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Magnetic Susceptibilities of UO_2–ThO_2 Solid Solutions

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The magnetic susceptibility of UO_2–ThO_2 solid solutions has been measured from room temperature to 2.0 K. The magnetic moment and the Weiss constant have been determined in the temperature range in which the Curie–Weiss law holds. For the solid solutions showing antiferromagnetic transition, the Néel temperature has been also determined. These values decrease monotonically with increasing ThO_2 concentration. The results were analyzed using the molecular field theory which includes the interaction between next-nearest neighbor spins. The interactions between nearest neighbor spins, J_1, and those between next-nearest neighbor spins, J_2, both decrease with increasing ThO_2 concentration. The change of J_1 with composition is larger than that of J_2. The effect of magnetic dilution with ThO_2 is considered to be stronger on the interaction between nearest neighbor uranium ions.

Introduction

The magnetic susceptibilities of UO_2–ThO_2 solid solutions have been measured by several researchers. Slowinski and Elliott (*1*) measured the magnetic susceptibilities in the temperature range of 66 ~ 296 K, and showed that the solid solutions obey the Curie–Weiss law. They also showed that the magnetic moment of the U^{4+} ion decreases with dilution with ThO_2 and approaches the "spin only value." The configuration of the valence electrons of the uranium ion was considered to be $6d^2$, because the quenching of the orbital angular mometum, which is characteristic of the *d* electrons, was thought to be responsible for the observed magnetic moment. Contrary to that, Hutchison and Candela (*2*) indicated that this "spin only value" could be interpreted in terms of a ground state configuration of $5f^2$ perturbed by the crystalline field with cubic symmetry. After a decade, Comly (*3*) made the magnetic susceptibility measurements down to 1.7 K. His results on the diluted samples of 5 ~ 10 mole% UO_2 in ThO_2 were explained on the basis of the paramagnetic ground state of the U^{4+} ion in UO_2 to be not singlet, but triplet, which was in accord with the results of the spin–wave dispersion branch experiments (*4*). Comly also observed a linear dependence of Néel temperature, T_N, on the concentration in the 60 ~ 100 mole% concentrated range of UO_2. By extrapolation, the critical concentration, at which antiferromagnetism disappears, was found to be 58 mole% UO_2.

However, there are some problems left to be clarified:

(*1*) *The problem of whether the reaction*

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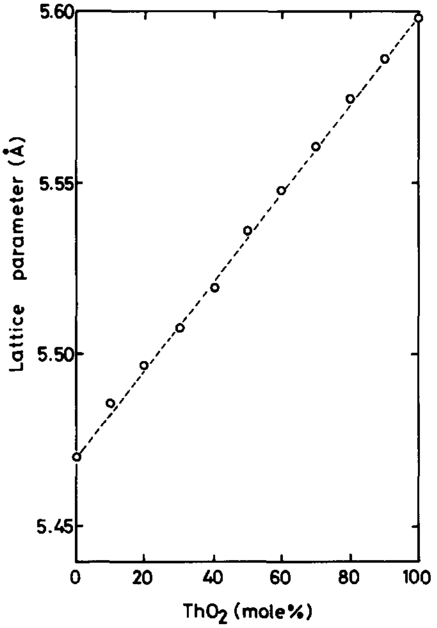

FIG. 1. Variation of lattice parameter with composition.

to form the solid solutions was complete or not. Regarding the relation between lattice parameter and composition, it has been known that the solid solutions of UO_2–ThO_2 obey Vegard's law, whereas at very high concentrations of UO_2, Cohen and Berman (*5*) reported deviation from the linearity. The lattice parameters of the samples used for magnetic susceptibility measurements by Trzebiatowski and Selwood (*6*) show scattering, and the samples of Slowinski and Elliott (*1*) were prepared by heating at 1000 ~ 1200°C for 2 ~ 4 hr. These reaction temperatures seemed not to be sufficiently high for forming UO_2–ThO_2 solid solutions.

(*2*) *Change of magnetic moment and Weiss constant with composition.* There have been few reports concerning this point. The magnetic moment obtained by Slowinski and Elliott (*1*) does not change up to 25 mole% ThO_2, whereas the Weiss constant decreases monotonically with increasing ThO_2 concentration (*1, 6, 7*).

