10^7 ohm-cm), and the isomorph $Na_2Sc_2Ti_6O_{16}$, a nonconductor at ordinary voltages. The iron compound shows the normal, field-independent paramagnetic susceptibility for Fe^{3+} ions (Figure 2), a $g = 2.00$ esr signal, and an electronic absorption spectrum typical of a spin-free d^5 ion with all electrons localized in an octahedral oxygen environment (curve B of Figure 1). The magnetic susceptibility per gram of $Na_2Fe_2Ti_6O_{16}$ is given by

$$\chi_g = \left(\frac{11,560}{T + 120.8} \pm 0.04\right) \times 10^{-6} \text{ cgs unit}$$

for the temperature range 200–370°K, with $\mu_{eff} = 5.73$ BM for each Fe^{3+} atom. Below 200°K the plot of χ_g^{-1} *vs.* T deviates from linearity, as expected from the relatively high Weiss constant. However, the Weiss constant of 120.8° is very close to the value of 125° observed for the (structurally different) compound $NaSc_{0.5}Fe_{0.5}TiO_4$,[15] the unit cell formulas being $Na_2Fe_2Ti_6O_{16}$ and $Na_4Fe_3Sc_2TiO_{16}$, respectively, and is consistent with the bulk concentration of Fe^{3+} ions. It is evident that for $Na_2Fe_2Ti_6O_{16}$ delocalization *via* band formation does not occur to any appreciable extent nor was it to be expected. In Na_xTiO_2 it is presumably, therefore, a function both of the presence of like atoms in the two sets of crystallographically equivalent metal atom positions and of the low donor ionization energy of Ti^{3+}. Failure to observe an esr signal for Ti^{3+} at 1.2°K suggests that the donor state may actually lie in the conduction band. It is probable that in Na_xTiO_2 all of the Ti atoms participate in band formation, but the character of the band, particularly whether d–pπ overlap between metal and oxygen atoms is involved as in ReO_3,[27] remains to be established. To this end, carrier density and carrier mobility measurements on single crystals would be most useful.

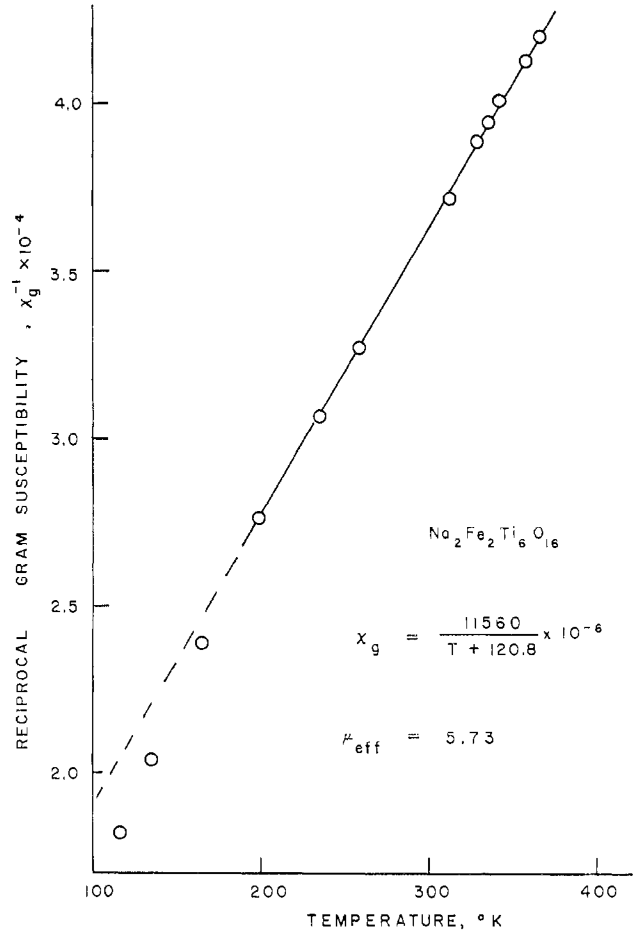

Figure 2.—Reciprocal gram susceptibility of $Na_2Fe_2Ti_6O_{16}$ as a function of temperature.

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(27) A. Ferretti, D. B. Rogers, and J. B. Goodenough, *Phys. Chem. Solids*, **26**, 2007 (1965).

