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Magnetic Susceptibilities of UO_2–ThO_2–ZrO_2 Solid Solutions

YUKIO HINATSU[1] AND TAKEO FUJINO

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

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Magnetic susceptibilities were measured from 2.2 K to room temperature for solid solutions of UO_2–ThO_2–ZrO_2 of which the lattice parameters are the same as that of UO_2, i.e., $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions. The Néel temperature decreases linearly with decreasing uranium concentration, the critical concentration being 69 mole% UO_2. The Néel temperatures of the present solid solutions are nearly in the middle of UO_2–ThO_2 solid solutions and UO_2–ZrO_2 solid solutions, which indicates that the magnetic dilution effect of ZrO_2 is larger than that of ThO_2. The effective magnetic moment decreases with decreasing uranium concentration, which is due to a decrease in the magnetic interactions with adjacent uranium ions, not due to a change of the strength of crystalline field. The Weiss constant decreases almost linearly with decreasing uranium concentration.

Introduction

Uranium dioxide crystallizes in the well-known fluorite structure in which U^{4+} ions order antiferromagnetically below ca. 30 K. According to neutron diffraction study (*1*), the antiferromagnetism is of type I that the magnetic moments of uranium ions are in the planes of ferromagnetic layers perpendicular to a crystal axis with the moments of each plane antiparallel to those of the neighboring planes. Another fact is that the paramagnetic–antiferromagnetic transition is of the first-order. Allen (*2, 3*) regarded the first-order transition as a consequence of a strong Jahn–Teller interaction between the ground triplet state and the lattice, which is comparable in magnitude to the exchange interaction between the neighboring uranium ions.

The magnetic studies on UO_2–ThO_2 solid solutions have revealed that the configuration of the valence electrons of uranium is $5f^2$ (*4, 5*) and that the paramagnetic ground state of the uranium ion in UO_2 is triplet (*6*). White and Sheard (*7*) measured the linear coefficient of thermal expansion of UO_2 and UO_2–ThO_2 solid solutions, and ascertained the magnetic transition at $T_N = 30.4$ K in UO_2 to be a first-order transition, which supports the theory of the first-order transition proposed by Allen. By measuring the intensity of the (100) magnetic reflection in neutron diffraction on both UO_2–ThO_2 and UO_2–ZrO_2 solid solutions, Sabine *et al.* (*8*) determined the Néel temperatures and localized magnetic moments on the uranium ions, and showed that the results were consistent with the spin–lattice interaction model.

In preceding papers (*9, 10*), we reported the variation of magnetic moment (μ_{eff}), Weiss constant (θ), and Néel temperature (T_N) with uranium concentration for UO_2–

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[1] To whom all correspondence should be addressed.

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ThO_2 and UO_2–ZrO_2 solid solutions. In both the solid solutions, the Néel temperature decreased linearly to the critical concentration with decreasing uranium concentration. The magnetic moment also decreased with dilution, which was considered to be due to decrease of the number of adjacent uranium ions. The linear relation between the Weiss constant and uranium concentration was shown by assuming that the exchange interaction for any one U^{4+} ion is proportional to the number of nearest and next-nearest neighbor U^{4+} ions.

In each of these solid solutions, the lattice parameter of the cubic cell varies with composition. Since the distance between uranium ions is responsible for the antiferromagnetic interaction and the distance between uranium ion and oxygen ion influences the crystalline field, the mixing of the lattice parameter factor complicates the problem.

In this paper, we prepared the solid solutions of UO_2, ThO_2, and ZrO_2 with fluorite structure of which the lattice parameters were equal to that of UO_2 and measured their magnetic susceptibilities from 2.2 K to room temperature. The variation of magnetic moment, Weiss constant, and Néel temperature with uranium concentration was investigated. The effect of lattice parameter change on these magnetic parameters was discussed by comparing the results of present solid solutions with those of UO_2–ThO_2 and UO_2–ZrO_2 solid solutions.

