JOURNAL OF SOLID STATE CHEMISTRY 110, 118–123 (1994)

Magnetic Susceptibility and Electron Paramagnetic Resonance Study of KUO_3 with Cubic Perovskite Structure

Yukio Hinatsu

Department of Chemistry, Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki 319-11, Japan

Received May 11, 1993; in revised form August 6, 1993; accepted August 9, 1993

KUO_3 (cubic perovskite structure) was prepared and its magnetic susceptibility was measured from 4.2 K to room temperature. It was found that a magnetic anomaly (magnetic transition) occurred at 16.8 K and that this transition temperature decreased with increasing magnetic field. The electron paramagnetic resonance spectrum due to the U^{5+} ion in the paramagnetic state was not observed even at 4.2 K. The magnetic susceptibility and the optical absorption spectrum were analyzed on the basis of an octahedral crystal field model. The crystal field parameters determined are discussed and compared with those reported for other f^1 compounds. © 1994 Academic Press, Inc.

INTRODUCTION

The magnetic and optical properties of actinides are characterized by the behavior of $5f$ electrons. For the $5f$ compounds, the crystal field, spin–orbit coupling, and electron–electron repulsion interactions are of comparable magnitude, which makes the analysis of the experimental results complicated. However, in the case of actinide ions having the $[Rn]5f^1$ electronic configuration, such as a U^{5+} ion, the situation is considerably simplified because there are no $5f$ electronic repulsion interactions. Therefore, the theoretical treatment of such ions is easier and we may then obtain a deeper understanding of the behavior of $5f$ electrons in solids.

In this paper, we focus our attention on the magnetic properties of KUO_3. X-ray structure analysis indicates that this uranate has a cubic-perovskite-type structure (space group: O_h^1-$Pm3m$) (1), i.e., a uranium ion is octahedrally coordinated by six oxygen ions. This high coordination symmetry around the U^{5+} ion, in addition to the simple f^1 configuration, enables us to more easily analyze the experimental results.

There have been several reports on the measurements of the magnetic susceptibility and electron paramagnetic resonance (EPR) spectrum for KUO_3. However, the results are inconsistent with each other and not sufficiently discussed. Kemmler-Sack *et al.* (2) measured the magnetic susceptibility of KUO_3 from 92 to 453 K and found that it did not obey the Curie–Weiss law, but could be represented by $\chi = 0.040/T + 390 \times 10^{-6}$ (emu/mole). Keller (3) extended the temperature range of the magnetic susceptibility measurements of KUO_3 down to 4.2 K and reported that there is no magnetic transition down to this temperature. Miyake *et al.* (4) prepared KUO_3 by heating a stoichiometric mixture of UO_2 and K_2CO_3 at 550 ~ 700°C *in vacuo* or in an argon atmosphere and measured its magnetic susceptibility in the temperature range between 2.0 K and room temperature. They found a sharp spike at 16 K in the magnetic susceptibility vs temperature curve. Later, Kanellakopulos *et al.* (5) made detailed measurements of the temperature and field dependence of the magnetic susceptibility of KUO_3 and obtained results quite similar to those reported by Keller (3), but found a weak field dependence of the susceptibility at low temperatures. As for the electron paramagnetic resonance (EPR) spectrum on KUO_3, Lewis *et al.* (6) reported that they could not observe any EPR spectrum for KUO_3 even at 4.2 K. On the contrary, Miyake *et al.* (4) measured a broad EPR spectrum at room temperature and 77 K and found a g-value of 2.42–2.61. Edelstein and Goffart (7) consider the magnetic susceptibility anomaly at 16 K and the EPR spectrum for KUO_3 measured by Miyake *et al.* to be incorrect.

In order to clarify the inconsistent experimental results and to study the magnetic properties of the $5f$ electron in an octahedral crystal field, we prepared KUO_3 and carried out its magnetic susceptibility measurements in the temperature range between 4.2 K and room temperature, and EPR measurements both at room temperature and at 4.2 K. EPR measurements were also made on KUO_3 diluted with $BaUO_3$ (a temperature-independent paramagnet (8)) and diluted with $BaCeO_3$ (a weakly temperature-independent paramagnet (9)). The crystal field parameters for KUO_3 were obtained from the analysis of its optical absorption spectrum reported earlier (10). The results of the magnetic susceptibility and the EPR measurements are discussed on the basis of an octahedral crystal field model.

