

MAGNETIC PROPERTIES OF
THE TRICHLORIDES, TRIBROMIDES, AND TRIIODIDES OF
U(III), Np(III), AND Pu(III)

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MAGNETIC PROPERTIES OF
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ABSTRACT - Magnetic susceptibilities of U^{3+} , Np^{3+} , and Pu^{3+} trichlorides, tribromides, and triiodides were measured from 2.7°K to as high as 240°K with a vibrating-sample magnetometer at applied fields up to 12 kOe. Antiferromagnetic transitions were observed in UCl_3 , $T_N = 22.0 \pm 1.0^\circ K$; in UBr_3 , $T_N = 15.0 \pm 0.5^\circ K$; in UI_3 , $T_N = 3.4 \pm 0.2^\circ K$; and in $PuCl_3$, $T_N = 4.5 \pm 0.5^\circ K$. A ferromagnetic transition at $T_C = 4.75 \pm 0.1^\circ K$ was found for PuI_3 , and a slight hysteresis was measured at 2.7°K. Temperature-independent paramagnetism was observed for $NpCl_3$ below 50°K, for α - $NpBr_3$ below 30°K, and for NpI_3 below 15°K. All these compounds, and $PuBr_3$, exhibited Curie-Weiss paramagnetism at higher temperatures, with effective moments near the free-ion moments. The experimental magnetic susceptibility of $PuCl_3$ from 10 to 100°K agrees with the susceptibility calculated from crystal field energy levels and wave functions.

INTRODUCTION

The magnetic susceptibility of UCl_3 was studied from 14 to 300°K by Handler and Hutchison,¹ who found an indication of anti-ferromagnetism at $\sim 20^\circ\text{K}$. Antiferromagnetism of UI_3 at 3.2°K was reported by Roberts and co-workers.^{2,3} Other studies of anhydrous actinide(III) halides^{4,5} have been above 77°K , where cooperative magnetic phenomena would not be expected. To explore the possibility that other actinide(III) halides might exhibit cooperative magnetic behavior at low temperatures, the magnetic susceptibilities of the chlorides, bromides, and iodides of U(III), Np(III), and Pu(III) were measured, and the results are described here. The ferromagnetic behavior of NpCl_4 ⁶ and PaCl_4 ⁷ at low temperatures was reported recently along with the temperature-independent paramagnetism of UCl_4 .⁸

EXPERIMENTAL

UCl_3 , NpCl_3 , UBr_3 , and $\alpha\text{-NpBr}_3$ were prepared by reduction of the corresponding actinide(IV) halide with zinc metal.⁹ In a typical preparation, powdered uranium tetrachloride and zinc were mixed and sealed in an evacuated glass tube. The entire tube was heated at 550 to 600°C for 16 to 20 hours, then one end of the tube was withdrawn from the furnace to allow excess zinc, zinc chloride, and unreacted uranium tetrachloride to sublime away from the uranium trichloride (UCl_3) product. For further

purification, the UCl_3 was sealed into a quartz tube and lowered at 8 mm/hr through a 950°C vertical furnace.

Plutonium trichloride (PuCl_3) was prepared by passing a stream of CCl_4 -saturated nitrogen over plutonium dioxide heated to 500 to 600°C .¹⁰ Plutonium trichloride sublimed to the cold portion of the apparatus as needle-like crystals. The PuCl_3 product and the other actinide(III) halides prepared for this study were characterized by their x-ray powder pattern and by metal analysis.

Plutonium tribromide (PuBr_3) and plutonium triiodide (PuI_3) were prepared by heating plutonium metal at 350 to 400°C with HgBr_2 and HgI_2 , respectively, in an evacuated, sealed, glass tube. The other product of the reaction, mercury metal, was sublimed from the plutonium halide by withdrawing one end of the reaction tube from the furnace. The products were further purified by sealing in an evacuated quartz tube and melting, as described in the preparation of UCl_3 .

Neptunium tribromide (NpBr_3) and neptunium triiodide (NpI_3) were prepared by the same method, except that the starting material was neptunium-aluminum alloy (30 wt % Np). AlBr_3 and AlI_3 sublimed from the reaction. The presence of oxygen was evident from the formation of trace amounts of NpOBr_2 and NpOI_2 , which were identified from x-ray diffraction patterns. Melting in quartz tubes was only partially successful in removing oxyhalide impurities, and subsequent magnetic measurements of NpBr_3 and NpI_3 were influenced by the presence of Np(IV) oxyhalides.

Magnetic susceptibilities were measured with a vibrating-sample magnetometer¹¹ at an applied field of 10 kOe in the temperature range 2.2 to 240°K. In both ferromagnetic and antiferromagnetic regions, the field dependence of the susceptibility was measured from 0.1 to 12 kOe. Details of the methods and techniques of the measurements have been previously reported.^{6,7}

RESULTS

Four compounds, UCl_3 , UBr_3 , UI_3 , and PuCl_3 , showed antiferromagnetic transitions with Néel temperatures of 22, 15, 3.4, and 4.5°K, respectively. PuI_3 has a ferromagnetic transition at 4.75°K. PuBr_3 exhibited Curie-Weiss (temperature-dependent) paramagnetism. NpCl_3 , NpBr_3 , and NpI_3 had temperature-independent paramagnetism (TIP) at low temperatures. Above their transition temperatures or regions of TIP, all compounds showed temperature-dependent paramagnetism expressed by $\chi = C/(T+\Theta)$, where C is the Curie constant and Θ is the paramagnetic Curie temperature. The magnetic data for all compounds are summarized in Table I.

Uranium Trihalides

The temperature dependence of the susceptibilities of UCl_3 and UBr_3 are shown in Figure 1, and that of UI_3 is shown in Figure 2. The characteristic maximum resulting from antiferromagnetism is apparent for all three compounds. Because earlier measurements on UCl_3 by Handler and Hutchison¹ suggested an

antiferromagnetic transition between 14 and 40°K, detailed measurements of its magnetic behavior were made in the present study. The Néel temperature for UCl_3 was determined as $22 \pm 1^\circ\text{K}$. UBr_3 had not previously been investigated in this temperature range; the results listed are the average of measurements on two samples from different preparations. Antiferromagnetic UI_3 has been previously investigated by Roberts and co-workers,^{2,3} who observed a maxima in differential susceptibility at 3.2°K , and a maxima in specific heat at 2.61°K on a single sample. Several samples of UI_3 were prepared and measured in the present study, yielding T_N values in the range from 3.2 to 3.7°K , depending on the sample purity. The sample of highest purity yielded identical maximum readings from 3.24 to 3.54°K , and $T_N = 3.4 \pm 0.2$ is assigned from these data. Measurements taken in applied fields of 1 and 10 kOe gave identical susceptibility curves.