Experimental

1. Sample Preparation

Samples were prepared by coprecipitation method. Chemically pure grade uranyl hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, thorium nitrate tetrahydrate, $Th(NO_3)_4 \cdot 4H_2O$, and zirconyl chloride octahydrate, $ZrOCl_2 \cdot 8H_2O$, were weighed out to the intended atom ratios of uranium, thorium, and zirconium as shown in Table I, and these were dissolved in dilute nitric acid. Fine coprecipitates obtained by adding ammonia water were filtered, washed with dilute ammonium nitrate solution, dried, and preliminary calcined in air at ca. 800°C. The mixtures thus obtained were pressed into pellets and heated in flowing hydrogen at 1650°C for about 7 hr. After cooling to room temperature, the products were crushed into powder, repressed, and heated under the same conditions to make the reaction complete. These procedures were repeated twice.

2. X-Ray Diffraction Analysis

X-Ray diffraction experiments on the solid solutions were performed using Cu$K\alpha$ radiation with a Philips PW 1390 diffractometer with curved graphite monochromator. The lattice parameter of the samples were determined by the Nelson–Riley extrapolation method for diffraction lines above 80° (2θ).

3. Magnetic Susceptibility Measurement

Magnetic susceptibilities were measured by the Faraday-type torsion balance in the temperature range from 2.2 K to room temperature. The apparatus was calibrated with Mn-Tutton's salt ($\chi_g = 10{,}980 \times 10^{-6}/(T + 0.7)$) as a standard. The temperature of the sample was measured by "normal" Ag vs Au–0.07 at% Fe thermocouple and Au–Co vs Cu thermocouple. Details of the experimental procedure have been described elsewhere (*9*).

Results and Discussion

1. Lattice Parameter

UO_2 and ThO_2 form a $Th_{y_1}U_{1-y_1}O_2$ solid solution for the whole composition range. The lattice parameter for the solid solution is expressed by the equation (*9*)

$$a(\text{Å}) = 5.4704 + 0.127 y_1. \qquad (1)$$

TABLE I

MAGNETIC PARAMETERS FOR $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ SOLID SOLUTIONS

Solid solutions	a (Å)	μ_{eff} (B.M.)	θ (K)	T_N (K)
UO_2[a]	5.4704	3.12	−220	31.0
$Th_{0.070}Zr_{0.030}U_{0.90}O_2$	5.4698	3.03	−190	17.1
$Th_{0.105}Zr_{0.045}U_{0.85}O_2$	5.4702	3.02	−180	15.2
$Th_{0.140}Zr_{0.060}U_{0.80}O_2$	5.4700	3.00	−169	11.0
$Th_{0.175}Zr_{0.075}U_{0.75}O_2$	5.4705	2.99	−158	6.3
$Th_{0.210}Zr_{0.090}U_{0.70}O_2$	5.4708	2.97	−149	—

[a] Parameters for UO_2 are given in Ref. (*9*).

The solubility of ZrO_2 into UO_2 is known to increase up to ca. 40 mole% ZrO_2 at 1650°C (*11*). The lattice parameter for these $Zr_{y_2}U_{1-y_2}O_2$ solid solutions (*10*) is given by the equation

$$a(\text{Å}) = 5.4704 - 0.301y_2. \quad (2)$$

In the absence of atomic ordering, therefore, the lattice parameter for the $Th_{y_1}Zr_{y_2}U_{1-y_1-y_2}O_2$ solid solutions will be expressed by

$$a(\text{Å}) = 5.4704 + 0.127y_1 - 0.301y_2. \quad (3)$$

Equation (3) shows that the solid solutions of which the lattice parameters are the same as that of UO_2 should be formed by mixing the ThO_2 and ZrO_2 in a ratio nearly 7 : 3. In Table I are listed the lattice parameters for $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions prepared in this study. They were in good agreement with the value of UO_2, which indicates that Th^{4+} and Zr^{4+} locate randomly at cation sites in the fluorite structure.