0022-4596/94 $6.00
Copyright © 1994 by Academic Press, Inc.
All rights of reproduction in any form reserved.

EXPERIMENTAL

1. *Preparation*

KUO_3 was prepared by the following reactions:

$$U_3O_8 + 3K_2CO_3 \xrightarrow{\text{in air}} 3K_2UO_4 + 3CO_2, \text{ and} \quad [1]$$

$$K_2UO_4 + UO_2 \xrightarrow{\textit{in vacuo}} 2KUO_3. \quad [2]$$

K_2UO_4 was prepared by firing finely ground mixtures of U_3O_8 and K_2CO_3 in air at 850°C for 1 day. After the mixtures were cooled, the same grinding and firing were repeated. KUO_3 was prepared by heating mixtures of UO_2 and an excess of K_2UO_4 in an evacuated quartz tube at 700°C for 10 hr. To avoid the reaction of the mixtures of K_2UO_4 and UO_2 with quartz, the mixtures were wrapped with molybdenum foil. After it cooled to room temperature, the sample was crushed into powder, pressed into pellets, and reacted under the same conditions.

The specimens, KUO_3 diluted with $BaUO_3$ (or $BaCeO_3$), were prepared by heating mixtures of the KUO_3 and $BaUO_3$ (or $BaCeO_3$) in evacuated quartz tubes at 700°C for 2 days. The ratios of the KUO_3 in $BaUO_3$ (or $BaCeO_3$) were 2–5 mole%.

2. *Analysis*

2.1. *X-ray diffraction analysis.* An X-ray diffraction study was performed with Cu$K\alpha$ radiation on a Philips PW 1390 diffractometer equipped with a curved graphite monochromator. The lattice parameters of the samples were determined by a least-squares method applied to the diffraction lines.

2.2. *Determination of oxygen content.* The oxygen nonstoichiometry in the specimen was checked by the back-titration method (11, 12). A weighed sample was dissolved in excess cerium (IV) sulfate solution. The cerium (IV) sulfate solution was standardized in advance with stoichiometric UO_2. Then, the excess cerium (IV) was titrated against a standard iron (II) ammonium sulfate solution with ferroin indicator. The oxygen content was determined for a predetermined K/U ratio.

3. *Magnetic Susceptibility Measurement*

The magnetic susceptibility was measured with a Faraday-type torsion balance in the temperature range between 4.2 K and room temperature. The apparatus was calibrated with a manganese Tutton's salt ($\chi_g = 10{,}980 \times 10^{-6}/(T + 0.7)$) standard. The temperature of the sample was measured by a "normal" Ag vs Au–0.07 at% Fe thermocouple (4.2 K ~ 40 K) (13) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). To examine the field dependence, the magnetic susceptibility was measured in each of the field strengths of 2800, 4700, 6900, 9000, and 10,600 G. Details of the experimental procedure have been described elsewhere (14). Furthermore, the magnetic susceptibility was also measured with a commercial SQUID magnetometer (Quantum Design, MPMS model) at 1000, 3000, 5000, 7000, 9000, 15,000, and 25,000 G.

4. *Electron Paramagnetic Resonance Measurement*

The EPR measurements were carried out both at room temperature and at 4.2 K for the specimen sealed in a quartz tube. The measurements were made using a Jeol RE-2X spectrometer operating at X-band frequency (~9.10 GHz) with 100 kHz field modulation. The magnetic field was swept from 100 to 13,000 G. Before measuring the specimen, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or sample tube.

RESULTS

The X-ray diffraction analysis shows the specimen KUO_3 prepared in this study is cubic and the lattice parameter is $a = 4.294$ Å. From the chemical analysis of the oxygen concentration, the sample was found to be $KUO_{2.993}$. In view of the error limits for this analysis, this result indicates that the specimen is oxygen stoichiometric.