The magnetic susceptibilities of both UCl_3 and UBr_3 follow the Curie-Weiss law above their transition temperatures, with effective moments of $3.70 \mu_B$ for UCl_3 and $3.57 \mu_B$ for UBr_3 . These values are near the value of $3.69 \mu_B$ calculated^{1,2} for the free-ion moment from

$$\mu_{\text{eff}} = g_J [J(J+1)]^{1/2}$$

where g_J is the intermediate-coupling Landé splitting factor, and for U^{3+} , g_J is equal to 0.743. For U^{3+} ions, whose ground-state

is nominally $^4I_{9/2}$, J is $9/2$. The observation of a free-ion moment above 25°K for both UCl_3 and UBr_3 indicates that the crystal field splitting is small in both compounds.

The inverse susceptibility of UI_3 (Figure 3) has two regions of constant slope on the graph of $1/\chi$ vs T above the antiferromagnetic transition temperature. From 5 to 14°K , $\mu_{\text{eff}} = 2.67 \mu_{\text{B}}$ indicating that the crystal field splitting is 10 to 15 cm^{-1} . Above 25°K , $\mu_{\text{eff}} = 3.65 \mu_{\text{B}}$, in excellent agreement with the expected value for the free-ion moment. Above 50°K , these data join smoothly with Dawson's⁴ earlier results. Crystal field splitting could be observed in UI_3 because of the low transition temperature; the antiferromagnetic regions for UCl_3 (below 22°K) and UBr_3 (below 15°K) obscure the effect of crystal field splittings in these compounds.

Neptunium Trihalides

The reciprocal magnetic susceptibilities of NpCl_3 , $\alpha\text{-NpBr}_3$, and NpI_3 are shown in Figure 4; all three compounds show a region of TIP susceptibility at low temperatures. At higher temperatures the susceptibility of NpCl_3 becomes temperature-dependent with an effective moment of $2.81 \mu_{\text{B}}$. Using the intermediate-coupling $g_J = 0.646$,¹² the free-ion moment is calculated to be $2.89 \mu_{\text{B}}$. The agreement between the experimental moment and the calculated moment indicates a small crystal field splitting for NpCl_3 , and is consistent with the results for UCl_3 .

The data for NpBr_3 and NpI_3 are affected by impurities present in the samples. X-ray diffraction data indicate that a small amount

of NpOBr_2 was present in the NpBr_3 samples and that an NpOI_2 impurity was present in the NpI_3 samples. Repeated attempts to purify both compounds succeeded only in reducing their impurity level. The low-temperature departure from TIP in the $\alpha\text{-NpBr}_3$ magnetic data varied from sample to sample and was reduced in the purer samples, and therefore is attributed to the NpOBr_2 impurity. The larger moment of Np^{4+} ions, compared to Np^{3+} ions, had a serious effect on both NpBr_3 and NpI_3 results; because of the Np^{4+} impurities, neither compound showed the free-ion moment for Np^{3+} expected at higher temperatures.

Plutonium Trihalides

The inverse magnetic susceptibilities of PuCl_3 , PuBr_3 , and PuI_3 are shown in Figures 5, 6, and 7. The inverse susceptibility of PuCl_3 has a minimum at 4.5°K resulting from antiferromagnetic behavior and above 10°K shows normal Curie-Weiss paramagnetism with $\mu_{\text{eff}}=1.11 \mu_{\text{B}}$. This value agrees closely with the free-ion moment of $1.25 \mu_{\text{B}}$ calculated using an intermediate-coupling g_J of 0.421, obtained from the 28-term Pu^{3+} wave function of Edelstein, et al.,¹³ and indicates that crystal field splitting is small. The magnetic susceptibilities from these measurements join smoothly with earlier measurements between 90 and 600°K.⁵

The inverse susceptibility of PuBr_3 has two regions of normal Curie-Weiss paramagnetism, but no cooperative effects were observed above 2.2°K. From 2.2 to 20°K, $\mu_{\text{eff}}=0.81 \mu_{\text{B}}$, and from 20 to 60°K,

$\mu_{\text{eff}}=1.01 \mu_{\text{B}}$, in fair agreement with the free-ion moment.

The magnetic susceptibility of PuI_3 shows normal Curie-Weiss paramagnetism from 5 to 50°K, with $\mu_{\text{eff}}=0.88 \mu_{\text{B}}$, a value that is somewhat less than the free-ion moment. At 4.75°K, a ferromagnetic transition was observed (Figure 8). The field dependence of the specific magnetization of PuI_3 is shown in Figure 9 for several temperatures between 3.2 and 10.85°K. Above 8°K, the susceptibility is independent of the field as indicated by the linear relationship between the specific magnetization (σ) and the field (H). As the temperature is decreased below 8°K, this relationship (between σ and H) deviates more and more from linearity.

The magnetization isotherms of PuI_3 do not extrapolate to zero with zero applied field, even above 5°K, and the initial rise in magnetization for the first 100 Oe of applied field is exceptionally large. A slight hysteresis was observed at 2.72°K (Figure 10). The detailed behavior between +100 Oe and -100 Oe is lost because of the inability to control the applied field in this range.

Two methods were used to locate the Curie temperature of PuI_3 . In the region immediately below the transition temperature, the small-argument expansion of the Brillouin function yields¹⁴ an equation in which the square of the specific magnetization is proportional to temperature and vanishes at $T = T_{\text{C}}$. Thus, the intercept of the line at zero magnetization gives the Curie temperature as seen in Figure 11, in which the intersection of the lines with the temperature axis determines the Curie temperature as 4.75°K.

