurements to the californium fluorides, CfF_3 and CfF_4. The californium fluorides studied here consisted of polycrystalline samples of CfF_3 (hexagonal and orthorhombic) and CfF_4, and were studied at the temperatures between 4.2 and 340 K and in fields up to 50 kG. CfF_3 crystallizes in both the LaF_3-type hexagonal and YF_3-type orthorhombic crystal forms.[4] In the hexagonal form (space group $P\bar{3}c1$) the actual site symmetry of the Cf ion is C_2, but it can be approximated as D_{3h} with a different choice of z axis. In the orthorhombic form (space group $Pnma$) the Cf site symmetry is C_s. The tetrafluoride has UF_4-type monoclinic symmetry[5] (space group $C2/c$) with two distinct Cf sites of approximate D_{4d} symmetry but different symmetry axes. In addition, we have looked closely at the effects of defects and/or chemical changes caused by self-irradiation fields of the samples. The results of these studies are reported here.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The californium-249 ($t_{1/2} = 345$ yr) was obtained as the β decay product of berkelium-249, which was synthesized in the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory. The CfF_3 samples were prepared by precipitation from a 0.1-mol/dm^3 HCl solution of trivalent californium with aqueous hydrogen fluoride and by thermal decomposition of anhydrous CfF_4. The CfF_4 was obtained by fluorination (F_2) of CfF_3 or Cf_2O_3 in sapphire or Ni dishes at 300–400 °C for 48 h followed by a programmed cooling cycle in F_2. The resulting products were loaded into fused silica capillaries in a He-atmosphere glove box. The microscale chemical procedures have been reported elsewhere.[6] The Cf samples had masses ranging from 30 to 90 μg. Sample masses were determined either by comparing the 388 keV γ-ray count rate of the samples with the count rate of a standard or by direct weighing.

B. Magnetic measurements

The susceptibility measurements were performed in a micromagnetic susceptometer employing a SQUID (Superconducting Quantum Interference Device) that was constructed specifically for use on radioactive samples with masses in the range of 1 μg to 1 mg.[7] A superconducting magnet provided applied magnetic fields of up to 50 kG and the sample temperature could be varied between 4.2 and 340 K.

In a typical measuring situation the quartz capillary containing the sample was placed inside a sapphire tube along with a second empty quartz capillary that acted as a blank. The latter established a means for correcting the sample's signal for contributions from the quartz. A gold wire fused into the end of the sapphire tube provided a thermal connection between the sample holder and the temperature sensors. The sample was moved back and forth through two oppositely wound flux-sensing coils

TABLE I. Summary of the polycrystalline Cf fluoride samples.

Sample	Crystal structure	Age (days)	μ_{eff} (μ_B) T > 150 K	μ_{eff} (μ_B) T < 150 K	Θ_P (K) T > 150 K	Θ_P (K) T < 150 K	Comments[a]
CfF$_3$ (No. 2)	ortho	2	10.1	9.6	14	8.3	5.8±0.6 K
CfF$_3$ (No. 3)	ortho	13	10.2	9.9	20	7.5	
CfF$_3$ (No. 3a)	ortho	15	10.2	9.9	20	7.5	No. 3 annealed 10.0±0.6 K
CfF$_3$ (No. 3b)	hex	28	10.3		19		No. 3a converted to hex, 7.3±1 K
CfF$_4$ (No. 1)	mono	1	9.0	8.4	35	20	
CfF$_4$ (No. 1a)	mono	35	9.1		32		10.0±1.2 K
CfF$_4$ (No. 2)	mono	1	9.4	8.6	51	20	
CfF$_4$ (No. 2a)	mono	13	9.0	8.7	27	20	
CfF$_4$ (No. 2b)	mono	23	9.2		33		8.7±0.9 K
CfF$_4$ (No. 3)	mono	2	9.4		54		10.4±1.2 K

[a]A temperature entry in this column indicates that a maximum in the magnetic susceptibility was observed at this temperature. Otherwise no maximum was observed.

that are part of a superconducting circuit monitored by the SQUID.

III. RESULTS AND DISCUSSION

The results of the magnetic measurements of the CfF$_3$ and CfF$_4$ samples are summarized in Table I.