Figure 1 shows the temperature dependence of the magnetic susceptibility of KUO_3 which was measured in a magnetic field of 4700 G. We have found that the susceptibility shows a sharp maximum (spike) at ca. 16 K. In the same figure, the susceptibility data measured by other research groups are also shown. Our susceptibility data are close to those of Kanellakopulos *et al.* (5), but a discrepancy between their data and ours has been found in the lower temperature region. Keller (3) and Kanellakopulos *et al.* (5) reported no magnetic ordering down to 4.2 K through their magnetic susceptibility measurements, while Miyake *et al.* (4) found a sharp spike at 16 K in the susceptibility vs temperature curve. The magnetic anomaly found in this experiment is consistent with that reported by Miyake *et al.* (4). A similar magnetic behavior has been found for the magnetic susceptibility of $NaUO_3$ (15) (the crystal structure of which is $GdFeO_3$-type (16)) and is supported by the finding of a heat capacity anomaly (17), although the transition temperature is 31.1 K. That transition is reported to be of long-range order of the ferromagnetic type (5). We believe that the magnetic anomaly found at ca. 16 K is due to the long-range magnetic ordering between uranium ions. Figure 2 shows the dependence of magnetic susceptibility on field strengths

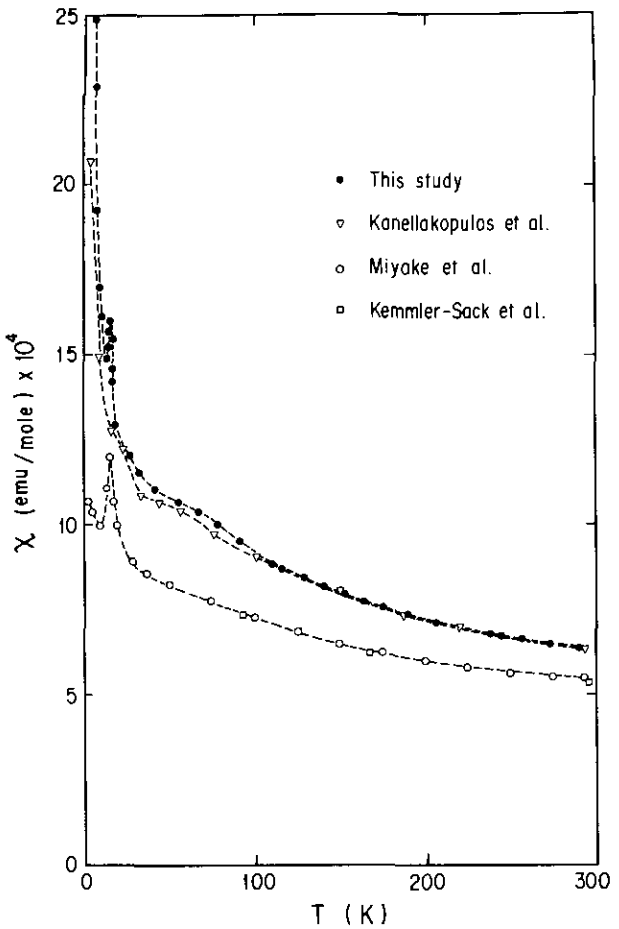

FIG. 1. Magnetic susceptibility vs temperature curve for KUO_3.