A second method for determining the Curie temperature is shown in the right half of Figure 11, where the applied field is plotted as a function of temperature for constant values of the magnetization obtained from the data of Figure 9. Usually the lines of constant magnetization converge at a common temperature for $H = 0$ and thus define the Curie temperature. For PuI_3 , the extrapolated lines converge only for an indicated negative magnetic field of 1 kOe. The convergence occurs at 4.75°K , giving the same Curie temperature as the other technique; the agreement between the two methods confirms the determination of the T_c .

DISCUSSION

The actinide(III) chlorides, bromides, and iodides have either the UCl_3 or PuBr_3 crystal structures.¹⁵ In the UCl_3 structure, the metal ion is coordinated with nine nearly equidistant chloride ions, arranged as a tricapped trigonal prism around the metal ion. UCl_3 , NpCl_3 , PuCl_3 , UBr_3 , and $\alpha\text{-NpBr}_3$ have this structure; the minimum metal ion to metal ion distance is about 4.3\AA for the chlorides and 4.4\AA for the bromides. The PuBr_3 structure is a lattice-layer structure in which the Pu^{3+} ion is 8-coordinated. UI_3 , NpI_3 , and PuI_3 also have the PuBr_3 structure. The minimum metal-ion to metal-ion distance is about 5.0\AA for PuBr_3 , and 5.4\AA for the three iodides.

In a qualitative assessment of the factors that lead to cooperative magnetic phenomena - ferromagnetism or antiferromagnetism -

electronic factors appear to be of major importance, crystal field splitting and metal-ion to metal-ion distance are of secondary importance, and the detailed structure of the crystal appears to be a minor factor. With a single exception, cooperative magnetic phenomena were found for the two ions with half-integer values of J , U^{3+} ($J=9/2$) and Pu^{3+} ($J=5/2$). $5f^n$ ions with half-integer J values necessarily have a magnetically degenerate lowest crystal field level (Kramers doublet), and thus will have a finite magnetic moment at low temperatures. Magnetic ordering can occur at temperatures sufficiently low that the exchange energy is greater than the thermal energy of the lattice. For Np^{3+} ($J=4$), the crystal field splitting leads to a singlet ground level which is magnetically inactive.¹⁶ Cooperative magnetic phenomena may also occur for ions of integer J values with a multiplet lowest state split by the crystal field, such as in uranium dioxide ($T_N=29^\circ K$).¹⁷

The exchange energy necessary for cooperative magnetic effects normally is considered to arise from metal ion -- anion -- metal ion (M-A-M) interactions, as the metal ion to metal ion distances are too large for direct interaction. M-A-M interactions will vary in strength with distance and the nature of the different ions. To some extent, M-A-M interactions parallel the changes in strength of the crystal field, and distinguishing between exchange energy and crystal field effects obviously is not entirely possible.

For the U^{3+} compounds, the decreasing temperatures of their antiferromagnetic transitions is consistent both with increasing

M-A-M distance and with less effective M-A-M interactions as the larger, less electronegative bromide and iodide ions serve as the exchanging anions. For the Pu^{3+} halides, the lower temperatures for a magnetic transition can be ascribed to the difference between $J=5/2$ and $J=9/2$. The antiferromagnetic transition for PuCl_3 at 4.5°K and a possible transition for PuBr_3 below 2°K are consistent with the results on U^{3+} halides. The ferromagnetic transition at 4.75°K for PuI_3 appears anomalous, compared with UI_3 , as crystal structure and ion distances are essentially the same for both UI_3 and PuI_3 . The difference in behavior is ascribed to a stronger interaction between Pu^{3+} and iodide ions than between U^{3+} and iodide ions. The contribution from the Pu^{3+} ion is tentatively assigned major responsibility.

The crystal field splitting of the ground states of Pu^{3+} and U^{3+} is small, as evidenced by the free ion moment for these compounds in the paramagnetic region immediately above the region of magnetic ordering. Considering PuCl_3 in detail, the C_{3h} crystal field splits the $J=5/2$ ground state of Pu^{3+} into three Kramers doublets. For PuCl_3 , the energies and wave functions of the crystal field levels are known from optical studies¹⁸ and are shown in Figure 12. From these eigenvalues and eigenfunctions a theoretical susceptibility can be calculated using the Van Vleck formalism:

$$\chi_{\parallel} = \frac{N(g_J)^2 (\mu_B)^2 y}{4hc} \left[\frac{1 + 9 \exp(-13y) + 25 \exp(-76y)}{1 + \exp(-13y) + \exp(-76y)} \right]$$

$$\chi_{\perp} = \frac{N(g_J)^2 (\mu_B)^2}{4hc} \left[\frac{(9y/2 + (16/13) - (16/13 - 10/63) \exp(-13y))}{1 + \exp(-13y) + \exp(-76y)} - \frac{(10/63) \exp(-76y)}{1 + \exp(-13y) + \exp(-76y)} \right]$$

where $y = hc/k_B T$. For a powdered sample, the average susceptibility is given by:

$$\chi_{av} = (\chi_{\parallel} + 2\chi_{\perp})/3$$

The susceptibility calculated in this manner is compared with experimental data for PuCl_3 in Figure 13 (solid curve). Theory and experiment agree up to about 100°K . At higher temperatures, the fit is improved (dashed curve) by including a small TIP contribution (approximately 236×10^{-6} emu/mole) from the $J=7/2$ state centered near 3200 cm^{-1} .

Second- and fourth-order crystal field parameters for PuCl_3 can be calculated from the known eigenvalues and eigenfunctions, using the operator-equivalent factors α and β given by Edelstein, et al.,¹³ giving

$$A_2^0 \langle r^2 \rangle = 97.6 \text{ cm}^{-1}; \quad B_0^2 = 195 \text{ cm}^{-1}$$

$$A_2^0 \langle r^4 \rangle = 127 \text{ cm}^{-1}; \quad B_0^4 = 1020 \text{ cm}^{-1}$$

Compared with crystal field parameters for C_{3h} rare-earth trichlorides,¹⁹ B_0^2 has about the same magnitude, but B_0^4 is approximately four times larger than the corresponding rare-earth values.