Contribution from the Baker Laboratory of Chemistry,
Cornell University, Ithaca, New York 14850

Magnetic Susceptibility of Uranium Trifluoride in the Range 2–300°K[1]

By MICHAEL BERGER and M. J. SIENKO

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The magnetic susceptibility of UF_3 has been measured by the Gouy method over the temperature range 1.9–300°K. Behavior follows the Curie–Weiss law $\chi = C/(T - \theta)$ with $\theta = -110 \pm 5°$. The effective moment is 3.67 ± 0.06 BM, corresponding closely to a $5f^3$ configuration. There is no sign of a Néel inversion even at the lowest temperature reached. Comparison of data for UF_3, UCl_3, and UBr_3 suggests that the ratio of spin–orbit coupling to ligand-field splitting increases in the order UF_3, UCl_3, UBr_3.

Introduction

The rather great carrier mobility (10 cm^2/v sec) observed in single-crystal specimens of WO_3 can be explained in terms of electron delocalization from overlap of d orbitals.[2] Occasional findings of lustrous fragments in powder preparations of UF_3 suggest that similar delocalization might also occur in UF_3. However, preparation of single crystals of UF_3 for conductivity

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[2] B. L. Crowder and M. J. Sienko, *J. Chem. Phys.*, **38**, 1576 (1963).

and Hall voltage studies proves to be very difficult. Instead, we examine the powder susceptibility of UF_3 as an indirect way of determining whether conduction band electron pairing exists in this compound to reduce its magnetic moment. It seems that, at the least, if a readily accessible conduction band exists in UF_3, strong antiferromagnetic interactions between U^{3+} moments should result.

Experimental Section

UF_3 was prepared by reduction of UF_4 with U and by reduction of UF_4 with Al. Also, through the kindness of Dr. Ellison H. Taylor and Dr. Warren Grimes, we had the good fortune of obtaining an independent sample of UF_3 from Oak Ridge National Laboratory. There was no difference at room temperature in the magnetic susceptibility of the various samples.[3] Only the Oak Ridge sample was investigated over the full range of temperature available. X-Ray powder photographs confirmed it to be UF_3 free of gross impurities, and a mass spectrographic analysis using spark source mass spectroscopy (courtesy of the Analytical Facility of the Materials Science Center, Cornell University) disclosed the following ppm-by-weight impurities: Mn, 1–10; Fe, 1–10; Co, 0.1–1; Ni, 0.1–1; Cu, 0.1–1; Cr, 1–10; V, 0.1–1; Ti, 1–10.

The magnetic susceptibility was measured by the Gouy method, using the cryogenic balance previously described.[4] UF_3 powder, ground to 325 mesh, was loaded in precision-bore, 4-mm i.d. quartz sample tubes and the magnetic force was determined at various field strengths at various temperatures, including the triple point of nitrogen and the boiling point of helium. Field calibration was done with "Special Low Cobalt" $NiCl_2$ solution. Measurements were made from 0 to 6000 gauss, with most in the range 2000–3000 gauss. A noticeable field dependence (up to 10% over the full range of field investigated both at room and nitrogen temperature) was corrected for by extrapolating observed susceptibilities to zero reciprocal field. The extrapolated UF_3 molar susceptibility, after correction for diamagnetism,[5] ranged from $(4318 \pm 83) \times 10^{-6}$ at 294.4 ± 0.1°K to $(440{,}000 \pm 17{,}600) \times 10^{-6}$ at 1.90 ± 0.01°K. The 1.90°K value was uncertain because the susceptibility was increasing with time, perhaps because of a slow transition to an ordered state A second sample gave values ranging from $(4174 \pm 82) \times 10^{-6}$ at 293.5 ± 0.1°K to $(91{,}700 \pm 4000) \times 10^{-6}$ at 4.26 ± 0.01°K. Results over the whole temperature range for the two samples are presented in Figure 1 as plots of reciprocal molar susceptibility against temperature. Both samples follow a Curie–Weiss law down to about 125°K, below which temperatures the susceptibility increases more rapidly than expected. Extrapolation of the linear portion to zero reciprocal susceptibility yields a Weiss constant, θ in $\chi = C/(T - \theta)$, of $-92 \pm 5°$ for sample I and $-110 \pm 5°$ for sample II. Sample II is considered to be the more reliable because of better field reproducibility. The corresponding effective moments calculated for samples I and II from the slopes of the χ^{-1} *vs.* T curves—hence, from the Curie constants $C = N\mu^2/3k = [d(1/\chi)/dT]^{-1}$—are, respectively, 3.65 ± 0.06 and 3.67 ± 0.06 BM.