(*3*) *Néel temperature change with composition.* According to the recent data of neutron diffraction (*8*) and thermal expansion (*9*) measurements, the linear dependence of T_N on the concentration of ThO_2 does not hold at high concentrations, which is inconsistent with magnetic susceptibility data (*3*).

We report here the results of the magnetic susceptibility measurements for UO_2–ThO_2 solid solutions prepared at 1650°C. The temperature range of the measurements was from room temperature to 2.0 K. In this paper, we will discuss the variation of three magnetic parameters, i.e., magnetic moment (μ_{eff}), Weiss constant (θ), and Néel temperature (T_N) with the concentration of uranium ion. The molecular field theory which includes interaction between next-nearest neighbor spins is used for discussing the results.

Experimental

1. Sample Preparation

Samples were prepared by the coprecipitation method. Chemically pure grade reagents of uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) and thorium nitrate tetrahydrate ($Th(NO_3)_4 \cdot 4H_2O$) were weighed out to the intended U/Th ratios, dissolved in water, and stirred well. By adding ammonia water, an intimate mixture of ammonium diuranate and thorium hydroxide was obtained. The precipitate was washed with dilute ammonium nitrate solution, dried, and preliminarily calcined in air. The mixtures thus obtained were pressed into pellets and reduced at 1650°C in flowing hydrogen for about 7 hr. After cooling, the samples were crushed into powder, repressed, and reduced under the same conditions.

2. X-Ray Diffraction Measurements

X-Ray diffraction study on the solid solutions was performed using Cu*Kα* radiation with a Philips PW 1390 diffractometer with curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson–Riley extrapolation method to the diffraction lines.

3. *Magnetic Susceptibility Measurements*

Magnetic susceptibility was measured by using the Faraday type torsion balance in the temperature range from room temperature to 2.0 K. The apparatus was calibrated with Mn–Tutton's salt ($\chi_g = 10980 \times 10^{-6}/T + 0.7$) as a standard. The temperature of the sample was measured by a "normal" Ag vs Au–0.07 at% Fe thermocouple (*10*) and an Au–Co vs Cu thermocouple. In order to minimize the error in measuring temperatures of the samples, the thermocouples were attached to the sample holder. Rapid thermal equilibrium was attained around the sample, by introducing helium gas into the system up to ca 10 mm Hg. To examine the field-dependence, magnetic susceptibilities were measured in each of the field strengths of 4700, 6900, 9000, and 10600 G. The measurements were also made on the blank quartz tube under the same conditions as in the case containing the samples. The magnetic susceptibilities for the samples were corrected for the blank, but not for the temperature-independent paramagnetism.

Results and Discussion

Figure 1 shows the variation of the lattice parameters of the samples used in this study. These solid solutions have a fluorite-type structure, and obey Vegard's law; the lattice parameters change linearly in the whole range of ThO_2 concentration between 5.4704 Å for UO_2 and 5.5975 Å for ThO_2.

The magnetic susceptibilities per mole uranium ion as a function of temperature for UO_2 and for the solid solutions in concentrated UO_2 range, i.e., $Th_{0.1}U_{0.9}O_2$, $Th_{0.2}U_{0.8}O_2$, $Th_{0.3}U_{0.7}O_2$, and $Th_{0.4}U_{0.6}O_2$ are shown in Fig. 2. For the solid solutions in the dilute range, the inverse magnetic susceptibilities per mole uranium ion versus temperature are shown in Fig. 3. For all the solid solutions examined here, the Curie–Weiss law holds over the temperature range from liquid nitrogen temperature to room temperature.