2. *Magnetic Susceptibility*

The results of magnetic susceptibility measurements are shown in Figs. 1 and 2. From the reciprocal susceptibility versus temperature curves in Fig. 1, the Curie–Weiss law is seen to hold in the wide temperature range from ca. 30 K to room temperature. The magnetic moment and Weiss constant are listed in Table I. Figure 2 indicates the temperature dependence of magnetic susceptibility in a lower temperature region. Solid solutions of which the uranium concentration, C, is 0.75 ~ 0.90, showed antiferromagnetic transition at low temperatures. It is characteristic for the solid solutions showing antiferromagnetic transition that the susceptibilities are almost constant in some temperature ranges below T_N. Because similar results have been obtained for UO_2–ThO_2 solid solutions (*6, 9*) and UO_2–ZrO_2 solid solutions (*10*), these constant magnetic susceptibilities are not due to the variation of lattice parameter and also insensitive to the kind of diamagnetic diluents.

3. *Néel Temperature*

In Fig. 3 is plotted the Néel temperature against uranium concentration. The Néel temperature decreases linearly with uranium concentration as in the case of UO_2–ThO_2 solid solutions (*9*) or UO_2–ZrO_2 solid solutions (*10*), though the point for $C = 0.9$ deviates slightly from the straight line. This indicates that the static ground state of U^{4+} is not singlet, but triplet, since the singlet ground state mechanism shows sharp curvature in T_N versus uranium concentration curve and a steep drop to much higher critical concentration (*6, 12*).

The difference in the Néel temperatures between the two solid solutions, UO_2–ThO_2 and UO_2–ZrO_2, suggests that the electronic structure of diamagnetic metal ions, i.e., $[Rn]5f^0$ and $[Kr]4d^0$ for Th^{4+} and Zr^{4+}, respectively, influences the dilution effect more than the lattice parameter. Otherwise, the Néel temperatures for UO_2–ZrO_2 solid solutions would be higher than those for UO_2–ThO_2 solid solutions, for the U^{4+}–U^{4+} distances in the former solid solutions are shorter than those in the latter. If composition ratio is taken into account, the Néel temperatures for $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions are between UO_2–ThO_2 and UO_2–