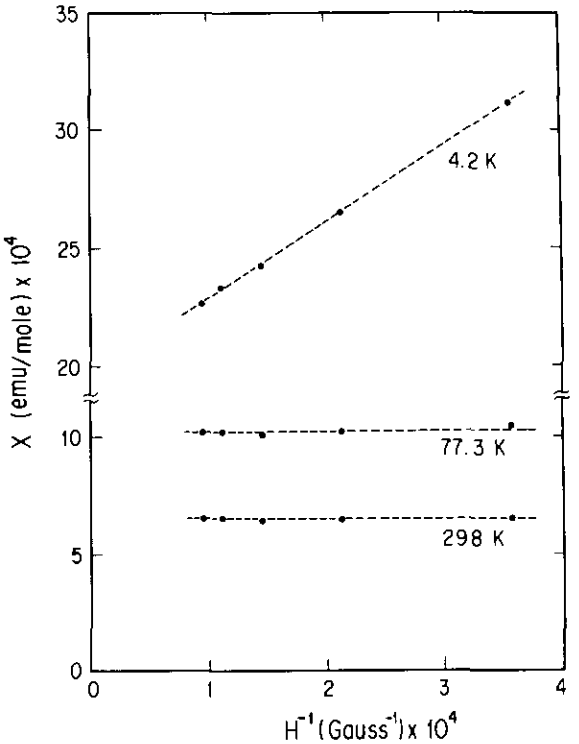

FIG. 2. Field dependence of magnetic susceptibility at 4.2, 77.3, and 298 K.

at 4.2, 77.3, and 298 K. A field dependence of the magnetic susceptibility is found at 4.2 K. This field dependence of the susceptibility must be related to the magnetic anomaly found at ca. 16 K. Kanellakopulos *et al.* also reported a similar field dependence of the susceptibility below 24.5 K (5).

Figure 3 shows the detailed susceptibility vs temperature curves in a lower temperature region at various magnetic fields. Clearly, the susceptibility below 25 K depends on the magnetic field and the magnetic transition temperature decreases with increasing magnetic field. Figure 4 shows the dependence of the transition temperature on field strength. In this figure, the data measured using a SQUID magnetometer are also included. From the extrapolation of the magnetic field to zero field, the transition temperature for KUO_3 was determined to be 16.8 K. In a magnetic field of 25,000 G, this sample shows no magnetic transition down to 4.2 K.

In this study, the EPR measurements for KUO_3 were made under various experimental conditions. The measurements for a concentrated (not diluted) KUO_3 showed

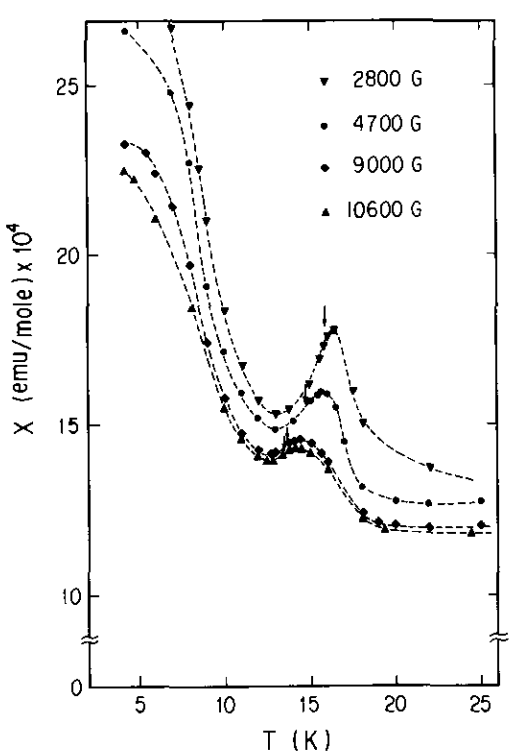

FIG. 3. Magnetic susceptibility vs temperature curves in a lower temperature region at various magnetic fields. Arrows show the transition temperatures at each magnetic field.

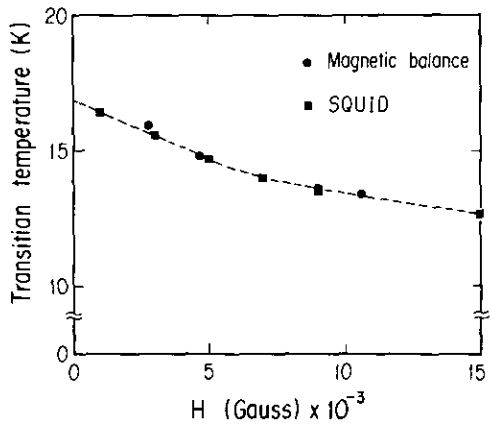

FIG. 4. Dependence of magnetic transition temperature on field strength.