In the previous reports, the Weiss constant decreased with increasing ThO_2 concentration, but the magnetic moment obtained by Slowinski *et al.* (*1*) did not vary up up 25 mole% ThO_2. However, the Néel temperature, as will be described later, decreased monotonically with increasing ThO_2 concentration (*3, 8, 9*). Therefore, the magnetic moment is also expected to vary at low ThO_2 concentrations. In Fig. 4, the magnetic moment determined in this work is plotted as a function of ThO_2 concentration. The magnetic moment decreases monotonically with increasing ThO_2 concentration. The magnetic moment of the U^{4+} ion infinitely diluted in ThO_2 is 2.78 B.M.[1] from Fig. 4, which is a little lower than that obtained by Slowinski *et al.* (*1*) and slightly larger than that of an infinitely diluted solid solution in UP–ThP system (*11*). Because the theoretical value of the moment for the ground state configuration $5f^2$ perturbed by the crystalline field with cubic symmetry is 2.83 B.M., our experimental moment agrees well with the theoretical value which is for the uranium ion without any magnetic interaction with the adjacent uranium ions. The larger magnetic moment in the concentrated range of UO_2 in Fig. 4 is due to the increased effect of adjacent uranium ions in this range as with the case of Fe_2O_3–Al_2O_3 (*12, 13*).

The effect of dilution on the Weiss constant, θ, is also shown in Fig. 4. There exists a nearly linear relation between θ and the concentration of uranium ions. In gen-

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[1] B.M.—Bohr magneton.

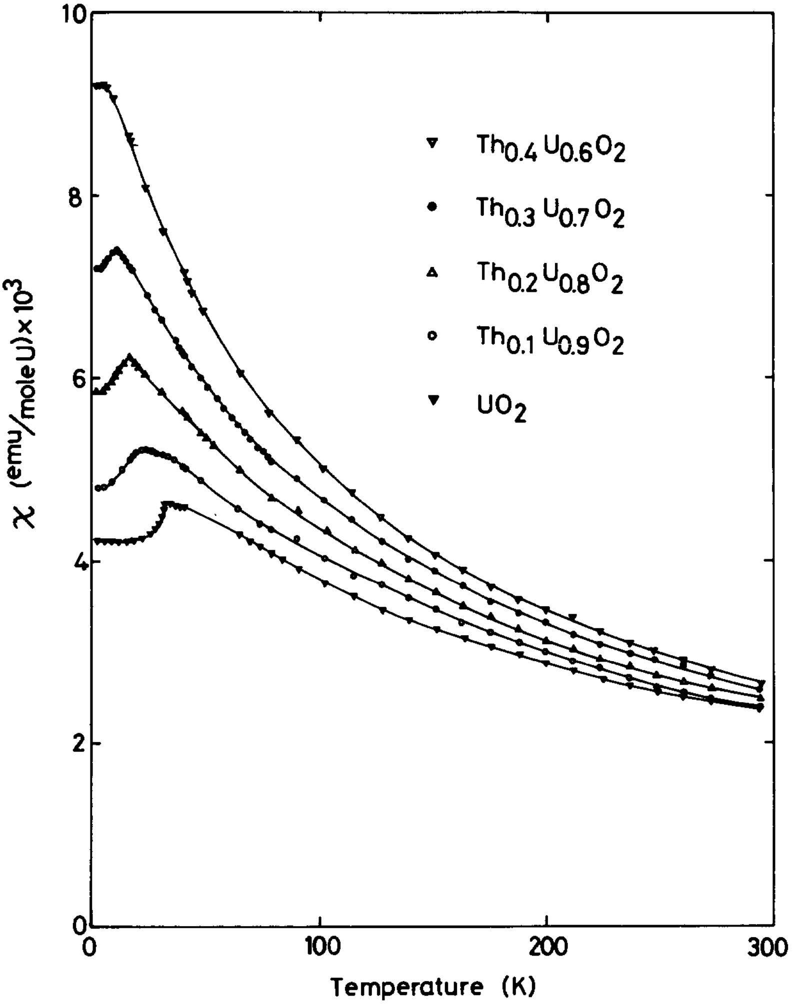

FIG. 2. Magnetic susceptibilities per mole uranium ion versus temperature for the solid solutions of the concentrated UO_2 range.

eral, the Weiss constant is indicative of the magnitude of the magnetic exchange interaction, so it can be said that as the ThO_2 concentration increases, the interaction is weakened. The linear dependence can be obtained 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.