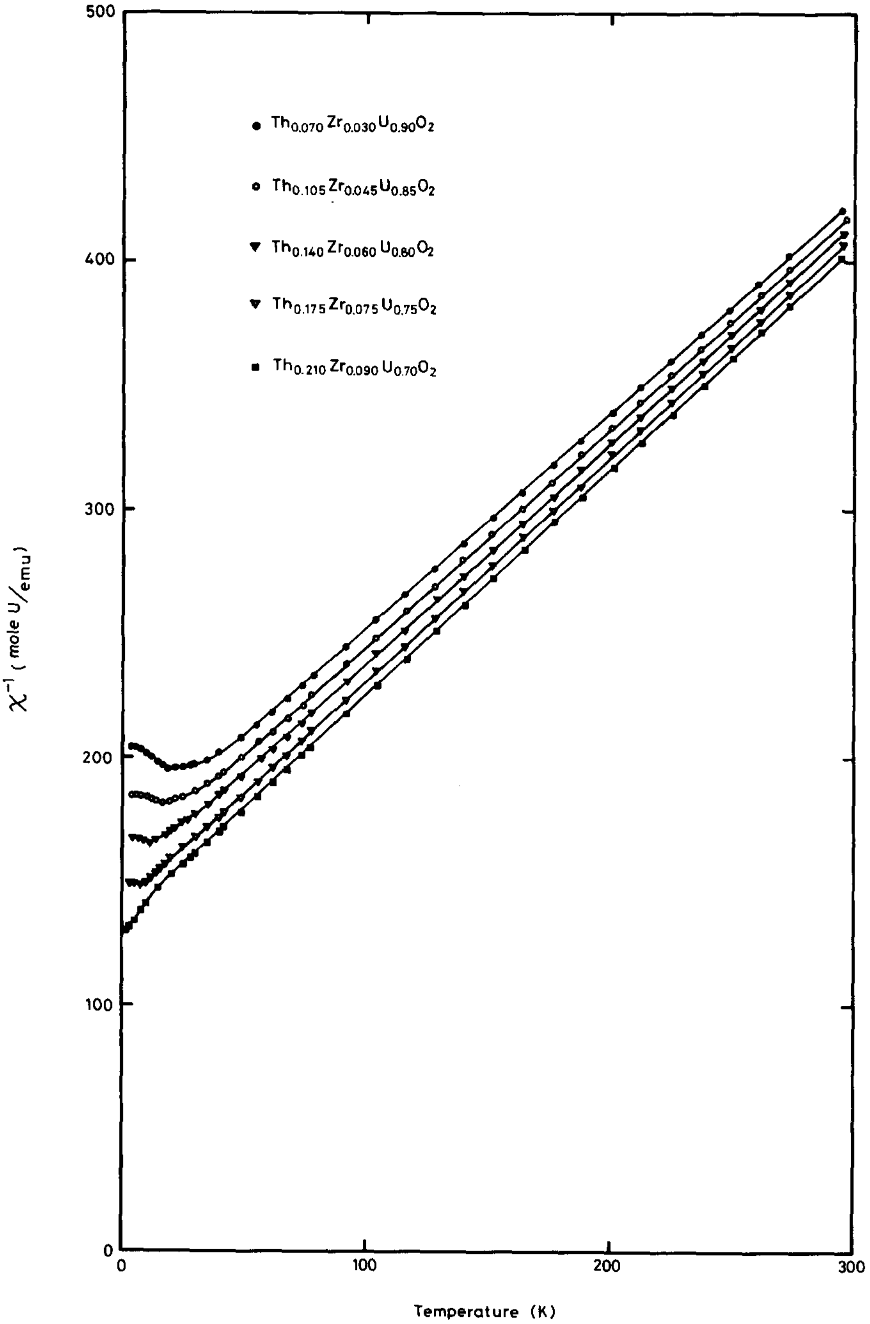

FIG. 1. Reciprocal magnetic susceptibility vs temperature.

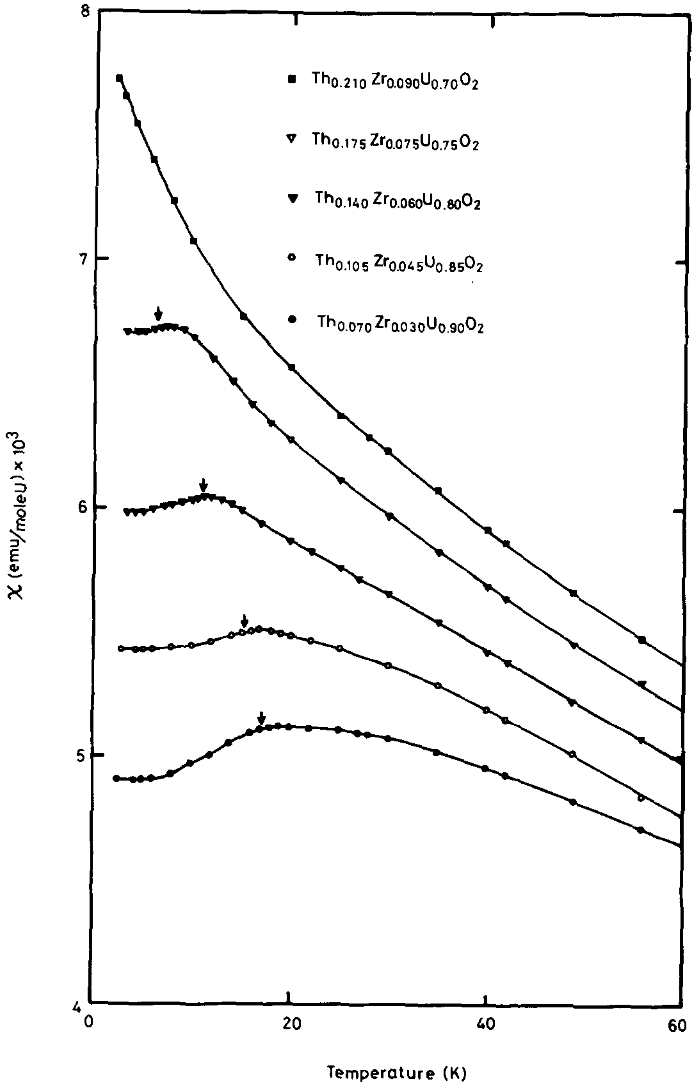

FIG. 2. Magnetic susceptibility vs temperature in lower temperature region. Downward arrows show T_N.