For $NpCl_3$ and $\alpha-NpBr_3$, the low symmetry of the crystal field splits the $J=4$ ground state into 3 singlet and 3 doublet levels;²⁰ for NpI_3 , the crystal field splits the ground state into 5 singlets and 2 doublets. The TIP behavior of the three Np^{3+} halides at low temperatures results from the interaction of a singlet ground level with some higher level, probably a singlet of the same character. The temperature of the transition from TIP to Curie-Weiss paramagnetism can be taken as a measure of the spacing of the crystal field splitting of the ground state. These temperatures (50, 30, and 15°K, for $NpCl_3$, $NpBr_3$, and NpI_3 , respectively) qualitatively conform to the expected decrease in the strength of the crystal field with an increase in Np^{3+} -halide ion distance. The decrease in electronegativity for the halides also could lead to the same trend; however, the increasing distance between the ions is judged to be the paramount factor.

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TABLE I. Magnetic susceptibility constants.

Compound	Temperature range (°K)	C^a (emu-deg mole ⁻¹)	θ^a (°K)	μ_{eff} (μ_B)	T_N (°K)	χ_{TIP} (10^{-6} emu/mole)
UCl ₃	25-117	1.70	89	3.70±0.08	22.0±1.0	-
UBr ₃	25-76	1.56	54	3.57±0.08	15.0±0.5	-
UI ₃	5-14	0.89	9.1	2.67±0.10	3.4±0.2	-
	25-200 ^b	1.66	34	3.65±0.05	-	-
NpCl ₃	3.5-50	-	-	-	-	6400±100
	75-240	0.99	83.5	2.81±0.09	-	-
α -NpBr ₃ ^c	10-30	-	-	-	-	10850±320
	50-125	1.33	86	3.26±0.40	-	-
NpI ₃ ^d	3-15	-	-	-	-	17000±7000
	25-60	1.26	42	3.17±0.40	-	-
PuCl ₃	5-100	0.16	7.9	1.11±0.04	4.5±0.5	-
PuBr ₃	2.2-20	0.082	0.55	0.81±0.08	-	-
	25-60	0.127	10.5	1.01±0.10	-	-
PuI ₃	5-50	0.097	-4.15	0.88±0.08	4.75±0.10 ^e	-

a. Constants from Curie-Weiss law, $\chi = C/(T+\theta)$.

b. Combined with data from Reference 4.

c. Contains NpOBr₂ impurity.

d. Estimated to contain 5% NpOI₂ impurity.

e. T_C listed for ferromagnetic PuI₃.

