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Magnetic Susceptibilities of UO_2–ZrO_2 Solid Solutions

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The magnetic susceptibility of cubic solid solutions of UO_2 and ZrO_2 with a fluorite structure has been measured from room temperature to 2.3 K. The magnetic moment and the Weiss constant have been determined in the temperature range where the Curie–Weiss law holds. These values decrease monotonically with increasing ZrO_2 concentration. The solid solutions of UO_2 diluted with 0 ~ 20 mole% ZrO_2 show an antiferromagnetic transition and have a linear dependence of Néel temperature on concentration, with a critical concentration of 78 mole% UO_2. The molecular field theory which includes next-nearest-neighbor interaction was applied to the results. The interaction between nearest-neighbor spins, J_1, decreases with increasing ZrO_2 concentration, whereas that between next-nearest-neighbor spins, J_2, increases. The behavior of J_1 against composition is thought to be caused from the direct effect of magnetic dilution with ZrO_2. Regarding the behavior of J_2, the effect of increasing magnetic interaction due to the smaller distance of uranium ions is considered to be stronger than the magnetic dilution effect.

Introduction

It is well known that UO_2 is paramagnetic, and changes to the antiferromagnetic state below 30.8 K (*1, 2*). Its antiferromagnetism is of type I, and the magnetic moments of uranium ions are in the planes of the ferromagnetic layers perpendicular to a crystal axis; the moments of each plane are antiparallel to those of the neighboring planes (*1–3*). On the other hand, ZrO_2 is a diamagnetic substance.

The magnetic study of UO_2–ZrO_2 solid solutions is interesting, because the lattice parameter of these cubic solid solutions with a fluorite structure decreases with increasing zirconium concentration, which is in contrast to the UO_2–ThO_2 solid solutions where the lattice parameter increases with thorium concentration. It is expected that the effect of lattice size on magnetic properties might become much clearer if the properties are compared in these two systems.

The magnetic susceptibility of $(U,Th)O_2$ has been measured by several investigators (*4–8*). However, that of $(U,Zr)O_2$ has not yet been reported. This is perhaps partly due to the lack of a reliable UO_2–ZrO_2 phase diagram and partly due to the difficulties in forming the solid solutions.

In this paper are reported the results of magnetic susceptibility measurement of $(U,Zr)O_2$ solid solutions from room temperature down to 2.3 K.

Experimental

1. Sample Preparation

Solid solutions $Zr_yU_{1-y}O_2$ with eight different y values of 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, and 0.35 were prepared. Chemi-

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cally pure grade uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$), and zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) were weighed to the intended ratio of uranium and zirconium, and were dissolved in water and well stirred. A fine coprecipitate of ammonium diuranate and zirconyl hydroxide was obtained by adding ammonia water. After filtering, the coprecipitate was washed with dilute ammonium nitrate solution, dried, and preliminarily calcined in air at 800°C. The mixture thus obtained was pressed into pellets and reduced at 1650°C in flowing hydrogen for about 7 hr. The samples were cooled to room temperature, crushed into powder, repressed, and reduced under the same conditions to make the reaction complete.

2. *X-Ray Diffraction Measurement*

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

3. *Magnetic Susceptibility Measurement*

Magnetic susceptibility was measured by a Faraday-type torsion balance in the temperature range from room temperature down to 2.3 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 "normal" Ag vs Au–0.07 at% Fe thermocouple (*9*) and Au-Co vs Cu thermocouple. Details of the experimental procedure were described elsewhere (*8*).

Results and Discussion

In spite of many investigations on the phase relation of UO_2–ZrO_2 (*10–15*), the agreement of these results is not necessarily good. According to the paper by Romberger *et al.* (*15*), only a very limited range of solid solutions can be formed at temperatures below 1500°C, which is due to the very considerable mismatch in ionic size between Zr^{4+} (= 0.794 Å) and U^{4+} (= 0.97 Å). However, at 1650°C the solubility of ZrO_2 into UO_2 increases up to 40 mole% ZrO_2.