ZrO_2 solid solutions, and are anticipated to be nearer to those for UO_2–ThO_2 solid solutions than those for UO_2–ZrO_2 solid solutions. However, the experimental results in Fig. 3, show that the Néel temperatures fall to nearly middle points between them, which is considered to be due to the larger dilution effect of ZrO_2. The critical concentration, C_0, at which antiferromagnetism disappears for $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions, was obtained to be $C_0 = 0.69$ by extrapolation in Fig. 3, though the antiferromagnetic transition has not been observed in $Th_{0.21}Zr_{0.09}U_{0.70}O_2$ solid solutions. As the Néel temperature is estimated to be ca. 1.2 K for this solid solution, it is reasonable that the transition has not been observed in our experimental temperature range. This critical concentration is much higher than the theoretical values for face-centered cu-

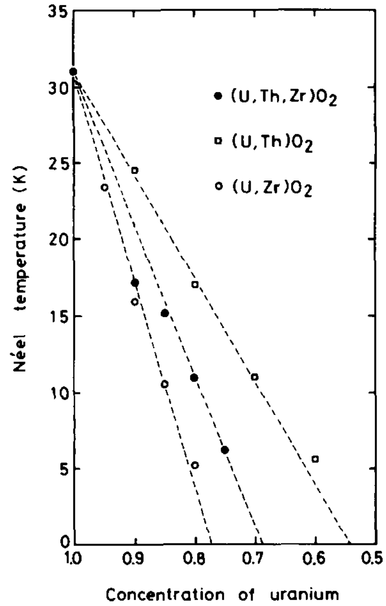

FIG. 3. Néel temperature vs uranium concentration.

bic lattice (*13–19*). The reason for this, we believe, is that the theoretical calculations do not take into account superexchange interactions where the paramagnetic ions are largely distant between each other and interact via anions such as oxygen ions intervening between them. We must consider the case of superexchange interactions, because in the fluorite structure the nearest-neighbor actinide ions are in an unfavorable orientation for direct $5f$–$5f$ overlap (*20*).

4. *Magnetic Moment*

The variation of magnetic moment with concentration of uranium is shown in Fig. 4. The magnetic moment was determined in the temperature range where the Curie–Weiss law holds. Data for UO_2–ThO_2 solid solutions (*9*) and for UO_2–ZrO_2 solid solutions (*10*) are also shown in this figure. The figure indicates that the magnetic moment decreases in all cases with decreasing uranium concentration. It is evident that the U^{4+}–U^{4+} distance (crystalline field) has no major effect on the variation of magnetic moment. If this is the case, the variation of magnetic moment with uranium concentration would be reversed in sign between UO_2–ThO_2 and UO_2–ZrO_2 solid solutions. This is ascertained by $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions which give decreasing magnetic moments in spite of unchanged lattice parameters. The reason for the larger magnetic moment in the case of solid solutions compared to the theoretical value for the ground state configuration of $5f^2$ perturbed by the crystalline field with cubic symmetry is believed to be due to the increased effect of adjacent uranium ions as reflected in the increase of Néel temperature with uranium concentration (Fig. 3). Larger magnetic moments observed in UO_2–ThO_2 solid solutions compared to those of UO_2–ZrO_2 solid solutions are consistent with higher Néel temperatures of UO_2–ThO_2 solid solutions, which indicates that the dilution effect is smaller in UO_2–ThO_2 than in UO_2–ZrO_2 solid solutions.