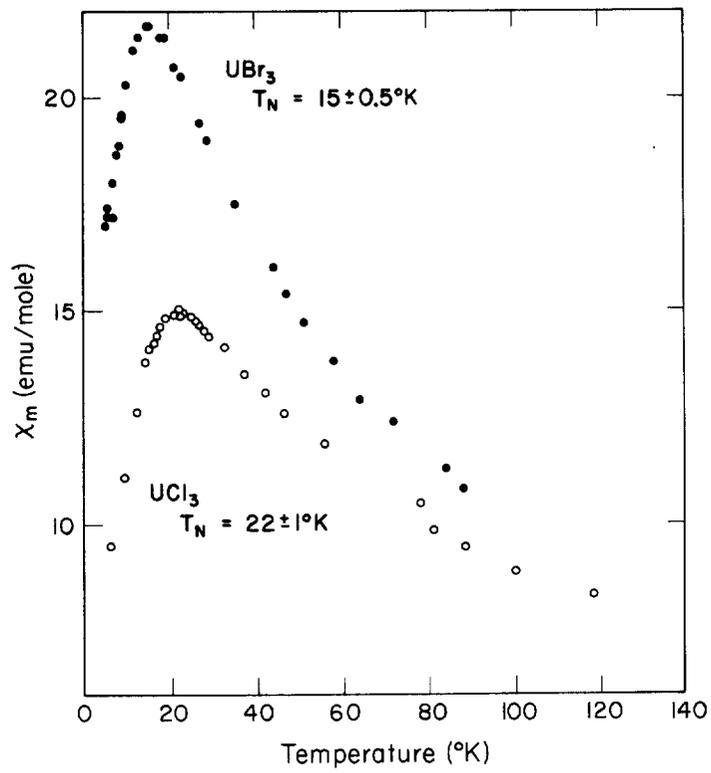


FIGURE 1. MAGNETIC SUSCEPTIBILITIES OF UCl_3 AND UBr_3

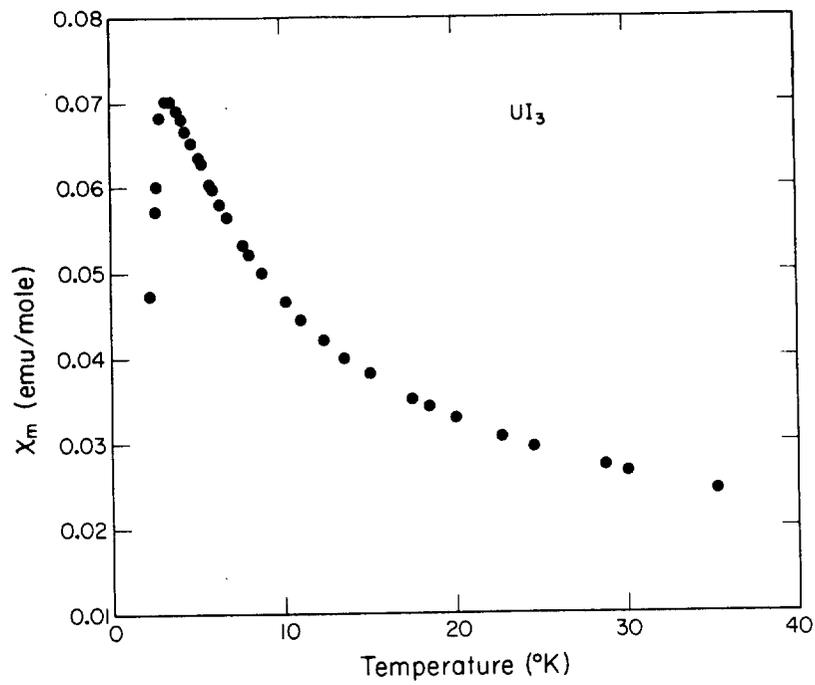


FIGURE 2. MAGNETIC SUSCEPTIBILITY OF UI_3

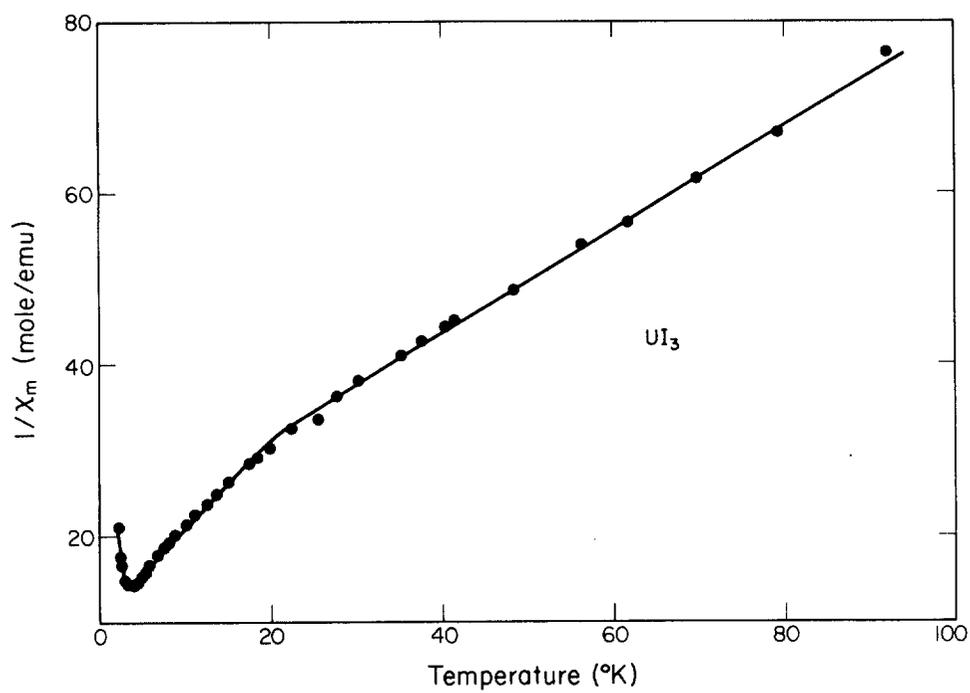


FIGURE 3. INVERSE MAGNETIC SUSCEPTIBILITY OF UI_3

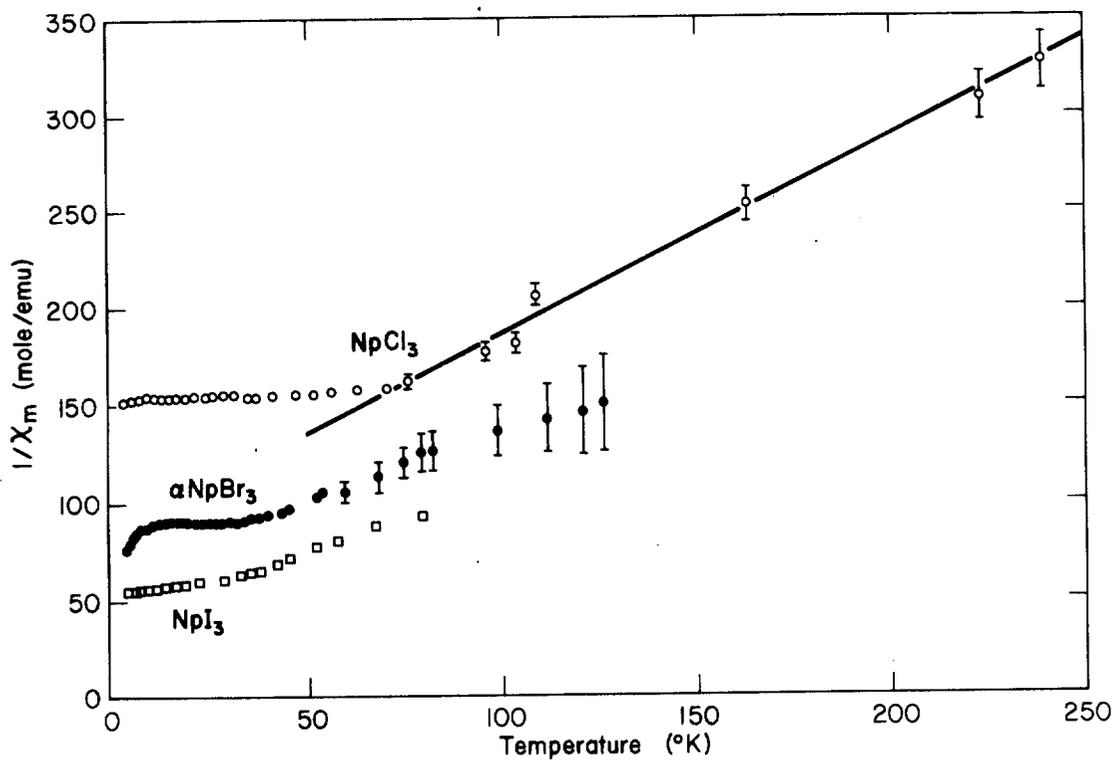


FIGURE 4. INVERSE MAGNETIC SUSCEPTIBILITIES FOR $NpCl_3$, $NpBr_3$, AND NpI_3 .
The straight line gives $\mu_{eff}=2.81 \mu_B$ for $NpCl_3$.