Figure 1 shows the results of the present experiment. The lattice parameter change of $Zr_yU_{1-y}O_2$ with y can be fitted to a linear equation, $a_0(\text{Å}) = 5.4704 - 0.301y$, which is in good agreement with the values of Cohen *et al.* (*14*).

In Fig. 2 are shown inverse magnetic susceptibilities of UO_2 and the $Zr_yU_{1-y}O_2$ solid solutions with low y values, i.e., $y = 0.05 \sim 0.2$. In these temperature-dependence curves, the susceptibilities are given per mole uranium. Those for higher y values, i.e., $y = 0.25 \sim 0.35$, are shown in Fig. 3. Addition of ZrO_2 to UO_2 diminishes antiferromagnetic interaction as seen in the behavior of the Néel temperature, T_N.

The variation of T_N with concentration of uranium ion is depicted in Fig. 4. In this

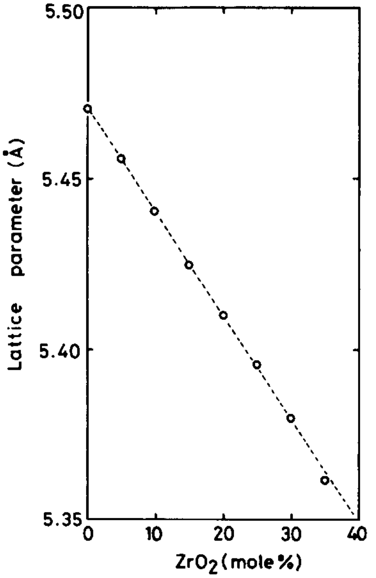

FIG. 1. Variation of lattice parameter of $Zr_yU_{1-y}O_2$ with composition.

