DP-MS-71-84

Conf- 720353--1

MAGNETIC PROPERTIES OF
UCl_3, UBr_3, $NpCl_3$, $NpBr_3$, AND $PuCl_3$

by

E. R. Jones, Jr. and M. E. Hendricks

Department of Physics and Astronomy
University of South Carolina
Columbia, South Carolina 29208

and

J. A. Stone and D. G. Karraker

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina 29801

To be presented at the March Meeting of the

American Physical Society

Atlantic City, N. J.

March 27-30, 1972

2/21/72

MASTER

MAGNETIC PROPERTIES OF UCl_3, UBr_3, $NpCl_3$, $NpBr_3$, AND $PuCl_3$*

by

E. R. Jones, Jr.[†] and M. E. Hendricks[‡]

Department of Physics and Astronomy
University of South Carolina
Columbia, South Carolina 29208

and

J. A. Stone and D. G. Karraker

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, South Carolina 29801

ABSTRACT

Magnetic susceptibilities of the isostructural compounds UCl_3, UBr_3, $NpCl_3$, α-$NpBr_3$, and $PuCl_3$ were measured from 3 to 100°K (nominal), with a vibrating-sample magnetometer at applied fields up to 12 000 Oe. U^{3+}, Np^{3+}, and Pu^{3+} have C_{3h} site symmetry in these compounds. Antiferromagnetic transitions were observed in UCl_3, $T_N=22.0 \pm 1.0$°K; in UBr_3, $T_N=20.0\pm 1.0$°K; and in $PuCl_3$, $T_N=4.5\pm 0.5$°K. Temperature-independent paramagnetism was observed in $NpCl_3$ below 50°K, and in α-$NpBr_3$ below 30°K. Each of the compounds exhibited Curie-Weiss behavior at higher temperatures, with effective moments closely approximating the free-ion moments. For $PuCl_3$, the experimental susceptibility from 10 to 100°K is in excellent agreement with values calculated from known crystal-field energy levels and wavefunctions.

2/21/72

INTRODUCTION

Magnetic susceptibility studies of a number of anhydrous actinide halide compounds have been reported,[1-9] mostly for temperatures above 77°K. As part of a study of the magnetic properties of actinide halides at lower temperatures, the magnetic susceptibilities of $NpCl_4$ and $PaCl_4$ were reported recently.[10,11] In this paper, low-temperature measurements of the magnetic susceptibilities of UCl_3, UBr_3, $NpCl_3$, α-$NpBr_3$, and $PuCl_3$ are described; for $PuCl_3$, calculations of the theoretical susceptibility are presented. The compounds are isostructural,[12] with the metal ion in a site of C_{3h} symmetry. The trivalent actinide ions are surrounded by nine ligands at nearly equal distances; there are three nearest neighbors and six others at slightly greater distances from the central ion.

EXPERIMENTAL

UCl_3, $NpCl_3$, UBr_3, and α-$NpBr_3$ were prepared by reduction of the corresponding actinide(IV) halide with zinc metal.[13] In a typical preparation, powdered UCl_4 and Zn were mixed and sealed in an evacuated Pyrex* tube. The entire tube was heated at 550-600°C for 16-20 hours, and then one end of the tube was withdrawn from the furnace to allow excess Zn, $ZnCl_2$, and unreacted UCl_4 to sublime away from the UCl_3 product. For further purification, the UCl_3 was

---

* Trademark of Corning Glass Works, Corning, N.Y.

sealed into a quartz tube and lowered at 8 mm/hr through a 950°C vertical furnace.

$PuCl_3$ was prepared by passing a stream of CCl_4-saturated nitrogen over PuO_2 heated to 500-600°C.[14] $PuCl_3$ 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) was characterized by its X-ray powder pattern by metal analysis.

Magnetic susceptibilities were measured with a vibrating-sample magnetometer[15] at an applied field of 10 000 Oe in the temperature range from 3 to approximately 100°K. For $PuCl_3$, the field dependence of the susceptibility was measured from 100 to 12 000 Oe. Details of the measurement technique have been given previously.[11]

RESULTS AND DISCUSSION

Magnetic susceptibility data for the trivalent actinide halides studied are shown in Slide 1. For three of the compounds, UCl_3, UBr_3, and $PuCl_3$, antiferromagnetic transitions were found, with Néel points of 22, 20, and 4.5°K, respectively. In contrast to this behavior, $NpCl_3$ and $NpBr_3$ exhibit temperature-independent paramagnetism (TIP) below about 50°K. Above their transition temperatures or regions of TIP, all of the compounds follow the Curie-Weiss law

$$\chi = C/(T+\theta)$$

where C is the Curie constant, and θ is the paramagnetic Curie temperature.