If no interaction exists between two kinds of paramagnetic ions in different electronic states, the magnetic moment is expressed as in the equation

$$\mu_{\text{eff}}^2 = C \cdot \mu_{\text{eff}}^{\text{I}2} + (1 - C) \cdot \mu_{\text{eff}}^{\text{II}2}, \quad (4)$$

where $\mu_{\text{eff}}^{\text{I}}$ and $\mu_{\text{eff}}^{\text{II}}$ represent the magnetic moments in electronic states I and II, respectively, and C is a ratio of paramagnetic

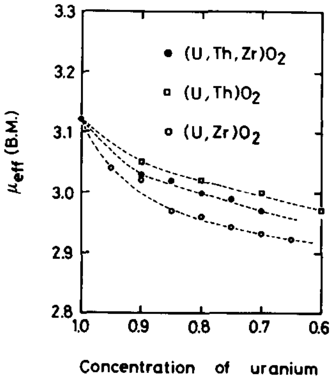

FIG. 4. Magnetic moment vs uranium concentration.

ion in electronic state I. Then, the magnetic moment of $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions will be given by

$$\mu^2_{\text{eff}}(Th_{0.7y}Zr_{0.3y}U_{1-y}O_2) = 0.7 \cdot \mu^2_{\text{eff}}(Th_yU_{1-y}O_2) + 0.3 \cdot \mu^2_{\text{eff}}(Zr_yU_{1-y}O_2), \quad (5)$$

where $\mu_{\text{eff}}(Th_{0.7y}Zr_{0.3y}U_{1-y}O_2)$, $\mu_{\text{eff}}(Th_yU_{1-y}O_2)$, and $\mu_{\text{eff}}(Zr_yU_{1-y}O_2)$ represent the magnetic moments of $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$, $Th_yU_{1-y}O_2$, and $Zr_yU_{1-y}O_2$ solid solutions, respectively. This equation indicates that the magnetic dilution effects by ThO_2 and ZrO_2 are additive in the paramagnetic temperature region. As shown earlier, the experimental Néel temperature for $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions was nearly in the middle of UO_2–ThO_2 and UO_2–ZrO_2 solid solutions. However, the magnetic moment was observed to satisfy the proportional distribution of the composition ratio as expressed by Eq. (5). The reason for this fact is considered as follow: below the Néel temperature, the magnetic interaction between uranium ions is predominant, whereas the magnetic moment was determined in the paramagnetic temperature range where the Curie–Weiss law holds. In this higher temperature range, the magnetic interaction between uranium ions is sufficiently weaker than the crystalline field effect.

Accordingly, two factors may contribute to the magnetic moment. Of these the major is calculated from the model in which a central uranium ion is in a crystalline field produced by eight oxygen ions, and the minor factor is the one to be derived by considering the interaction between U^{4+} ions which is dependent on the concentration of uranium ion.

5. *Weiss Constant*

The variation of Weiss constant with concentration of uranium is shown in Fig. 5. In this figure are also shown the data for UO_2–ThO_2 solid solutions (*9*) and UO_2–ZrO_2 solid solutions (*10*). The Weiss constants of $Th_{0.7y}Zr_{0.3y}U_{1-y}O_2$ solid solutions do not differ much from those of UO_2–ThO_2 and UO_2–ZrO_2 solid solutions. Roughly speaking, it can be taken that the Weiss constant decreases linearly with decreasing uranium concentration. This linearity can be explained by assuming that the exchange interaction for any one U^{4+} ion is proportional to the number of nearest and next-nearest neighbor U^{4+} ions (*9*).

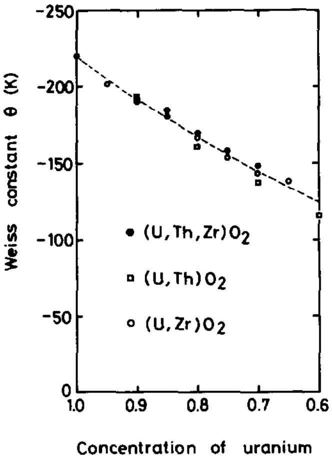

FIG. 5. Weiss constant vs uranium concentration.

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