First, we consider only nearest neighbor spins (*14*). The U^{4+} ions are divided into groups having 0, 1, · · · , 12 nearest neighbors. The average value of θ will then be given by

$$\bar{\theta} = \sum_{k=0}^{12} f_k \cdot k \cdot \delta, \quad (1)$$

where f_k is the fraction of the U^{4+} ions having k U^{4+} nearest neighbors and δ represents the contribution to the total θ of one of the equivalent nearest neighbors. The fraction f_k is expressed as

$$f_k = \frac{12!}{k! \cdot (12 - k)!} x^k \cdot (1 - x)^{12-k}, \quad (2)$$

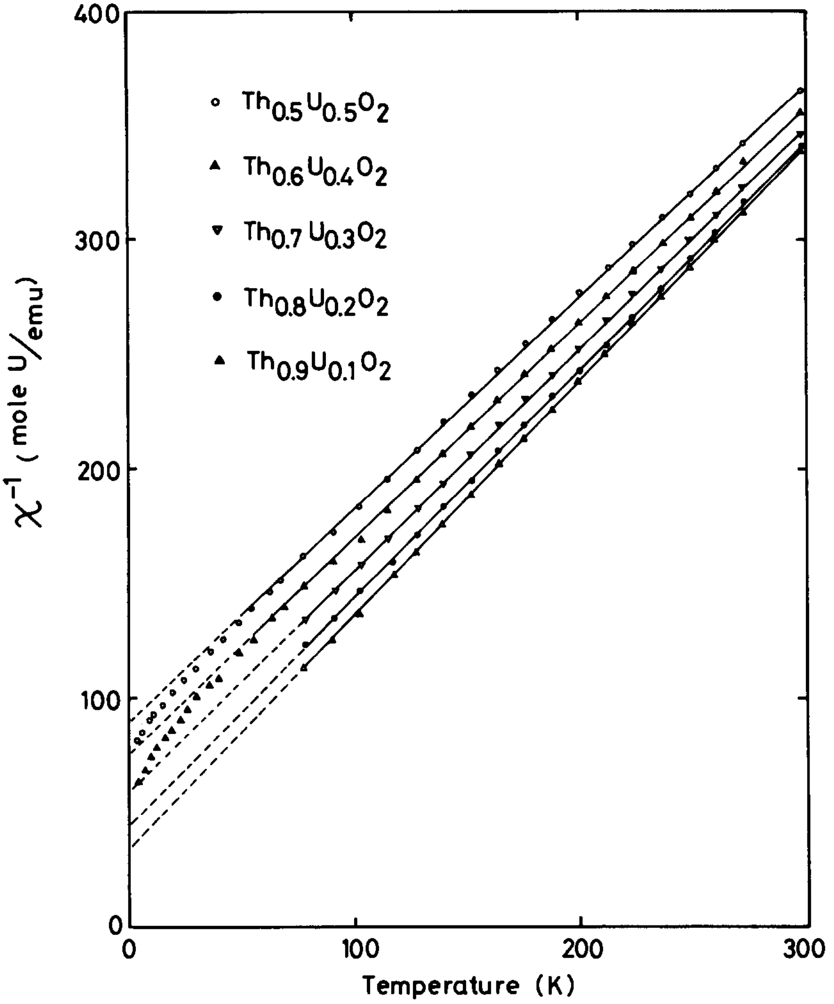

FIG. 3. Inverse magnetic susceptibilities per mole uranium ion versus temperature for the solid solutions of the dilute UO_2 range.

where x is the mole fraction of UO_2. By direct summation, $\bar{\theta}$ is obtained as

$$\bar{\theta} = x \cdot 12\delta = x \cdot \theta_{\text{pure } UO_2}. \qquad (3)$$

In the case where next-nearest neighbor interaction also significantly contributes to the Weiss constant, the average value of θ will be given by

$$\bar{\theta} = \sum_{k=0}^{12} f_k \cdot k \cdot \delta + \sum_{k=0}^{6} f'_k \cdot k \cdot \delta', \qquad (4)$$

where f'_k is the fraction of the U^{4+} ion having k U^{4+} next-nearest neighbors and δ' represents the contribution of one of the equivalent next-nearest neighbors to the total θ. The fraction f'_k is given by

$$f'_k = \frac{6!}{k! \cdot (6-k)!} x^k \cdot (1-x)^{6-k}. \qquad (5)$$

The average value of θ is obtained as

$$\begin{aligned} \bar{\theta} &= x(12\delta + 6\delta') \\ &= x \cdot \theta_{\text{pure } UO_2}. \end{aligned} \qquad (6)$$