A. Paramagnetic behavior

The polycrystalline susceptibilities of CfF$_3$ and CfF$_4$ exhibit Curie-Weiss behavior, ie., $\chi_M = N_A \mu_{eff}^2 / 3k(T + \Theta_p)$, at temperatures from 150 to 340 K. The experimental values for μ_{eff} and Θ_p listed in Table I were determined from a linear least-square fit to the inverse susceptibility versus temperature data. Figures 1 and 2 show the plots of such data for representative samples of CfF$_3$ (orthorhombic) and CfF$_4$, respectively. Theoretical values for μ_{eff} were determined using an intermediate-coupling model with a spin-orbit coupling constant and Slater integrals, as determined by Carnall et al.[8,9] to give a best fit to optical absorption data. Californium in the 3+ charge state (nominally the f^9 electronic configuration) has a theoretical μ_{eff} of 10.2μ_B, whereas in the 4+ charge state (nominally the f^8 configuration) it has a theoretical μ_{eff} of 9.3μ_B.

Both the hexagonal and orthorhombic crystal forms of the trifluoride were studied and no significant differences were observed in the high-temperature susceptibility (> 150 K) with either age or crystal structure of the samples. The experimental effective paramagnetic moment of (10.2±0.1)μ_B for Cf^{3+} is in agreement with the intermediate coupling value for the 3+ state; the Θ_p value of 20±3 K did not vary, within the experimental uncertainty, as a function of the sample's crystal structure or age (radiation damage). However, for the tetrafluoride two distinct sets of values for μ_{eff} and Θ_p were observed depending on the sample age. Two of the three freshly prepared samples had $\mu_{eff} = 9.4±0.1\mu_B$ and $\Theta_p = 51±3$ K. The third, and the first two after aging at least two weeks, had $\mu_{eff} = 9.1±0.1\mu_B$ and $\Theta_p = 33±3$ K. The effective

paramagnetic moments for the freshly prepared CfF$_4$ were in good agreement with the intermediate-coupling value for the 4+ state.

It is found that CfF$_4$ samples stored (unsealed) in an inert-atmosphere glove box changed to crystalline CfF$_3$ in a period of a month, while those sealed in a small volume capillary containing an inert gas or vacuum became amorphous (as indicated by x-ray diffraction). Magnetic measurements indicated that in the latter case the samples remained in the tetravalent state although the slight change in values for μ_{eff} and Θ_p may indicate a change in chemical state.

B. Magnetic ordering

Both Cf compounds showed evidence of antiferromagnetic ordering at low temperatures with maxima observed
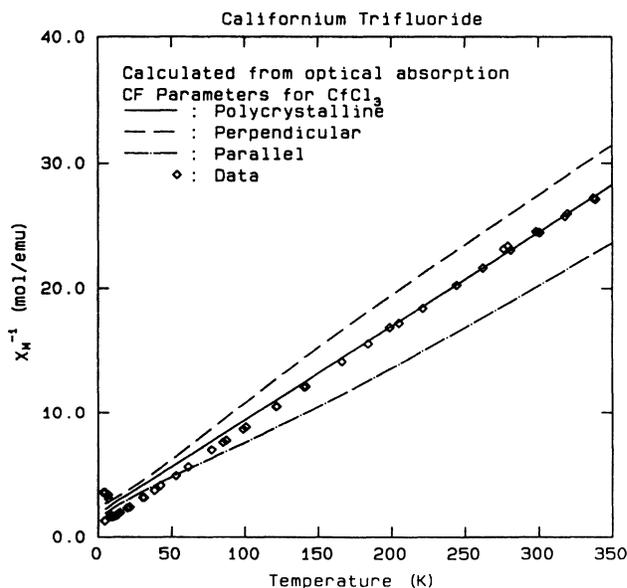