The difference in behavior of the odd-electron ions, U^{3+} ($5f^3$, J=9/2) and Pu^{3+} ($5f^5$, J=5/2), from the even-electron Np^{3+} ($5f^4$, J=4) is apparent. Because the ground states of the odd-electron ions are split into Kramers doublets by the crystal field, a finite magnetic moment exists even at low temperatures. Thus, the odd-electron actinide trihalides are expected to undergo magnetic ordering at temperatures sufficiently low that the exchange energy exceeds k_BT. For even-electron ions, the crystal-field splitting can result in a singlet ground level, which would have no magnetic moment, but which could interact with higher levels to give TIP behavior.

The temperature dependence of the susceptibilities of UCl_3 and UBr_3 is shown in Slide 2. The characteristic maximum associated with antiferromagnetism is apparent for both compounds. For UCl_3, the magnetic susceptibility was measured from 6.2 to 117.5°K, and for UBr_3 the range measured was from 2.9 to 76°K. Because earlier measurements on UCl_3 by Handler and Hutchison[2] suggested the possibility of an antiferromagnetic transition near 25°K, detailed measurements were made in the region 15-30°K to determine the magnetic behavior in this vicinity and to locate the transition temperature. The higher transition temperature for UCl_3 than for UBr_3 is consistent with the smaller unit cell[12] and shorter uranium-uranium distances in UCl_3.

Both UCl_3 and UBr_3 follow the Curie-Weiss law above their transition temperatures, with effective moments of 3.70 μ_B for

UCl_3 and 3.76 μ_B for UBr_3. These are near the theoretical value of 3.69 μ_B calculated[16] for the free-ion moment, from

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

where g_J is the intermediate-coupling Lande factor; for U^{3+}, g_J=0.743. The observation of the free-ion moment above 25°K suggests that the crystal-field splitting is small in both UCl_3 and UBr_3.

The magnetic susceptibilities of $NpCl_3$ and α-$NpBr_3$ are shown in Slide 3, plotted as reciprocal susceptibility versus temperature. For $NpCl_3$, the measurements spanned the temperature range from 3.5 to 240°K, and for α-$NpBr_3$ from 3.5 to 126°K. Both compounds display a TIP below 50°K, with the larger TIP susceptibility of α-$NpBr_3$ indicating more closely spaced crystal-field levels than $NpCl_3$. Within experimental uncertainties, the two compounds follow the Curie-Weiss law with the same effective moment, 2.81 μ_B, above 50°K. This may be compared with the free-ion moment of 2.89 μ_B, calculated[16] using the intermediate-coupling g_J =0.6457; the proximity of the experimental moment to the free-ion moment suggests small crystal-field splittings in $NpCl_3$ and α-$NpBr_3$ and is consistent with the results for UCl_3 and UBr_3.

The presence of a low-temperature TIP in $NpCl_3$ and α-$NpBr_3$ is indicative of a crystal-field singlet as the ground level. (The susceptibility of α-$NpBr_3$ deviates from TIP below 10°K; this is probably due to a small amount of paramagnetic impurity in the sample, but could be from a lower-lying level with a very small effective moment.) The crystal-field levels of Np^{3+} in isostructural $LaBr_3$ have been studied by optical spectroscopy;[17] however, the present results disagree with the optical data both as to the presence of a low-lying singlet and the magnitude of the overall crystal-field splitting. These differences between the optical and magnetic data are not fully understood, but the evidence suggests that the crystal-field parameters in the pure compound differ from those in the doped material.

The susceptibility of $PuCl_3$, measured from 2.6 to 100°K, is shown in Slide 4. The minimum in the inverse susceptibility curve at 4.5°K indicates a magnetic transition, which by analogy with isostructural UCl_3 and UBr_3 is assumed to be antiferromagnetic. The possibility of ferromagnetic ordering was eliminated by field studies below 4°K that showed no hysteresis and no saturation behavior in the field dependence of the magnetization. Although it has smaller lattice constants[12] than UCl_3, $PuCl_3$ has a lower transition temperature; this may indicate that the transition temperatures depend on J as well as the internuclear distances.