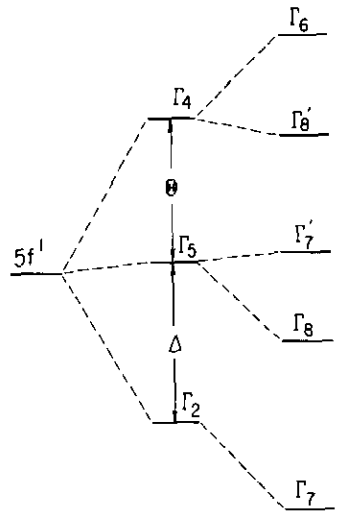

FIG. 5. f^1 orbital splitting perturbed by octahedral crystal field and spin–orbit coupling.

a broad EPR spectrum even at room temperature. The g-value was 2.39 and the peak-to-peak linewidth was ca. 1600 G. This result is similar to that reported by Miyake *et al.* (4). With decreasing temperature, the spectrum becomes broader. As will be discussed later, we believe that this EPR spectrum with large g-value ($g > 2$) is not ascribable to the paramagnetic behavior of the U^{5+} ion perturbed by the octahedral crystal field, but that it may be related to the magnetic interaction between uranium ions, as was found at low temperatures. To decrease the effect of this magnetic interaction and to measure the EPR spectrum ascribable to the U^{5+} ion just perturbed by the crystal field, KUO_3 was diluted with $BaUO_3$ or $BaCeO_3$. Both the specimens, however, showed no EPR signal, even at 4.2 K.

DISCUSSION

KUO_3 is a suitable compound to study the behavior of $5f$ electron in solids, because it has a cubic-perovskite-type structure, in which a U^{5+} ion is octahedrally coordinated by six oxygen ions. This high coordination symmetry, in addition to the one-electron configuration ([Rn]$5f^1$), enables us to analyze the magnetic properties of KUO_3 theoretically.

Figure 5 shows the effects of perturbing the f^1 orbital energy levels successively by an octahedral crystal field, and spin–orbit coupling. In the crystal field with octahedral symmetry, the sevenfold degenerate energy state of the f orbitals is split into Γ_2, Γ_5, and Γ_4 states, where Δ and Θ are parameters that represent the intensity of the crystal field. If spin–orbit coupling is taken into account, the Γ_2 orbital state is transformed into Γ_7, whereas the Γ_5 and Γ_4 states are split into Γ_7^* and Γ_8, and Γ_6 and Γ_8^*, respectively. The ground-state Kramers doublet is the Γ_7 state and is coupled to the excited Γ_7^* state arising from the Γ_5 orbital, by spin–orbit coupling. The energy matrices for the Γ_7, Γ_8, and Γ_6 states are:

$$\begin{aligned}
\Gamma_7&: \begin{vmatrix} 0 & \sqrt{3k}\,\zeta \\ \sqrt{3k}\,\zeta & \Delta - \tfrac{1}{2}k\zeta \end{vmatrix} \\
\Gamma_8&: \begin{vmatrix} \Delta + \tfrac{1}{4}k\zeta & \tfrac{3}{4}\sqrt{5kk'}\,\zeta \\ \tfrac{3}{4}\sqrt{5kk'}\,\zeta & \Delta + \Theta - \tfrac{3}{4}k'\zeta \end{vmatrix} \\
\Gamma_6&: |\Delta + \Theta + \tfrac{3}{2}k'\zeta|.
\end{aligned} \qquad [3]$$

Here ζ is the spin–orbit coupling constant and k and k' are the orbital reduction factors for an electron in Γ_5 and Γ_4 orbital states, respectively (18, 19). Diagonalization of the energy matrix produces the ground state Γ_7 and the excited state Γ_7', and the corresponding wavefunctions are written

$$\begin{aligned}
|\Gamma_7\rangle &= \cos\theta|^2F_{5/2}, \Gamma_7\rangle - \sin\theta|^2F_{7/2}, \Gamma_7^*\rangle, \\
|\Gamma_7'\rangle &= \sin\theta|^2F_{5/2}, \Gamma_7\rangle + \cos\theta|^2F_{7/2}, \Gamma_7^*\rangle,
\end{aligned} \qquad [4]$$

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state with the relation

$$\tan 2\theta = \frac{2\sqrt{3k}\,\zeta}{\Delta - \tfrac{1}{2}k\zeta}. \qquad [5]$$

Similarly, diagonalization of the Γ_8 matrix produces the two levels Γ_8 and Γ_8'.