FIG. 1. Experimental and calculated inverse magnetic susceptibility of CfF$_3$ (orthorhombic) vs temperature.
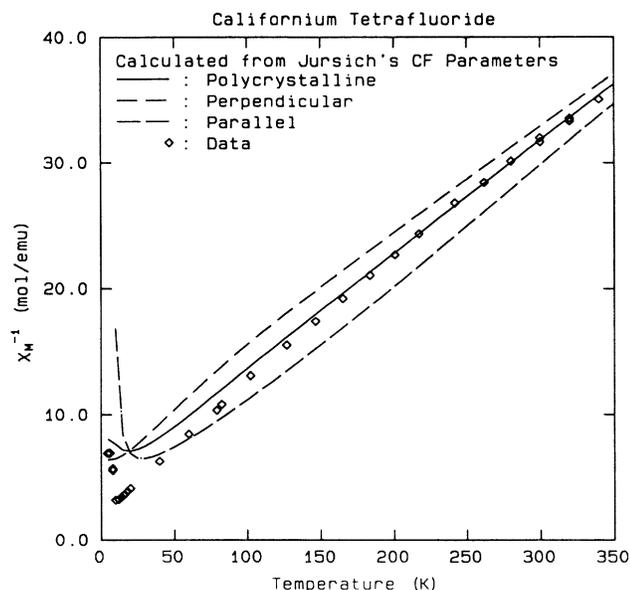
FIG. 2. Experimental and calculated inverse magnetic susceptibility of CfF_4 vs temperature.

in the susceptibility as a function of temperature. The temperatures observed for this transition in CfF_3 (6–7 K) and in CfF_4 (9–12 K) were dependent on the sample's history. In one case, although initially not observed, the transition appeared after annealing an aged trifluoride sample as shown in Fig. 3. While $CfCl_3$ exhibits metamagnetic behavior[3], neither CfF_3 nor CfF_4 shows evidence of such behavior; i.e., the disappearance of the antiferromagnetic transition at higher fields. Furthermore, unlike $CfCl_3$ for which the magnetization curve approaches saturation by 50 kG, the magnetization curves for both CfF_3 and CfF_4 at 4.2 K are still increasing at 50 kG. The antiferromagnetic transition in the CfF_3 samples indicates stronger superexchange than in the lanthanide homologue, TbF_3,[10] which has a ferromagnetic transition at 3.9 K. If the ferromagnetic dipole-dipole interactions were stronger than the antiferromagnetic superexchange interactions, then ferromagnetism would be favored as it is in terbium trifluoride. The dipole-dipole interaction is even stronger in californium trifluoride due to its larger magnetic moment and therefore the superexchange interaction must be considerably larger.

C. Crystal-field effects

Deviations from linearity in the plots of the inverse susceptibility with temperature are indicative of large

splitting of energy levels by crystal fields. For trivalent californium a study has been performed on both polycrystalline and single-crystal samples of trichlorides.[3] The magnetic results have been compared with the anisotropy in the magnetic susceptibility calculated from the optical-absorption crystal-field parameters (CFP). The polycrystalline susceptibilities of these magnetically anisotropic materials were found to be very close to the free-ion susceptibilities. The CfF_3, in analogy to $CfCl_3$, has both hexagonal and orthorhombic crystal structures. However, the susceptibility of the trifluoride was found to be less sensitive to the crystal structure than the trichloride. In the trichloride Θ_P (150 K $< T <$ 350 K) changes from 13 to 37 K in going from the hexagonal to orthorhombic form, while there was no change in the susceptibility for the trifluoride with crystal structure. In view of this difference, it is interesting to compare the extent of the orthorhombic distortion for the two compounds. The near neighbors of both hexagonal structures consist of six halides at the apices of a trigonal prism and three more beyond the midpoints of the lateral faces. In the trifluoride two more exist on the prism axis. The orthorhombic distortion involves moving one of the three halides above the faces of the prism farther away from the anion, and this displacement is significantly larger with the trichloride than with the trifluoride. Since the single-crystal x-ray structure has been determined[11] for both forms of $CfCl_3$, the bond lengths are known. One may calculate the approximate fluorine positions in the two forms of CfF_3 by using the relative positions determined for LaF_3 (Ref. 12) and YF_3 (Ref. 13) and the published[4] lattice parameters for the californium compounds, as determined from x-ray powder patterns. In the orthorhombic trichloride structure each californium has eight halide neighbors at about 2.81 Å and another at 4.01 Å, compared with eight at about 2.36 Å and the ninth at 2.52 Å in the orthorhombic trifluoride. Therefore, it is likely that the smaller orthorhombic distortion in the trifluoride makes the change in the susceptibility with crystal structure less significant.