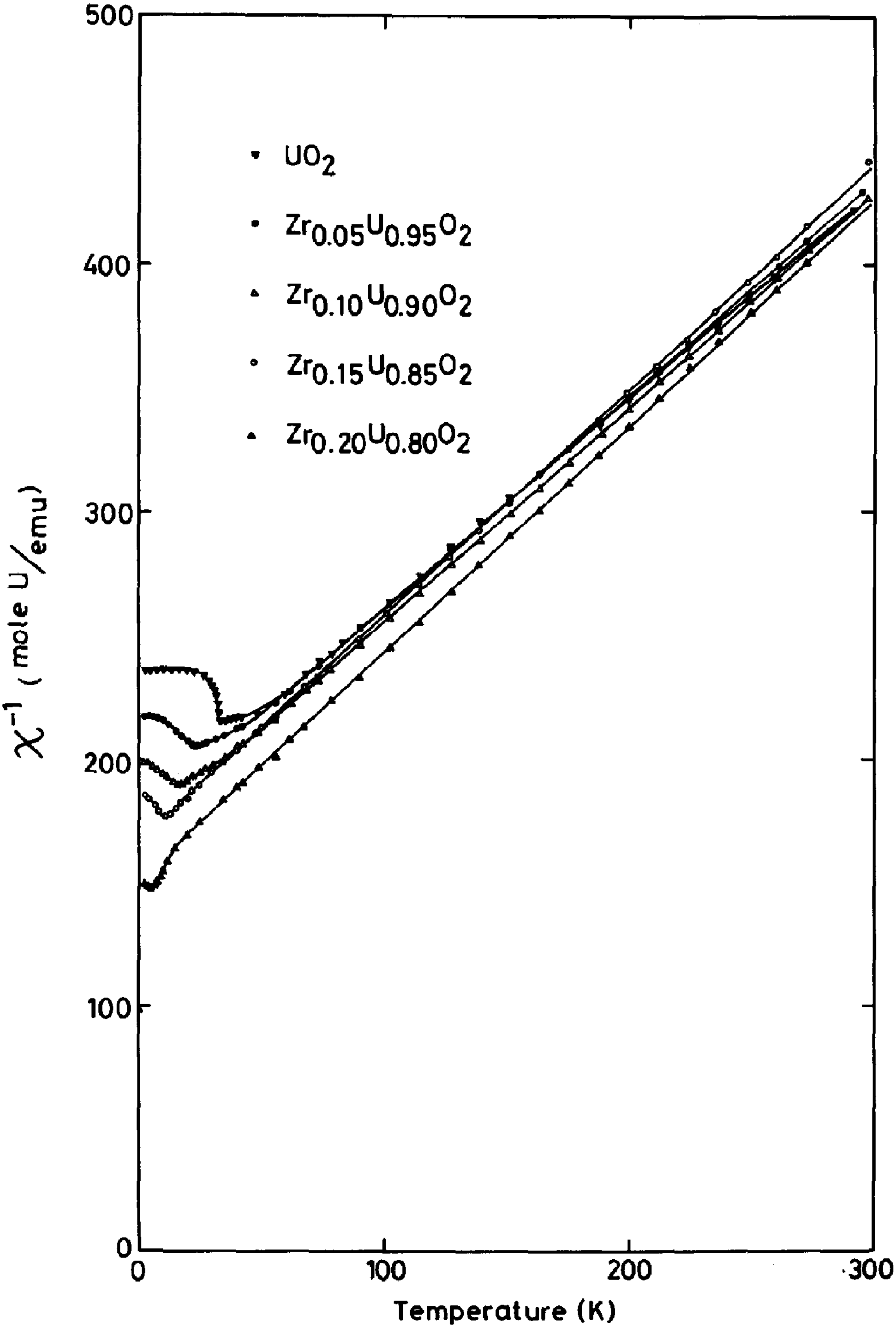

FIG. 2. Inverse magnetic susceptibilities per mole uranium versus temperature for solid solutions of $y = 0 \sim 0.20$.