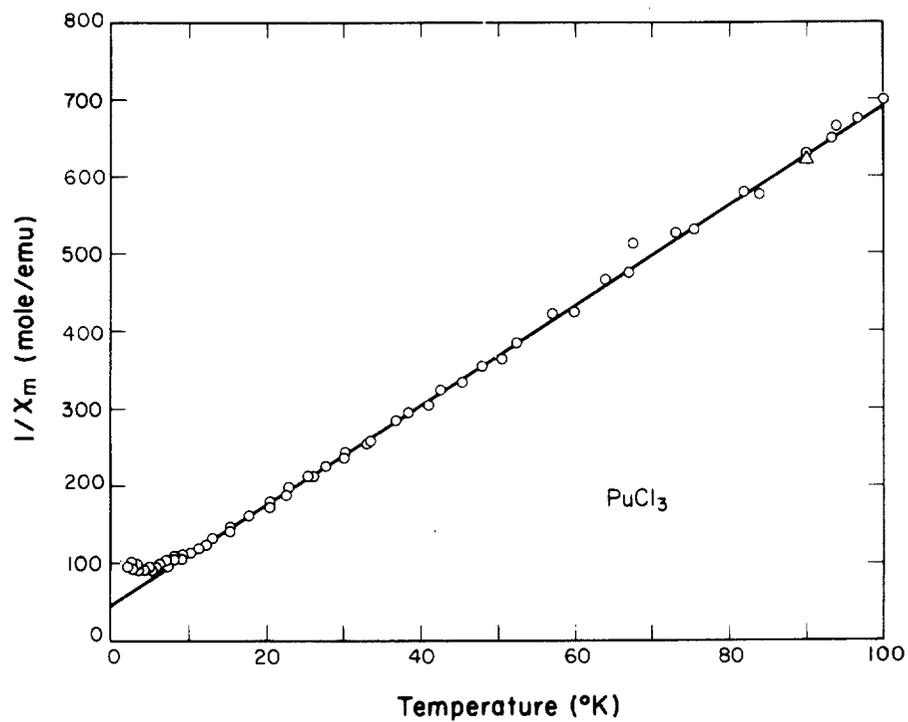


FIGURE 5. INVERSE MAGNETIC SUSCEPTIBILITY OF PuCl₃

The solid line corresponds to the Curie-Weiss law, with $\mu_{eff} = 1.11 \mu_B$. o, this work; Δ , from Reference 5.