The interpretation of the magnetic measurements for the fluorides is hampered by both the difficulty of preparing single crystals and lack of spectroscopically determined crystal-field splitting information. The magnetic susceptibility of CfF_3 is calculated using the set of CFP for $CfCl_3$, which have been determined by Carnall and Crosswhite[9] from optical absorption measurements. The calculated curves have been shifted to correspond to a molecular-field constant of 1.5 mol/emu that gives the best fit between the calculated polycrystalline curve and

TABLE II. Comparison of crystal-field parameters of Na^{3+}.

Source of parameters	Approximate site symmetry	B_0^2	B_0^4 (cm^{-1})	B_0^6	B_6^6
Nd:LaCl$_3^a$	C_{3h}	163	-366	-713	462
Nd:LaF$_3^b$	D_{3h}	201	1249	1573	809

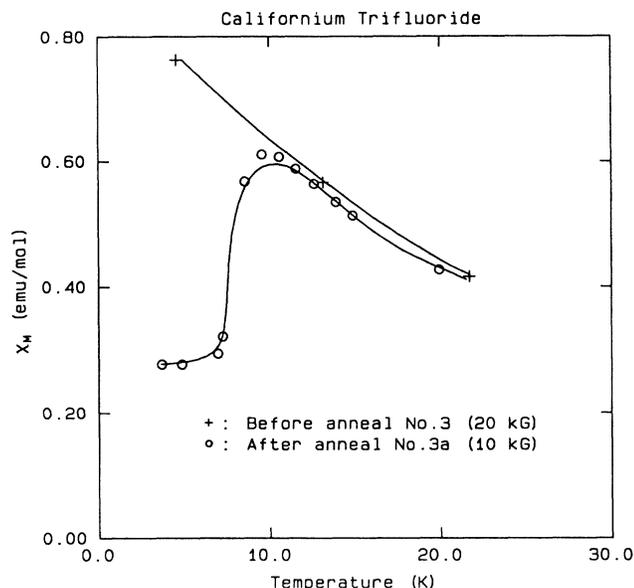[a]Reference 14.
[b]Reference 15.

FIG. 3. Magnetic susceptibility of polycrystalline CfF_3 (orthorhombic) at low temperatures.

the magnetic data and are shown in Fig. 1 for comparison to the experimental data. The lack of agreement between the experimental low temperature susceptibility and the calculated curve (see Fig. 1) means that there may be significant differences in the CFP of $CfCl_3$ and CfF_3. This is consistent with spectroscopic results for the analogous lanthanide compounds. As shown in Table II, the differences between the two sets of CFP for Nd^{3+} in $LaCl_3$ and LaF_3 are quite significant.

Jursich et al.[16] have determined the crystal-field parameters for Bk^{4+} in a CeF_4 matrix from fluorescence measurements. The susceptibility for CfF_4 was calculated using this set of CFP and assuming an approximate single, antiprismatic site symmetry (D_{4d}) for the californium ion. The results of the calculation are shown in Fig. 2, in which the calculated curves have been shifted to correspond to a molecular-field constant of 2.7

mol/emu that gives the best fit between the solid line (representing the polycrystalline susceptibility) and the magnetic data. However, it should be pointed out that there are two possible problems in using the CFP of Bk^{4+} for Cf^{4+}. In comparing the CFP of lanthanide compounds, Carnall et al.[17] have noted that there is a discontinuity in magnitude for many of them in going from f^6 to f^8 configuration. In addition, there is an indication of a set of fluorescence lines that Jursich et al.[16] attribute to a second site for the Bk^{4+}, and thus it may be inappropriate to use CFP for a single average site.

In both the trifluoride and the tetrafluoride the experimental inverse susceptibility data deviates below the calculated value at temperatures below 150 K. This may be attributed to the lack of an accurate set of CFP for these compounds. In spite of the problems with the CFP used for the calculations, the results demonstrate that there exists a region where the polycrystalline susceptibility follows an approximate Curie-Weiss Law and are important for that reason. The calculated susceptibility curves indicate the presence of substantial anisotropy in the susceptibility and, therefore, single crystals would be of help in investigating the effects of the crystal field. A better interpretation of the magnetic results for californium fluorides due to the effects of crystal fields will require further spectroscopic studies. These should include CfF_3, BkF_4, $Bk:CeF_4$, CfF_4, and $Cf:CeF_4$ to determine the existence of multiple sites and the change in the CFP as a function of the number of f electrons and bond lengths.

ACKNOWLEDGMENTS

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