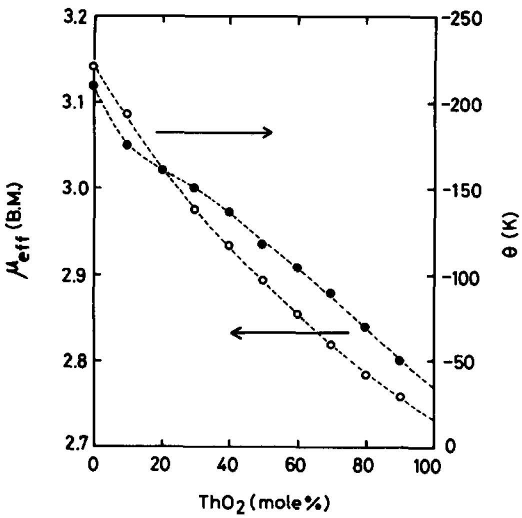

FIG. 4. Variation of magnetic moment and Weiss constant with composition.

Equation (6) shows that θ is a linear function of UO_2 concentration in the solid solutions even if the next-nearest interaction is taken into account. It also shows that the Weiss constant is zero if UO_2 is infinitely diluted with ThO_2. The experimental curves, however, do not approach 0 K at 100% ThO_2. This discrepancy has been observed fairly often in the other systems, and in some cases it is discussed by means of clustering of magnetic ions in the dilute limit (*11*, *15*), but there is no reason that clustering of uranium ions occurs in this case, i.e., Vegard's law holds in the lattice parameter change. It is likely that Van Vleck's temperature-independent susceptibility contributes to the experimental susceptibility to some extent. In this paper, however, this correction was not made because the error would be large and it seemed to have no quantitative meaning.

The variation of T_N with concentration of uranium ion is shown in Fig. 5. The data seem to be followed by a straight line which falls to $T_N = 0$ at ~54 mole% UO_2, although the point at 60% UO_2 deviates slightly from the line. According to the experimental results for the samples with 50% UO_2 shown in Fig. 3, antiferromagnetism does not appear at this concentration of the solid solution. From these facts, it can be safely estimated that the critical concentration is between 50 ~ 55 mole% UO_2. This value is close to the results of Comly and the linear dependence of T_N on concentration supports the idea that the static ground state of UO_2 is triplet (*3*, *16*). The T_N change in the UO_2–ThO_2 system has been also determined by the measurements of the linear thermal expansion coefficient (*9*) and by the measurements of intensity of the (100) magnetic reflection in neutron diffraction (*8*). These two reports indicated that a linear dependence of T_N on concentration does not hold at low UO_2 concentrations and that the critical concentration of uranium ion is lower than that determined by magnetic susceptibility measurements. The reason for this difference is not very clear, but one possibility is that the oxidation of

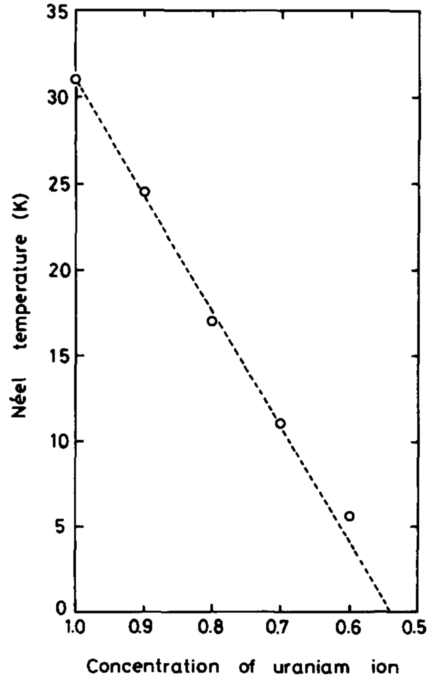

FIG. 5. Variation of Néel temperature with concentration of uranium ion.