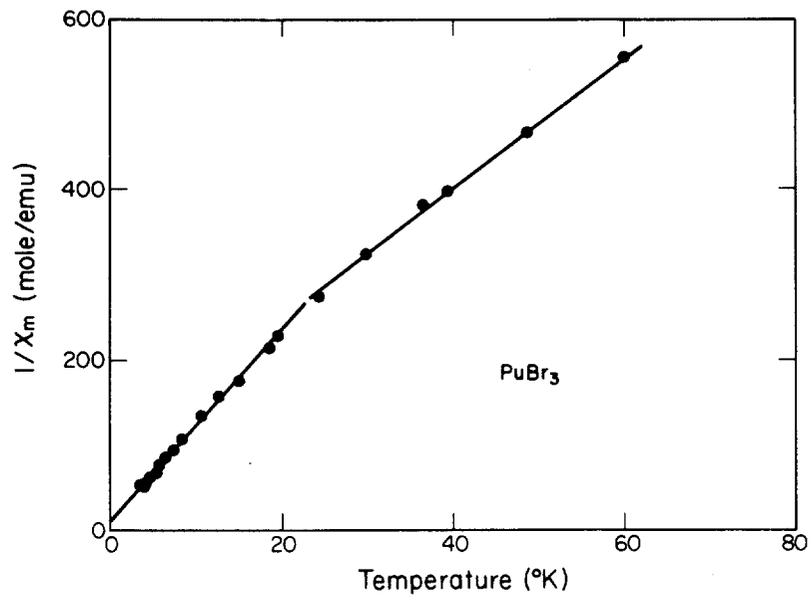


FIGURE 6. INVERSE MAGNETIC SUSCEPTIBILITY OF PuBr_3

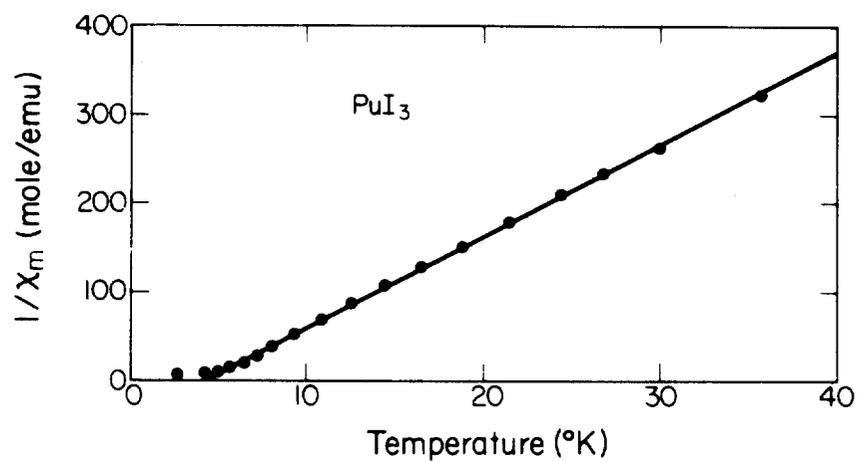


FIGURE 7. INVERSE MAGNETIC SUSCEPTIBILITY OF PuI₃

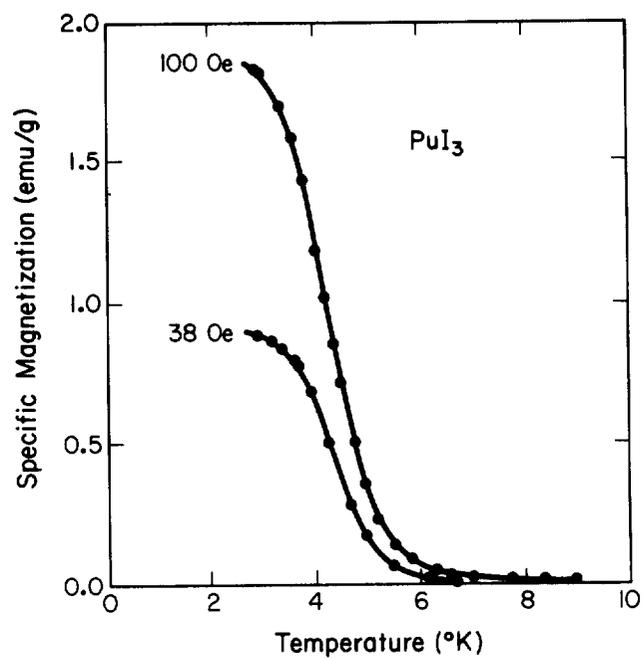


FIGURE 8. SPECIFIC MAGNETIZATION VERSUS TEMPERATURE FOR PuI₃

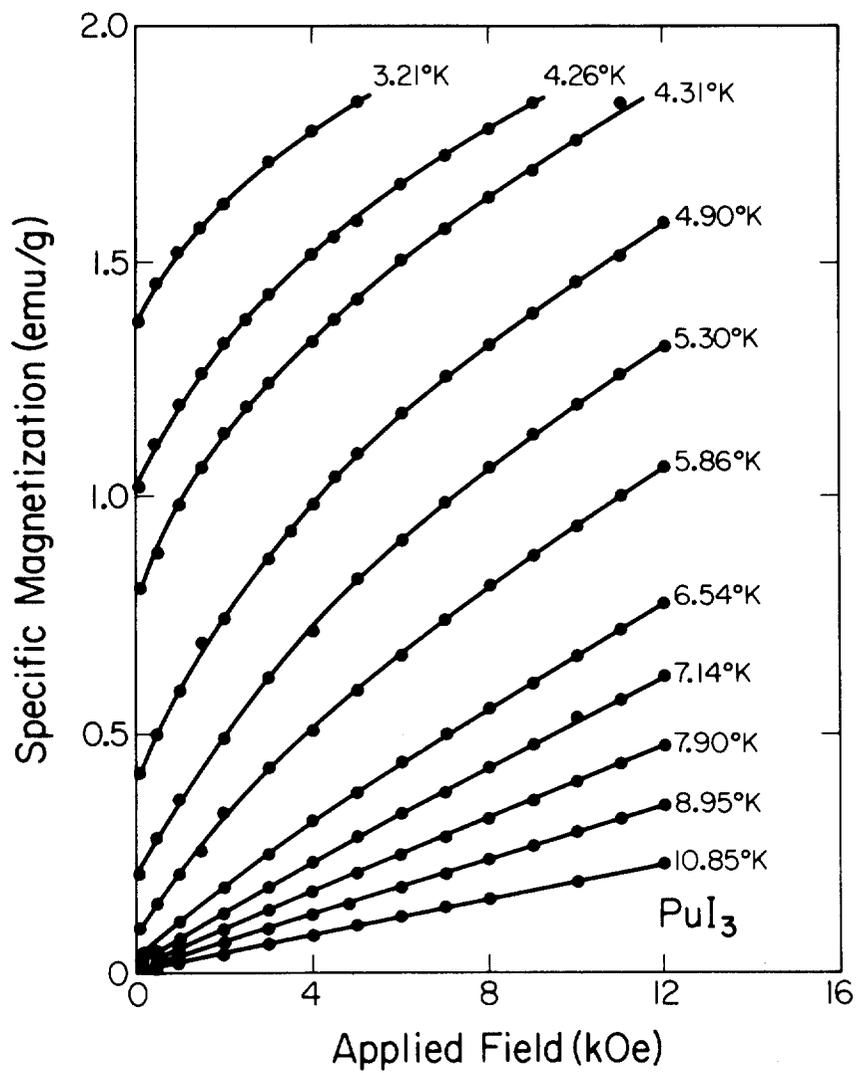


FIGURE 9. MAGNETIZATION ISOTHERMS FOR PuI₃

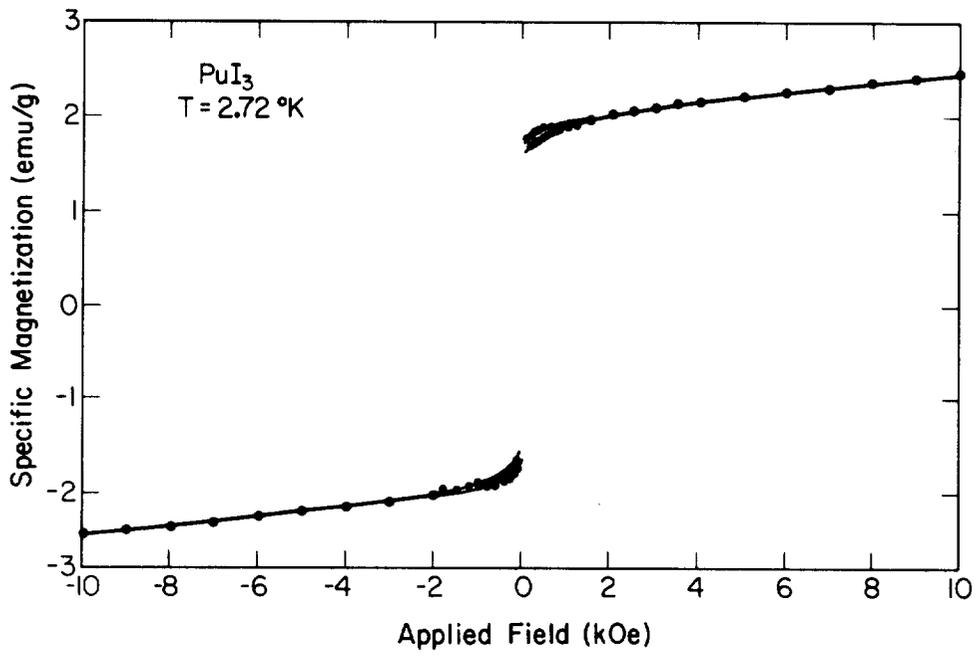


FIGURE 10. HYSTERESIS EFFECT IN PuI₃

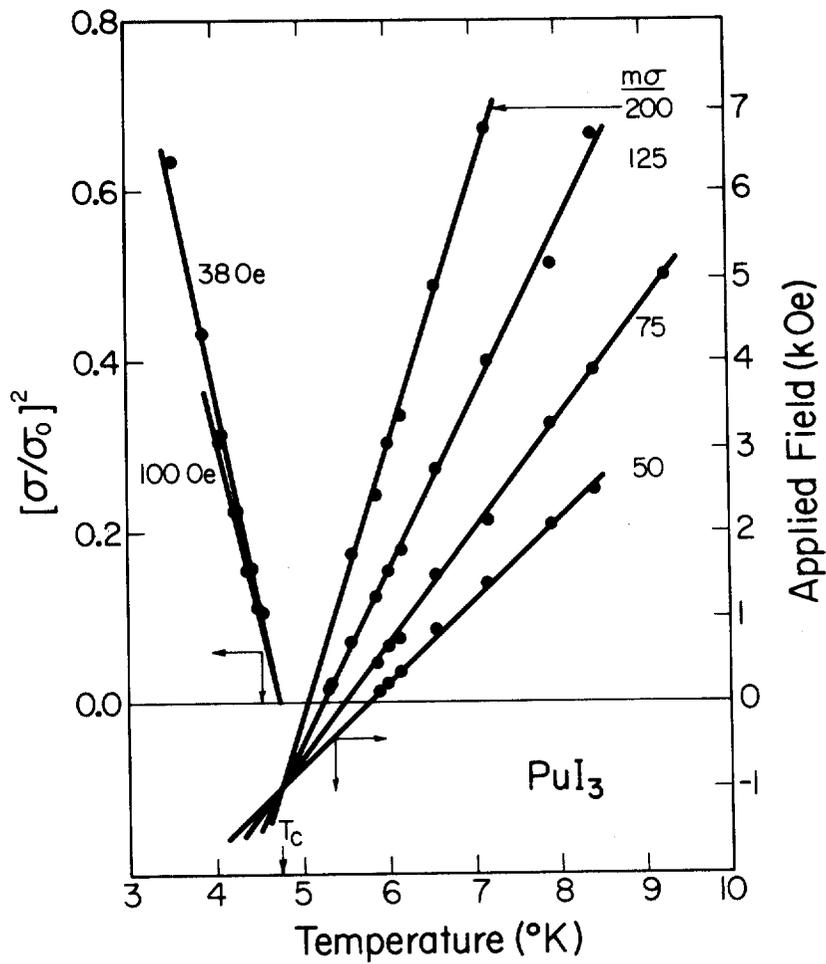


FIGURE 11. DETERMINATION OF CURIE POINT OF PuI_3