Above 10°K, $PuCl_3$ obeys the Curie-Weiss law with an effective moment of 1.11 μ_B. This value agrees closely with the free-ion moment of 1.17 μ_B calculated using an intermediate-coupling g_J=0.392, obtained from the 28-term Pu^{3+} wave function given by Edelstein, Mollet, Easley, and Mehlhorn.[18] Again, this agreement suggests small crystal-field splitting. The magnetic data for

$PuCl_3$ join smoothly to measurements between 90 and 600°K reported earlier.[5]

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 studies[19] and are shown in Slide 5. From these eigenvalues and eigenfunctions, a theoretical susceptibility can be calculated using the Van Vleck formalism[20]:

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

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

where $y = hc/k_BT$. For a powered 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 Slide 6 (solid curve). There is excellent agreement between theory and experiment 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.*,[18] giving

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

$$A_4^0\langle r^4\rangle = 127\ \text{cm}^{-1}; \qquad B_0^4 = 1020\ \text{cm}^{-1}$$

Compared with crystal-field parameters for C_{3h} rare-earth trichlorides,[21] B_0^2 has about the same magnitude, but B_0^4 is approximately four times larger than the corresponding rare-earth values.

FOOTNOTES

*The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

†Faculty Research Participant at Savannah River Laboratory, Summer, 1971.

‡AEC Special Fellow in Nuclear Science and Engineering; present address: Eisenhower College, Seneca Falls, New York.

[1] J. K. Dawson, J. Chem. Soc. 1951, 429.

[2] P. Handler and C. A. Hutchison, J. Chem. Phys. 25, 1210 (1956).

[3] L. D. Roberts, D. E. Lavalle, and R. A. Erickson, J. Chem. Phys. 22,1145 (1954).

[4] M. Berger and M. J. Sienko, Inorg. Chem. 6, 324 (1967).

[5] J. K. Dawson, C. J. Mandleberg, and D. Davies, J. Chem. Soc. 1951, 2047.

[6] R. Stoenner and N. Elliott, J. Chem. Phys. 19, 950 (1951).

[7] W. Trzebiatowski and J. Mulak, Bull. Acad. Pol. Sci., Ser. Sci. Chem. 18, 121 (1970).

[8] J. K. Dawson, J. Chem. Soc. 1952, 1882.

[9] W. B. Lewis and N. Elliott, J. Chem. Phys. 27, 904 (1957).

[10] J. A. Stone and E. R. Jones, Jr., J. Chem. Phys. 54, 1713 (1971).

[11] M. E. Hendricks, E. R. Jones, Jr., J. A. Stone, and D. G. Karraker, J. Chem. Phys. 55, 2993 (1971).

[12] W. H. Zachariasen, Acta Cryst. 1, 265 (1948).

[13] J. J. Katz and E. Rabinowitch, The Chemistry of Uranium, National Nuclear Energy Series VIII-5 (McGraw-Hill, New York, 1951), p. 452.

[14] J. J. Katz and G. T. Seaborg, The Chemistry of the Actinide Elements (Methuen, London, 1957), p. 285.

[15] S. Foner, Rev. Sci. Instr. 30, 548 (1959).

[16] M. E. Hendricks, Ph.D. Dissertation, Univ. of South Carolina, 1971.

[17] W. F. Krupke and J. B. Gruber, J. Chem. Phys. 46, 542 (1967).

[18] N. Edelstein, H. F. Mollet, W. C. Easley, and R. J. Mehlhorn, J. Chem. Phys. 51, 3281 (1969).

[19] H. Lämmermann and J. G. Conway, J. Chem. Phys. 38, 259 (1963).

[20] J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities (Oxford University Press, London, 1932).

[21] G. H. Dieke, Spectra and Energy Levels of Rare Earth Ions in Crystals (Interscience, New York, 1968), p. 149.