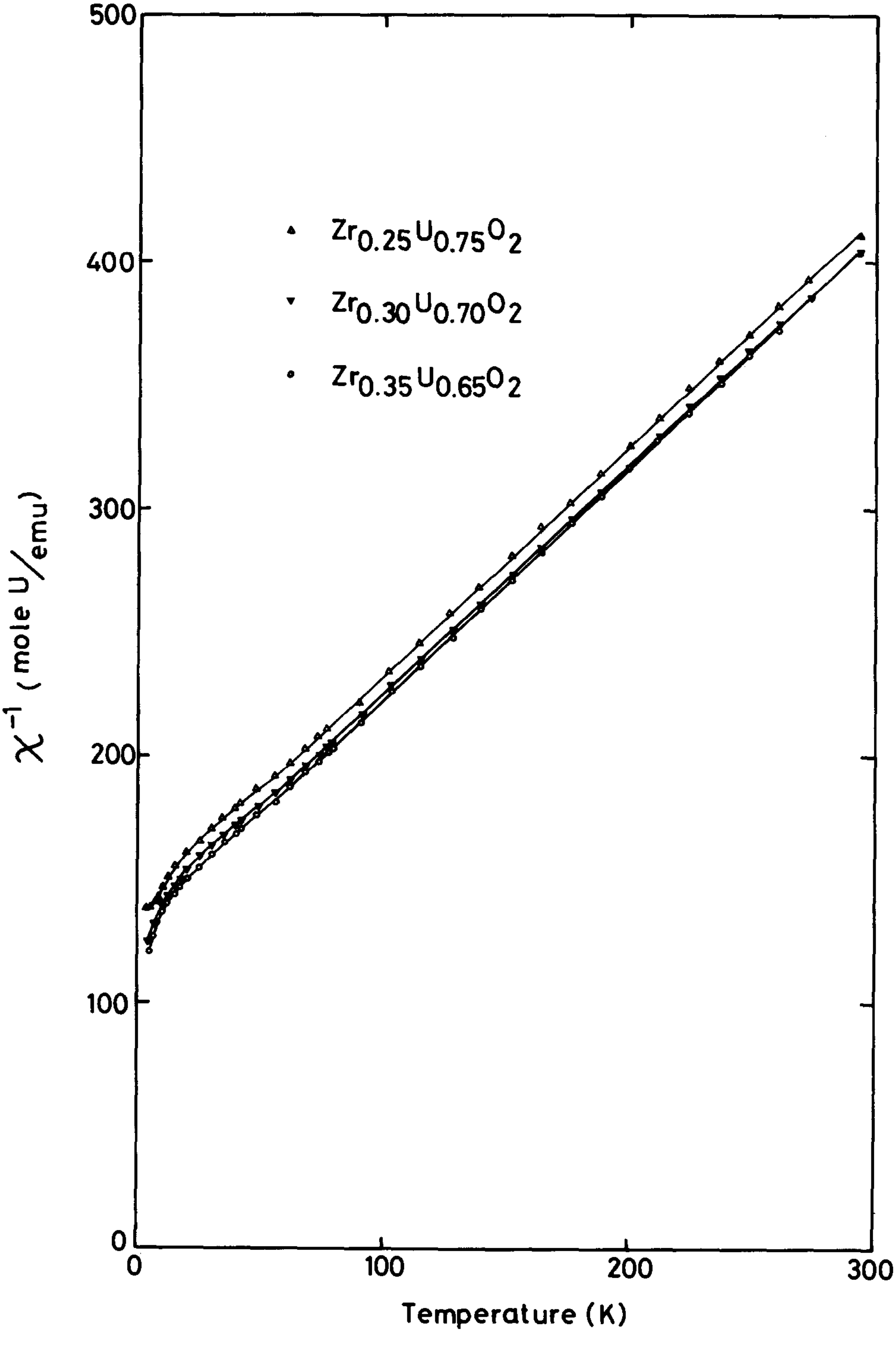

FIG. 3. Inverse magnetic susceptibilities per mole uranium versus temperature for solid solutions of $y = 0.25 \sim 0.35$.

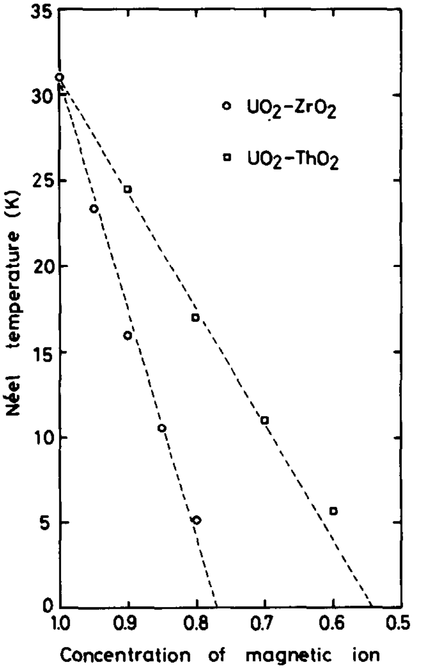

FIG. 4. Variation of Néel temperature with concentration of uranium ion.

figure is also shown the variation of T_N in UO_2–ThO_2 solid solutions. The figure shows that T_N decreases linearly to the critical concentration, at which antiferromagnetism disappears. This fact agrees with measurements on ordinary antiferromagnets and supports the static ground state of UO_2 to be triplet (*7*, *16*). The critical concentration, C, of magnetic ions is 0.78. This value is well in accord with ca. 0.8 of Sabine *et al.* (*17*) obtained by neutron diffraction methods.

The problem of localized moment types of magnetic ions diluted with nonmagnetic ions has been discussed by several researchers (*18–21*). If only nearest-neighbor interaction is considered, theoretical values of the critical concentration depend on the spin, S, per magnetic ion and the coordination number, Z, of each magnetic ion. Smart (*19*) gives

$$C = 1/(Z - 1), \tag{1}$$

whereas Elliott (*20*) gives a formula which for $S = 1$ reduces to

$$C = 2.4/(Z - 1). \tag{2}$$

The value experimentally obtained for the present system is much larger than that from these relations. Therefore, it seems that for this system we need to consider a model including more than nearest-neighbor interactions.