Discussion

Two reasonable configurations for U^{3+} are $5f^3$ and $5f^26d^1$. Assuming L–S coupling, the predicted moment for the ground state of $5f^3$ is 3.62 BM, while that for $5f^26d^1$ is 4.62. If the 6d orbital moment is quenched, the latter value reduces to 2.65 BM. Clearly the observed effective moment, 3.67 BM, for UF_3 is more consistent with a $5f^3$ configuration than with a $5f^26d^1$ configuration. This finding is consistent with that of O'Brien,[6] who on the basis of a crystal-field calculation for UF_3 concludes that a fit to the observed g values ($g_{\|} \cong 2.8$ and $g_{\perp} \cong 2.1$) of Ghosh, Gordy, and Hill[7] can only be made with a $5f^3$ configuration.

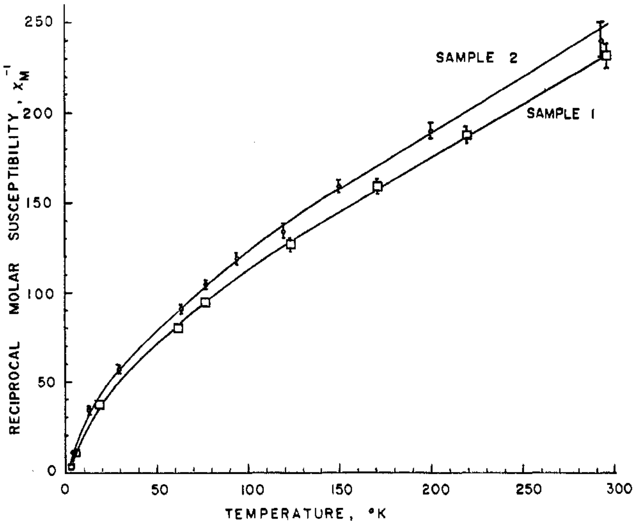

Figure 1.—Reciprocal molar susceptibility of UF_3 as a function of temperature.

If the state of U^{3+} in UF_3 contains appreciable admixture of $5f^26d^1$, then it would be reasonable to expect either direct overlap of the $d(t_{2g})$ orbitals between neighboring U^{3+} ions or indirect d overlap through the intermediacy of pπ interaction with intervening nonmetal atoms. One or the other of these possibilities seems certainly to be the explanation of the high conductivity observed in the tungsten bronzes.[8] Overlap of d orbitals in UF_3 would lead to a collective electron assembly as opposed to localized electrons, hence to a conducting state in which magnetic moments would be significantly reduced. The fact that no appreciable conductivity occurs in UF_3 taken together with the observation that no apparent reduction of the free-ion magnetic moment has occurred suggests that UF_3 is best considered as a normal, nonbanded solid containing independent $U^{3+}(5f^3)$ ions.

The rather appreciable, negative Weiss temperature, $\theta = -110°$, observed for UF_3 would suggest an antiferromagnetic coupling of the local moments. This at first sight is supported by the observation that θ for the series UF_3, UCl_3,[9] UBr_3[10] shows a regular progression from -110 to -75 to $+25°$, as expected for decreasing uranium–uranium exchange interaction with increasing anionic size. However, unlike UCl_3 which has a Néel temperature[9] of 23°K, UF_3 shows no evidence of an antiferromagnetic transition down to 1.9°K. If anything, there is a suggestion of ferromagnetic ordering in UF_3 at very low temperatures. Further, the work of Handler and Hutchison[9] on solid solutions

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[3] Preliminary measurements on UF_3 at room temperature were carried out by Diane Gutterman.

[4] M. J. Sienko and J. B. Sohn, *J. Chem. Phys.*, **44**, 1369 (1966).

[5] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., 2nd ed. New York, N. Y., 1956, p 78.

[6] M. C. M. O'Brien, *Proc. Phys. Soc.* (London), **A68**, 351 (1955).