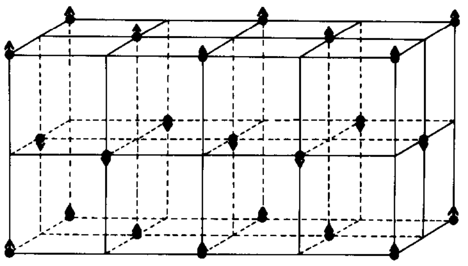

FIG. 6. Magnetic structure of UO_2. The directions of ordered moments on the uranium ions are depicted by arrows. Oxygen ions are not shown.

the solid solution during heating can be considered. The deviation from linearity is observed if U^{5+} ion is contained in the solid solution composed basically of U^{4+} ion (*17*).

The magnetic structure of UO_2 obtained by neutron diffraction experiments (*18–21*) is of type I as depicted in Fig. 6. Smart (*22*) gave the molecular field relation for θ and T_N in terms of two exchange interactions J_1 and J_2 for various lattices and for various types of order. J_1 and J_2 represent magnetic interactions between nearest neighbor spins and next-nearest neighbor spins, respectively. For face-centered cubic lattices with the first kind of magnetic ordering, the molecular field relations between T_N, θ, J_1, and J_2 are given by

$$T_N = \tfrac{2}{3}(S + 1)(-4J_1 + 6J_2), \tag{7}$$

$$\theta = \tfrac{2}{3}(S + 1)(12J_1 + 6J_2), \tag{8}$$

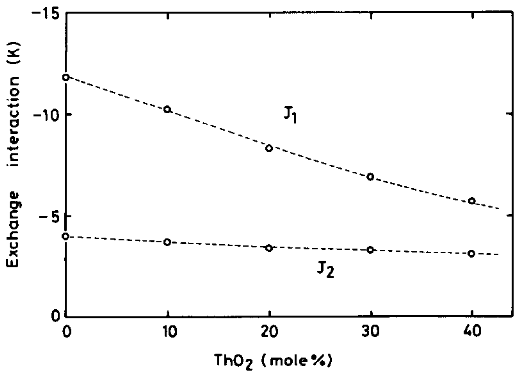

FIG. 7. Variation of J_1 and J_2 with composition.

TABLE I

MAGNETIC PARAMETERS OF $Th_yU_{1-y}O_2$ SOLID SOLUTIONS

Solid Solutions	μ_{eff} (B.M.)	θ (K)	T_N (K)	$\frac{\chi(T \to 0)}{\chi(T_N)}$	J_1 (K)	J_2 (K)
UO_2	3.12	−220	31.0	0.90	−11.8	−4.0
$Th_{0.1}U_{0.9}O_2$	3.05	−193	24.5	0.92	−10.2	−3.7
$Th_{0.2}U_{0.8}O_2$	3.02	−160	17.0	0.94	−8.3	−3.4
$Th_{0.3}U_{0.7}O_2$	3.00	−137	11.0	0.97	−6.9	−3.3
$Th_{0.4}U_{0.6}O_2$	2.97	−116	5.6	0.99_7	−5.7	−3.1

where J_1 and J_2 are given in Kelvin. It can be said that T_N is a lattice-dependent quantity which is a measure of the lowest energy of the magnetic ions in the lattice, whereas θ gives the strength of total interactions of which the signs are not considered. By using these equations, J_1 and J_2 can be obtained from the experimental values of T_N and θ. In Table I are listed the values of J_1 and J_2. The variation of J_1 and J_2 with composition is indicated in Fig. 7. Both J_1 and J_2 decrease monotonically with increasing ThO_2 concentration. This is considered to reflect the dilution effect with ThO_2. Compared to J_1, the value of J_2 decreases more slowly. This may be because the magnetic interaction between next-nearest uranium ions is through oxygen ions intervening between them. The effect of dilution with ThO_2 should be alleviated in the indirect interaction of J_2. Consequently, the effect would be much smaller on the interaction between next-nearest neighbor spins than on that between nearest neighbor spins.

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