The g-value for the ground Γ_7 doublet is calculated as follows:

$$g = 2\langle\Gamma_7|\mathbf{L} + 2\mathbf{S}|\Gamma_7\rangle = 2\cos^2\theta - 4\sqrt{k/3}\sin 2\theta - \tfrac{2}{3}(1-k)\sin^2\theta. \quad [6]$$

This equation indicates that the g-value should be between -1.43 and 2.00, even if the covalency effect k is included (20). Therefore, the EPR spectrum with large g-value ($g > 2$) measured for concentrated KUO_3 is not ascribable to the paramagnetic behavior of U^{5+} ion. The KUO_3 diluted with $BaUO_3$ (or $BaCeO_3$) in which the U^{5+} ion is perturbed by the octahedral crystal field shows no EPR signal, even at 4.2 K. Although the g-value for the ground crystal field state of U^{5+} ion was not determined from EPR measurements, this value can be evaluated from the temperature-dependent part of the magnetic susceptibility, as will be described in the following.

The magnetic susceptibility of the molecule is given by the equation

$$\chi = \frac{N\Sigma_{n,m}\{(E^{(1)}_{n,m})^2/kT - 2E^{(2)}_{n,m}\}\exp(-E^0_{n,m}/kT)}{\Sigma_{n,m}\exp(-E^0_{n,m}/kT)}, \quad [7]$$

where N is Avogadro's number, $E^0_{n,m}$ is the zero-field energy, $E^{(1)}_{n,m}$ and $E^{(2)}_{n,m}$ are the first- and second-order Zeeman terms, and n and m are quantum numbers. If the separation of levels within the ground state is much smaller than kT, and the energy of the next excited state is much larger than kT, the susceptibility is expressed by the form (21)

$$\chi = \frac{Ng^2\beta^2}{4kT} + \chi_{TIP} \quad [8]$$

where

$$\chi_{TIP} = 2N\beta^2\sum_i \frac{|\langle\Gamma_i|\mathbf{L} + 2\mathbf{S}|\Gamma_7\rangle|^2}{E(\Gamma_i) - E(\Gamma_7)}. \quad [9]$$

The g-value in Eq. [8] is the same g-value obtained from EPR measurements on the ground crystal field state (Eq. [6]), i.e., the g-value can be determined from this temperature-dependent part of the susceptibility. From the extrapolation of $1/T$ to 0 for the measured magnetic susceptibility (χ_{exp}) vs reciprocal temperature ($1/T$) curve, we may obtain the temperature-independent paramagnetic susceptibility $\chi_{TIP} = 450 \times 10^{-6}$ (emu/mole). The resulting temperature-dependent susceptibility ($\chi(T) = \chi_{exp} - \chi_{TIP}$) follows the equation $\chi(T) = 0.054/T$ except at very low temperatures. From the temperature-dependent part of the susceptibility (using Eq. [8]), the g-value for the ground state of the U^{5+} ion in this KUO_3 is calculated to be 0.76. This g-value is quite reasonable for the value of an f^1 electron perturbed by the octahedral crystal field and comparable g-values are found in many $5f^1$ compounds (22–25).

