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MAGNETIC SUSCEPTIBILITY OF $CfCl_3$ AND ITS DEPENDENCE ON CRYSTAL STRUCTURE

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Summary

Magnetic measurements are presented for polycrystalline samples of californium trichloride in both a hexagonal (UCl_3 type; Cf(III) C.N. = 9) and orthorhombic ($PuBr_3$ type; Cf(III) C.N. = 8) crystal form. In the Curie-Weiss temperature region the Weiss constant, θ_p, is significantly larger for the orthorhombic form. The susceptibility of the orthorhombic form deviates from Curie-Weiss behavior at a higher temperature than the hexagonal form indicating a larger crystal field splitting in the former. At temperatures below 15 K a field dependent transition is observed. In a field of 5 kG an antiferromagnetic maximum in the susceptibility is observed at 7 K and 13 K for the hexagonal and orthorhombic forms, respectively. For 30 kG both types exhibit monotonically increasing susceptibilities with lower temperature and the

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hexagonal form shows saturation behavior in the susceptibility versus temperature plots with a saturation moment of $\sim 7\ \mu_B$/atom.

1. Introduction

Magnetic measurements have been made on the californium compounds Cf_2O_3 (bcc and monoclinic forms), CfO_2 (fcc), Cf_7O_{12} (rhombohedral), and $BaCfO_3$ (perovskite structure) [1]. In a program to investigate the effects of crystal structure on the magnetic properties of ionic compounds of heavy actinides, we have extended these measurements to $CfCl_3$ in different crystal forms. $CfCl_3$ exists in both a hexagonal (UCl_3 type; Cf(III) C.N. = 9) and orthorhombic ($PuBr_3$ type; Cf(III) C.N. = 8) crystal form. Magnetic measurements have been made on polycrystalline samples of both of these forms in the temperature range 4.2–340 K and in fields up to 40 kG.

2. Experimental Methods

2.1 Sample Preparation

The californium-249 ($t_{\frac{1}{2}}$ = 351 years; alpha emitter) was obtained as the daughter in the beta-decay of berkelium-249 ($t_{\frac{1}{2}}$ = 320 days) which was synthesized in the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory. The $CfCl_3$ was obtained by hydrochlorination of small, solid chunks of CfO_{2-x} (total mass of $\sim 20\ \mu g$) in a fused silica capillary. The capillary containing the $CfCl_3$ sample under an atmosphere of ~ 76 kPa HCl gas was then flame sealed. The microscale

chemical procedures required have been described more completely elsewhere [2]. The $CfCl_3$ product in each capillary was then characterized by X-ray powder diffraction, absorption spectrophotometric analysis, and magnetic susceptibility measurements.

2.2 Crystal Form Characterization and Transformation

As described by Peterson et al. [3], it is possible to distinguish between the hexagonal (UCl_3 type) crystal form and the orthorhombic ($PuBr_3$ type) modification by room-temperature absorption spectrophotometry. Typical spectra of the two types are given in Figure 1 and were obtained using a single beam microscope-spectrophotometer described elsewhere [2]. The spectra cover the wavelength range 320-1100 nm where one sees the Laporte forbidden f-f transitions of the Cf ion. The orthorhombic form is believed to be the high-temperature form and was obtained by quenching from the melt (mp = 818 K). The hexagonal form was obtained initially as a powdered product of the low-temperature hydrochlorination process (<775 K), but conversion of the orthorhombic form to the hexagonal structure can be accomplished by annealing at a temperature near the melting point. Detection of complete transformation was greatly facilitated by the use of optical absorption spectrotometry. The transformations were carried out in the sealed capillary and allowed magnetic study of both forms using the same sample material. This leads to a more reliable determination of the effects of crystal structure on magnetic properties. After confirmation of a phase change by optical absorption the sample structure was also confirmed by X-ray powder diffraction using CuK X-rays. X-ray analysis also

indicated that the unmelted powder (hexagonal form) was microcrystalline but the melted orthorhombic and hexagonal samples were macrocrystalline.

2.3 Magnetic Measurements

The susceptibility measurements were performed in a micromagnetic susceptometer employing a SQUID (Superconducting Quantum Interference Device) [5]. A superconducting magnet provided applied magnetic fields of up to 50 kilogauss and the sample temperature was varied between 4.2 and 340 K.

The magnetic measurements were made on the samples contained in the same quartz capillary in which X-ray and spectrophotometric measurements were performed. In a typical sample holder, the quartz capillary containing the sample was placed inside a sapphire tube along with another empty quartz capillary which acted as a spacer. The sapphire tube was thermally connected to temperature sensors through a gold wire that was bonded inside one end of the tube. This arrangement is described in detail elsewhere [4].