[7] S. N. Ghosh, W. Gordy, and D. Hill, *Phys. Rev.*, **96**, 36 (1954).

[8] See, for example, J. B. Goodenough, *Bull. Soc. Chim. France*, **4**, 1200 (1965).

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

[10] J. K. Dawson, *J. Chem. Soc.*, 429 (1951).

of UCl_3 in isomorphous $LaCl_3$ showed almost no change of the Weiss constant with dilution. This would appear to indicate that the Weiss constant for the uranium trihalides owes its origin, not to exchange interaction, but to crystal-field splitting of the 5f orbitals.

Crystal-field splittings, generally ignored for the lanthanides, are expected to be greater in the actinides because of the greater radial extent of 5f compared to 4f wave functions. However, the splittings of 5f orbitals are difficult to predict because of the complexity of the f distributions, the relatively greater importance of interelectronic repulsion parameters, and because the crystal-field splittings in the actinides are probably comparable in magnitude to the spin–orbit couplings.[11] In a strictly ionic picture, the spin–orbit coupling constant λ for U^{3+} would be the same in UF_3, UCl_3, and UBr_3. However, partial electron delocalization, which probably increases in the order UF_3, UCl_3, UBr_3, would reduce λ, leading to the sequence $\lambda_{UBr_3} < \lambda_{UCl_3} < \lambda_{UF_3}$. On the other hand, the crystal-field splitting, $Dq + Fr$, probably increases significantly in the order UBr_3, UCl_3, UF_3. UF_3, reported to be isostructural with LaF_3, has a structure different from UCl_3 and UBr_3, though unresolved discrepancies in the X-ray and nmr-esr data on LaF_3 make specification of the site symmetry at the U^{3+} somewhat uncertain.[12] Still, the near- and next-nearest-neighbor environment is not grossly different in the three halides except for the distances. The U–F distance is on the average 10% less than the U–Cl or U–Br spacing, so the effect on Dq (fourth order in radius) and Fr (sixth order in radius) would be substantial.

The ground state of U^{3+} is ${}^4I_{9/2}$ and, in a low-symmetry crystal field such as obtains in these structures, is split so that the lowest state is orbitally nondegenerate—*i.e.*, orbitally nonmagnetic. The spin-only moment for this lowest state would be 3.87 BM. Admixture of higher orbital states would probably reduce this moment. The extent to which higher orbital states contribute to the total wave function is roughly proportional to the ratio of the spin–orbit coupling to the crystal-field splitting. In the sequence UF_3, UCl_3, and UBr_3, $\lambda/(Dq + Fr)$ is probably smallest in UF_3, so the magnetic moment in UF_3 would be expected to be least removed from the spin-only value. In fact, on this simple qualitative basis we would expect the moments to decrease in the order UF_3, UCl_3, or UBr_3. Table I summarizes the present experimental situation for these compounds. The data of this investigation for UF_3 taken in conjunction with those of Dawson would appear to support the foregoing arguments. However, there is a discrepancy for UCl_3 between Dawson's findings and those of Handler and Hutchison, major enough to make uncertain in which direction the observed moments increase. It would appear that the Handler and Hutchison value for UCl_3 might be preferred, on the basis that the investigation was a consistent part of a more extended study on solutions of UCl_3 in $LaCl_3$. For the current situation, it is difficult to speculate further until the above discrepancy is resolved and further data (spectral, esr, and magnetic) become available so as to establish more firmly the relevant spin–orbit coupling and ligand-field parameters for these compounds.

TABLE I

MAGNETIC CONSTANTS OF URANIUM TRIHALIDES

Compd	μ_{eff} at 300°K, BM	θ in $\chi = C/(T - \theta)$, deg	Remarks
UF_3	3.67	−110	This investigation
UCl_3	3.76	−75	Handler and Hutchison[9]
	3.03	−29	Dawson[10] concludes $5f^26d^1$
UBr_3	3.29	+25	Dawson[10] concludes $5f^26d^1$

Acknowledgments.—We wish to thank George Bouchard for assistance in making the low-temperature magnetic measurements and Diane Gutterman for the preliminary room-temperature studies.

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(11) B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966, p 327.

(12) See, for example, M. B. Schulz and C. D. Jeffries, *Phys. Rev.*, **149**, 270 (1966).