The optical spectrum on KUO_3 was measured by Kemmler-Sack in the range between 4000 and 40,000 cm^{-1} (10). The spectrum shows no splitting of $\Gamma_7 \rightarrow \Gamma_8$ and $\Gamma_7 \rightarrow \Gamma_8'$ transitions, i.e., the central U^{5+} ion is in a crystal field with octahedral symmetry. The transition energies are listed in Table 1. The crystal field parameters and orbital reduction factors in Eq. [3] are determined by fitting the transition energies calculated to those determined experimentally, and by fitting the calculated g-value (Eq. [6]) to the g-value obtained from the magnetic susceptibility measurements ($|g| = 0.76$). We have considered that the transition $\Gamma_7 \rightarrow \Gamma_8'$ is a least reliable one because it is known to be broad and sometimes split. The transition energies calcualted, and the crystal field parameters and orbital reduction factors determined here are also listed in Table 1. The spin–orbit coupling constant is 1896 cm^{-1}, which is a reasonable value for U^{5+} ions in solids (26–29), and is close to the value obtained from linear interpolation of the ζ values between Pa^{4+} and Np^{6+} compounds, 1950 cm^{-1} (30). From the orbital reduction factors k and k', a considerable degree of covalency is found to exist in this uranate. For comparison, the crystal field parameters and spin–orbit coupling constants for $LiUO_3$ and $BaPrO_3$ (20, 31) are listed in Table 2 (32). They were also determined from the analysis of their magnetic and optical properties on the basis of the octahedral crystal field model. Parameters obtained for KUO_3 are comparable to those for $LiUO_3$ (20). The spin–orbit coupling constant for the U^{5+} ion in KUO_3 is much larger than that for the Pr^{4+} ion ([Xe]$4f^1$ electronic configuration) in

TABLE 1
Crystal Field Parameters and Orbital Reduction Factors

	Experiment	Calculation
$\Gamma_7 \rightarrow \Gamma_8$ (cm^{-1})	4,386	4,365
$\Gamma_7 \rightarrow \Gamma_7'$ (cm^{-1})	6,849	6,849
$\Gamma_7 \rightarrow \Gamma_8'$ (cm^{-1})	9,808	10,715
$\Gamma_7 \rightarrow \Gamma_6$ (cm^{-1})	12,500	12,500
g-value	$\lvert g\rvert = 0.76^a$	$g = -0.76$
ζ (cm^{-1})		1,896
Δ (cm^{-1})		3,335
Θ (cm^{-1})		4,683
k		0.95
k'		0.80

[a] This value was determined from the temperature-dependent part of the magnetic susceptibility (see text).

TABLE 2
Spin–Orbit Coupling Constant and Crystal Field Parameters

Compound	ζ	Δ	Θ
KUO_3	1896	3335	4683
$LiUO_3$	1938	3543	6145
$BaPrO_3$	865	1686	2521

Note. All values are given in cm^{-1}.

$BaPrO_3$ (31). The magnitude of the crystal field splitting ($\Delta + \Theta$) of the U^{5+} ion in KUO_3 is also much larger than that for the Pr^{4+} ion in the same octahedral symmetry. This result shows that the $5f$ electrons of actinides are not so effectively shielded from their environment by the completed $6s$ and $6p$ subshells.

Next, the magnetic susceptibility of KUO_3 in the paramagnetic temperature region is evaluated. Since we have already obtained the wavefunctions for the ground doublets (Eq. [4]) and excited states, the magnetic susceptibility of KUO_3 is easily calculated from Eq. [8] as follows:

$$\chi = 0.054/T + 225 \times 10^{-6}. \qquad [10]$$

The discrepancy between the calculated results and experimental results is found in the temperature-independent part of the susceptibility. The χ_{TIP} obtained experimentally is larger than that calculated. This result suggests that some of the uranium ions are in the tetravalent state. The electronic configuration of the U^{4+} ion is $[Rn]5f^2$. If the $5f^2$ ion is octahedrally coordinated by six anions, its susceptibility is known to show a temperature-independent paramagnetism over a wide temperature range (33).