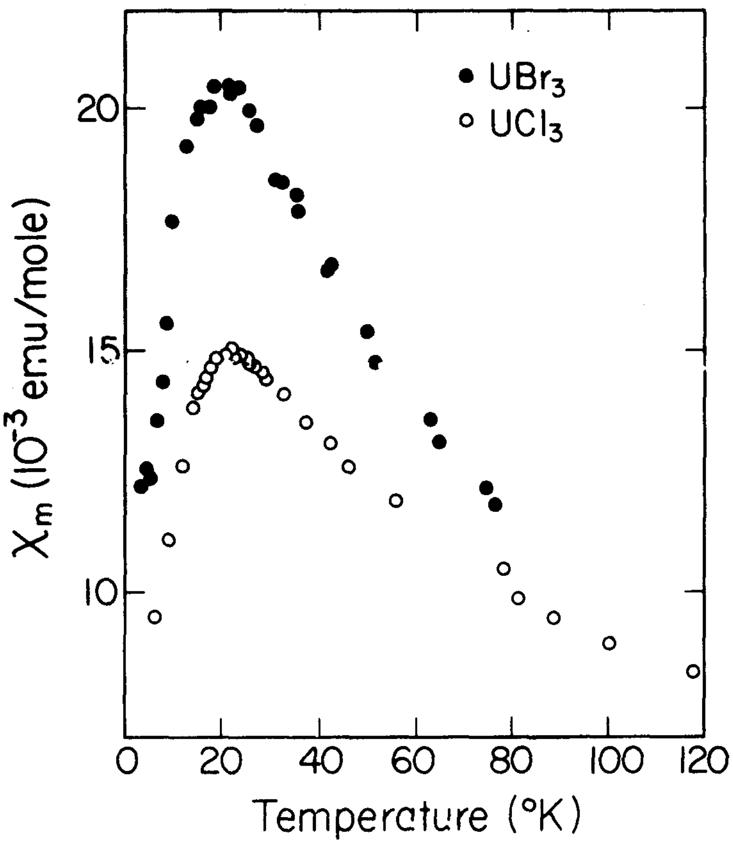
MAGNETIC SUSCEPTIBILITY CONSTANTS

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^{-1})
UCl_3	25-117	1.70	89.3	3.70±0.08	22±1	-
UBr_3	25-76	1.77	63.8	3.76±0.08	20±1	-
$NpCl_3$	3.5-50	-	-	-	-	6 400±100
	75-240	0.99	83.5	2.81±0.09	-	-
α-$NpBr_3$	10-30	-	-	-	-	10 850±320
	50-126	0.99	45.0	2.81±0.20	-	-
$PuCl_3$	5-100	0.16	7.9	1.11±0.04	4.5±0.5	-