3. Results and Discussions

The magnetic susceptibility as a function of temperature was determined for two samples with masses of 12.5 and 19.3 microgram. Each $CfCl_3$ sample was measured first in the unmelted hexagonal form (microcrystalline state), then after melting in the orthorhombic form, and finally in the hexagonal phase again (both in a macrocrystalline state due to the melting process). The magnetic results for both the

micro- and macrocrystalline hexagonal phases are in good agreement and are characterized by Curie-Weiss behavior in the range 60–340 K with deviation from this behavior at lower temperatures. Average values of 10.3 ± 0.1 μ_B and 12 ± 5 K were determined for μ_{eff} and θ_p, respectively, for the hexagonal samples in the Curie-Weiss region. The orthorhombic phase exhibits Curie-Weiss behavior in the temperature range 100-340 K; below 100 K a significant deviation from Curie-Weiss behavior was observed. For the orthorhombic phase a fit to the data in the Curie-Weiss region (100-340 K) gave average values for the samples of μ_{eff} = 10.3 ± 0.1 μ_B and θ_p = 30 ± 5 K. This described behavior is evident in the plots of the inverse susceptibility versus temperature for the two crystal forms at 5 and 30 kilogauss as given in Figure 2. The low-temperature susceptibility for both crystal forms at low field (5 kG) and at high field (30 kG) is shown in Figure 3. At low fields there is a suceptibility maximum in the range 7–13 K which is indicative of antiferromagnetism, while at high fields the susceptibility monotonically increases below ∿15 K. The hexagonal form appears to have a slightly lower antiferromagnetic transition temperature than the orthorhombic form (7 K versus 13 K). The susceptibility versus field plot for the hexagonal form at 4.2 K is shown as an inset of Figure 3 and indicates a saturation of behavior with a saturation moment of 7 μ_B/atom. This behavior which appears to be a change from antiferromagnetism at low fields to ferromagnetism at high fields is termed metamagnetism.

The paramagnetic effective moment (10.3 μ_B) determined from the data in the Curie-Weiss region is independent of the crystal phase of $CfCl_3$ and is in agreement with the free ion value for trivalent Cf ($5f^9$

configuration), as calculated based on an intermediate coupling model. A value of 10.3 μ_B was calculated for this configuration using a ground state wave function obtained from the intermediate coupling model, using Slater integrals and a spin-orbit coupling parameter as determined by Carnall et al. [5] to give a best fit to optical absorption data for $CfCl_3$.

The major distinction in the magnetic properties of the two crystal forms of $CfCl_3$ is a difference in their θ_p values. The hexagonal form gives a smaller θ_p than the orthorhombic form (12 ± 5 versus 30 ± 5 K). The reliability of the measured difference is greater due to the fact that the measurements involved the same material in different crystal forms. This difference in θ_p reflects a large difference in the susceptibility at low temperatures and, it is possible to distinguish between the two crystal forms based on susceptibility measurements. At this time, we cannot rule out the possibility that a change in θ_p may result from a preferred orientation in the macrocrystalline samples coupled with an anisotropic susceptibility. However, this seems unlikely in view of the fact that both the unmelted (microcrystalline) and melted (macrocrystalline) hexagonal samples gave comparable θ_p values. Since θ_p reflects magnetic interaction between the local moments of near-neighbor Cf(III) ions, such a sensitivity to crystal structure must indicate some superexchange coupling via the Cl^- anion. Such a model has also been proposed to explain very low temperature magnetic ordering in the rare earth trichlorides $CeCl_3$, $PrCl_3$, and $NdCl_3$ [6] which have values of θ_p less than 3 K. It is reasonable to believe

that the superexchange coupling and θ_p values would be greater in the 5f series due to the larger spatial extent of the 5f orbitals.

One may obtain an estimate of the magnitude of the crystal-field interactions by determining the temperature at which deviations from Curie-Weiss behavior become significant. For the orthorhombic form of $CfCl_3$ this occurs below ∿100 K, while for the hexagonal form it occurs below ∿60 K. Thus the crystal-field splitting appears to be larger in the orthorhombic form. This is also supported by the increase in the number of peaks in each absorption envelope of the orthorhombic form and the greater baseline width of each orthorhombic envelope versus the corresponding hexagonal envelope (see Figure 1).

The metamagnetic behavior of the low-temperature ordered state is also similar to that observed in some rare earth trichlorides (hexagonal form) [6]. In this reference it is postulated that the rare earth moments align along the c axis in a sheet structure with the sheets perpendicular to the c axis. In the antiferromagnetic state the two adjacent sheets are aligned in an opposite sense. The coupling to these sheets is postulated to be small and is overcome by modest fields to give a ferromagnetic state.

In conclusion it should be emphasized that there is an strong degree of similarity in the magnetic properties of $CfCl_3$ with those of the light rare earth trichlorides $CeCl_3$, $PrCl_3$, and $NdCl_3$. However, in contrast, the larger superexchange coupling and crystal-field interactions make $CfCl_3$ an interesting system for further study. Such study would be facilitated by measurements on single crystals and this possibility is being pursued.

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References

1. J. R. Moore, S. E. Nave, R. G. Haire, and Paul G. Huray, J. Less-Common Met., in press.
2. J. P. Young, R. G. Haire, R. L. Fellows, and J. R. Peterson, J. Radioanal. Chem. 43 (1978) 479-488.
3. J. R. Peterson, J. P. Young, D. D. Ensor, and R. G. Haire, Inorg. Chem., in press.
4. S. E. Nave and Paul G. Huray, Rev. Sci. Instrum. 51 (1980) 253.
5. W. T. Carnall, Sherman Fried, and Frank Wagner, Jr., J. of Chem. Phys., 58 (1973) 1938-1949.
6. J. C. Eisenstein, R. P. Hudson, and B. W. Mangum, Phys. Rev. A, 137 (1965) A1886-1895.