REFERENCES

1. W. Rüdorff, S. Kemmler, and H. Leutner, *Angew. Chem.* **74,** 429 (1962).
2. S. Kemmler-Sack, E. Stumpp, W. Rüdorff, and H. Erfurth, *Z. Anorg. Allg. Chem.* **354,** 287 (1967).
3. C. Keller, *in* "MTP International Review of Science," Vol. 7, "Lanthanides and Actinides" (K. W. Bagnall, Ed.), Series I, p. 47. Butterworths, London, 1972.
4. C. Miyake, K. Fuji, and S. Imoto, *Chem. Phys. Lett.* **61,** 124 (1979).
5. B. Kanellakopulos, E. Henrich, C. Keller, F. Baumgärtner, E. König, and V. P. Desai, *Chem. Phys.* **53,** 197 (1980).
6. W. B. Lewis, H. G. Hecht, and M. P. Eastman, *Inorg. Chem.* **12,** 1634 (1973).
7. N. M. Edelstein and J. Goffart, *in* "The Chemistry of the Actinide Elements" (J. J. Katz, G. T. Seaborg, and L. R. Morss, Eds.), 2nd ed., Chap. 18. Chapman & Hall, London/New York, 1986.
8. Y. Hinatsu, *J. Solid State Chem.* **102,** 566 (1993).
9. J. B. Bulman, M. V. Kuric, R. P. Guertin, S. Foner, E. J. McNiff, Jr., G. Cao, J. O'Riely, J. E. Crow, P. P. Wise, and T. Yuen, *J. Appl. Phys.* **69,** 4874 (1991).
10. S. Kemmler-Sack, *Z. Anorg. Allg. Chem.* **363,** 295 (1968).
11. S. R. Dharwadkar and M. S. Chandrasekharaiah, *Anal. Chim. Acta* **45,** 545 (1969).
12. T. Fujino and T. Yamashita, *Fresenius' Z. Anal. Chem.* **314,** 156 (1983).
13. L. L. Sparks and R. L. Powell, *J. Res. Natl. Bur. Stand. U.S. A.* **76,** 263 (1972).
14. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **60,** 195 (1985).
15. C. Miyake, K. Fuji, and S. Imoto, *Chem. Phys. Lett.* **46,** 349 (1977).
16. S. F. Bartram and R. E. Fryxell, *J. Inorg. Nucl. Chem.* **32,** 3701 (1970).
17. W. G. Lyon, D. W. Osborne, H. E. Flotow, and H. R. Hoekstra, *J. Chem. Thermodyn.* **9,** 201 (1977).
18. J. C. Eisenstein and M. H. L. Pryce, *Proc. R. Soc. Ser. A* **255,** 181 (1960).
19. H. G. Hecht, W. B. Lewis, and M. P. Eastman, *Adv. Chem. Phys.* **21,** 351 (1971).
20. Y. Hinatsu, T. Fujino, and N. Edelstein, *J. Solid State Chem.* **99,** 182 (1992).
21. J. H. Van Vleck, "The Theory of Electronic and Magnetic Susceptibilities." Oxford Univ. Press, London, 1932.
22. C. A. Hutchison, Jr. and B. Weinstock, *J. Chem. Phys.* **32,** 56 (1960).
23. P. Rigny and P. Plurien, *J. Phys. Chem. Solids* **28,** 2589 (1967).
24. M. Dryfford, P. Rigny, and P. Plurien, *Phys. Lett. A* **27,** 620 (1968).
25. J. Selbin and H. J. Sherrill, *Inorg. Chem.* **13,** 1235 (1974).
26. D. G. Karraker, *Inorg. Chem.* **3,** 1618 (1964).
27. M. J. Reisfeld and G. A. Crosby, *Inorg. Chem.* **4,** 65 (1965).
28. N. Edelstein, D. Brown, and B. Whittaker, *Inorg. Chem.* **13,** 563 (1974).
29. "Gmelin Handbook of Inorganic Chemistry," Uranium, Supplement Volume A6. Springer-Verlag, New York/Berlin, 1983.
30. J. Selbin and J. D. Ortego, *Chem. Rev.* **69,** 657 (1969).
31. Y. Hinatsu and N. Edelstein, *J. Solid State Chem.*, in press.
32. There are a number of different conventions used for the crystal field parameters. We believe that for the f^1 system the strong crystal field convention using parameters Δ and Θ is the most convenient. Some researchers use the formalism which is used in the theory of tensor operators. The parameters B_k^q have the relationship given by the equations $b_4 = B_0^4/33$, $b_6 = (-5/429)B_0^6$, $\Theta = 8b_4 - 56b_6$, and $\Delta = 10b_4 + 84b_6$. From these equations, $B_0^4 = 15{,}291\ cm^{-1}$ and $B_0^6 = 1403\ cm^{-1}$ are obtained.
33. C. A. Hutchison, Jr., and G. A. Candela, *J. Chem. Phys.* **27,** 707 (1960).