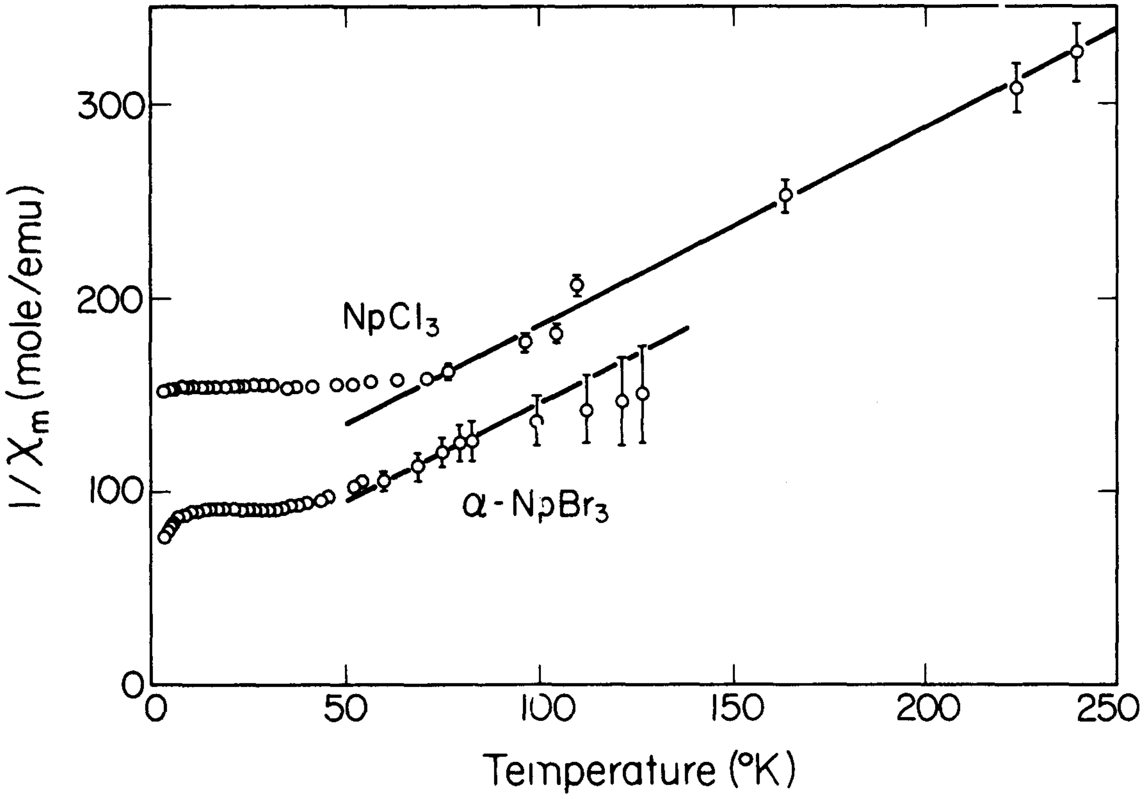
---

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

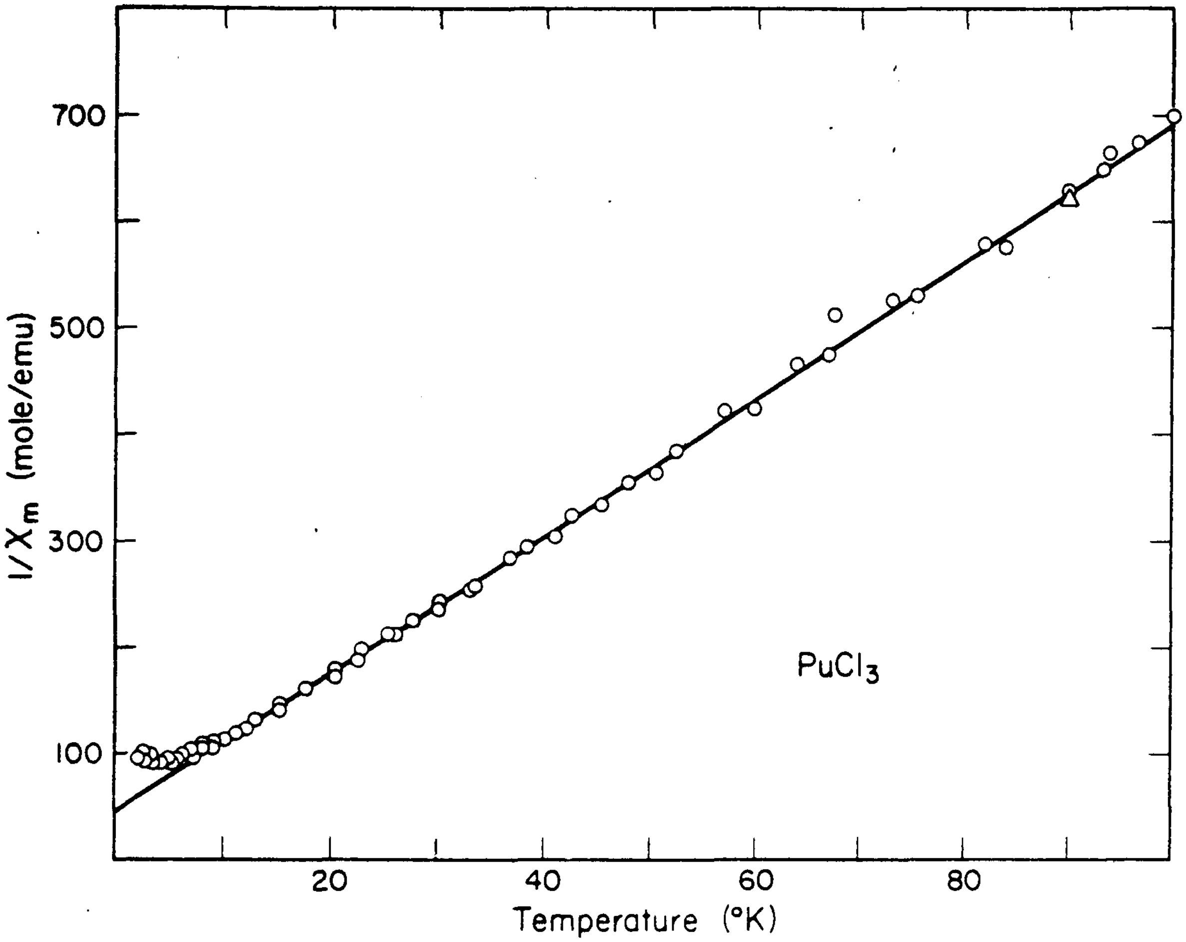
SLIDE 1. Magnetic data for some trivalent actinide halides.