Data at 38 and 100 Oe refer to left ordinate, as explained in text. Lines of constant magnetization ($m\sigma$) refer to the right ordinate.

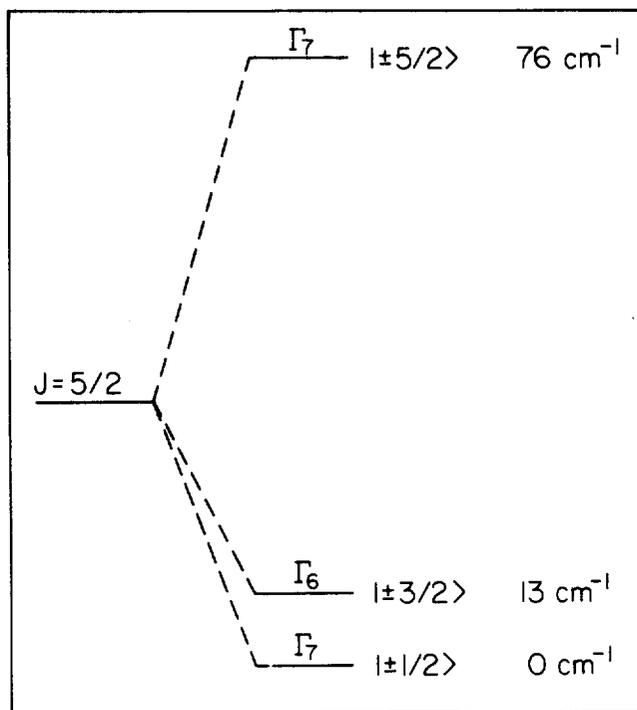


FIGURE 12. CRYSTAL FIELD LEVELS OF Pu^{3+} in PuCl_3

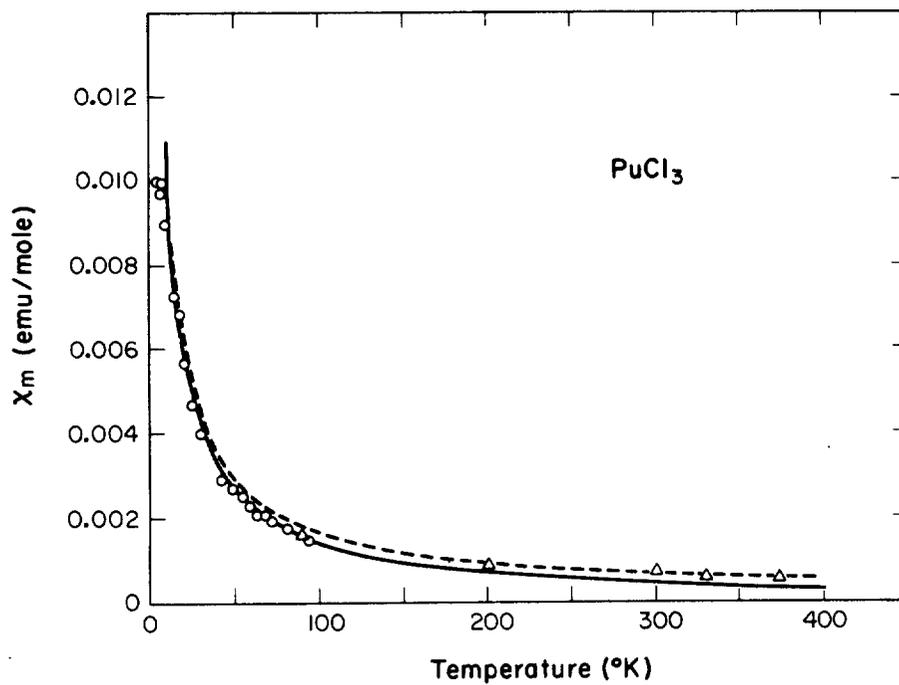


FIGURE 13. MAGNETIC SUSCEPTIBILITY OF PuCl_3

o, this work; Δ , Ref. 5. The solid curve gives the calculated susceptibility, considering only the crystal-field levels of the ground state. The dashed curve includes a correction for the temperature-dependent paramagnetism of the $J=7/2$ first-excited state.