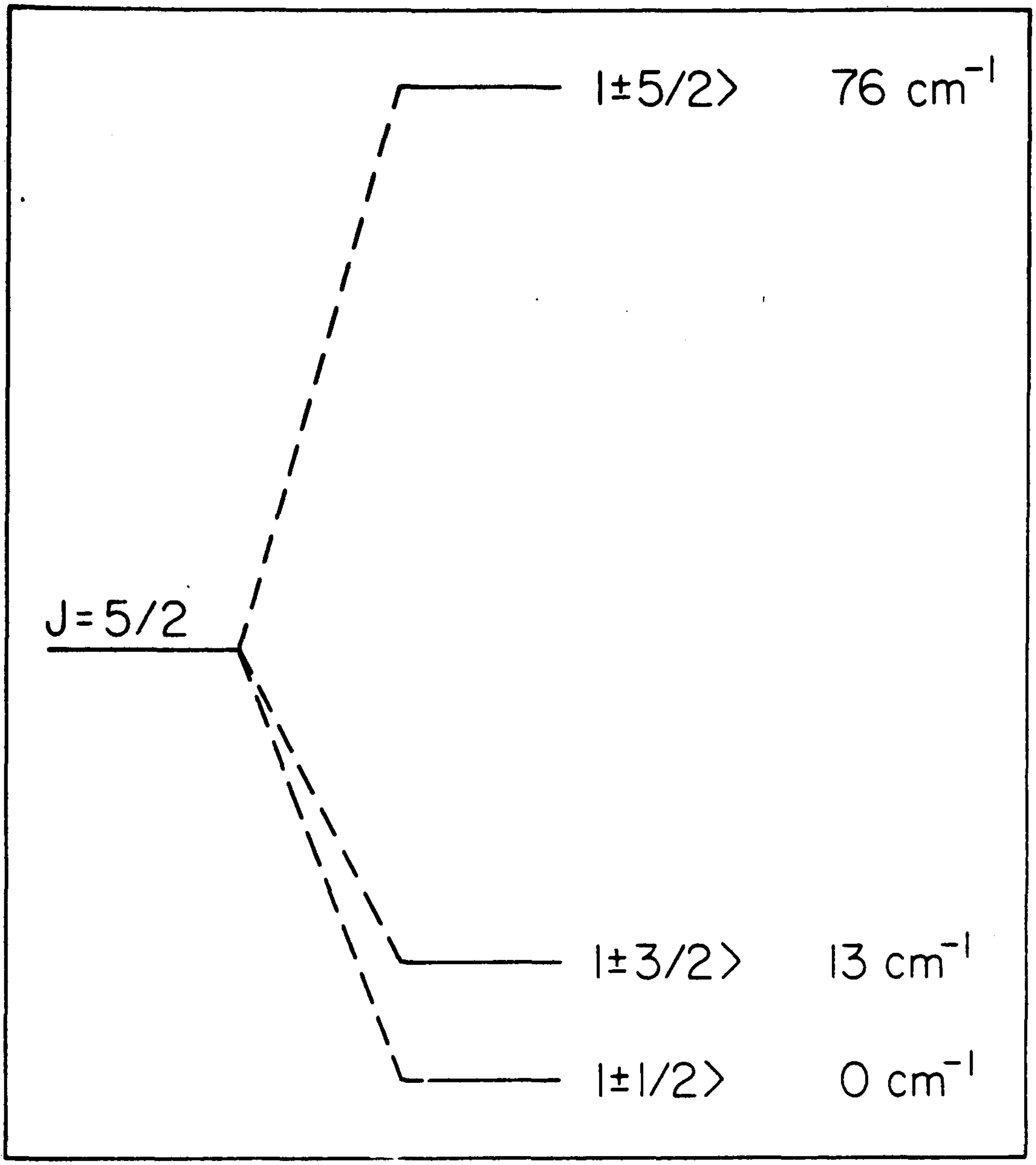
SLIDE 2. Molar susceptibilities of UCl_3 and UBr_3.



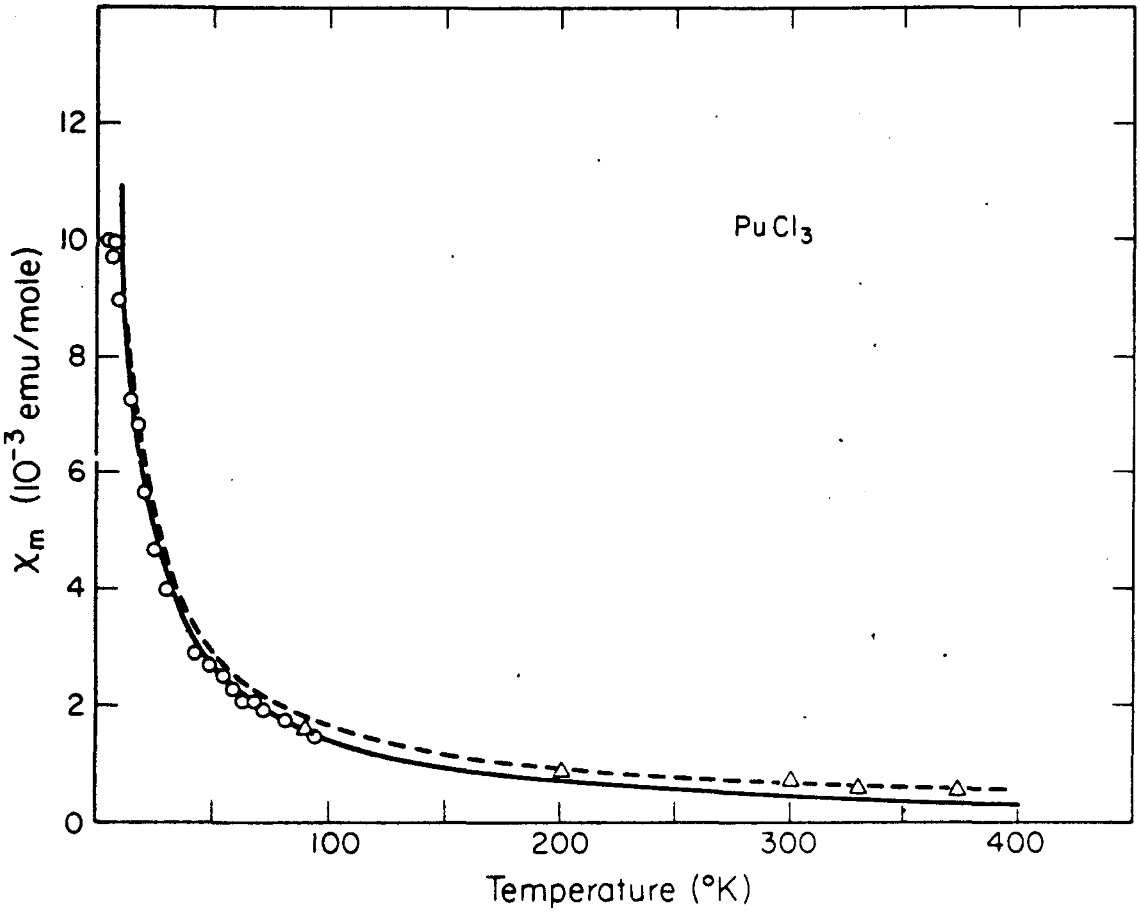
SLIDE 3. Reciprocal molar susceptibilities of $NpCl_3$ and α-$NpBr_3$.



SLIDE 4. Reciprocal molar susceptibility of $PuCl_3$.



SLIDE 5. Crystal-field splitting of the ground state of $PuCl_3$.



SLIDE 6. Calculated molar susceptibility of PuCl$_3$.