In Fig. 5 are plotted the magnetic moments calculated from the temperature range in which the Curie–Weiss law holds as a function of ZrO_2 concentration. The magnetic moment decreases with increasing ZrO_2 concentration. This is because the exchange interaction between magnetic ions is weakened due to isolation of uranium ions. Then, as the concentration of ZrO_2 increases, the magnetic moment of U^{4+} with two $5f$ unpaired electrons approaches to 2.828 B.M. which corresponds to that for a ground state configuration $5f^2$ perturbed by the crystalline field produced by eight oxygen ions located at the corners of a cube (*22*). The fact that the reduction of the magnetic moment in UO_2–ZrO_2 solid solutions is larger than that in UO_2–ThO_2

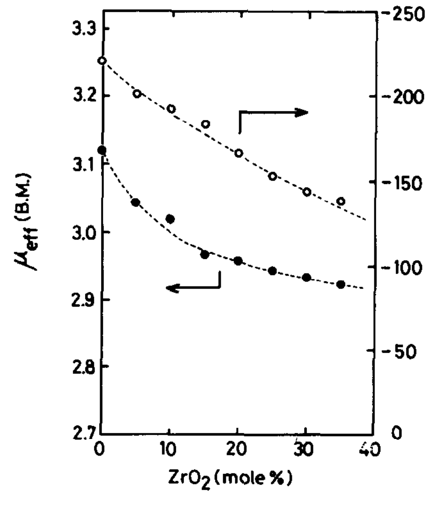

FIG. 5. Variation of magnetic moment and Weiss constant with composition.

solid solutions (*8*), together with the change of T_N against the concentration of magnetic ion, which is depicted in Fig. 4, shows that the effect of ZrO_2 diluent is stronger than that of ThO_2. The moment of UO_2 infinitely diluted with ZrO_2, however, could not be obtained because UO_2 and ZrO_2 do not form a continuous series of solid solutions at the experimental temperatures.

Next, we discuss the behavior of magnetic susceptibility below the Néel temperature. In the solid solutions with low ZrO_2 concentrations ($y = 0.05$ and 0.1), the decrease of magnetic susceptibilities ceases below some temperatures and they attain constant values, while in the solid solutions with higher ZrO_2 concentrations, the magnetic susceptibilities decrease monotonically with decreasing temperature. This behavior is somewhat different from that of UO_2–ThO_2 solid solutions where the susceptibilities attain constant values at very low temperatures in the whole range of uranium ion concentration examined.

The ratio of susceptibility at $T \rightarrow 0$ divided by that at $T = T_N$, $\chi(T \rightarrow 0)/\chi(T = T_N)$, was calculated for each concentration in Table I. All these values are much larger than $\frac{2}{3}$ which is derived for powder samples by Weiss's molecular field theory. In general, the following reasons can be considered for this type of misfit (*23*): (1) the incorrectness of Weiss's approximation for χ at $T = T_N$; (2) the existence of more than two sublattices; and (3) the effect of anisotropic energy and anisotropy in the *g* factor. In the compounds with face-centered cubic lattice as UO_2, we can by no means divide the lattice into two simple sublattices, each sublattice having the property that it contains no nearest neighbors of its own members, but all of the nearest neighbors of the members of the other sublattice. For this reason, Weiss's molecular field theory can not simply be applied to this case, and it is therefore reasonable that the experimental ratios do not satisfy Van Vleck's relation $\chi(T \rightarrow 0)/\chi(T = T_N) = \frac{2}{3}$.

TABLE I

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

Solid solutions	μ_{eff} (B.M.)	θ (K)	T_N (K)	$\frac{\chi(T \rightarrow 0)}{\chi(T_N)}$	J_1 (K)	J_2 (K)
UO_2	3.12	−220	31.0	0.90	−11.8	−4.0
$Zr_{0.05}U_{0.95}O_2$	3.04	−202	23.4	0.93	−10.6	−4.1
$Zr_{0.10}U_{0.90}O_2$	3.02	−192	15.9	0.95	−9.8	−4.5
$Zr_{0.15}U_{0.85}O_2$	2.97	−184	10.6	0.91	−9.1	−4.7
$Zr_{0.20}U_{0.80}O_2$	2.96	−166	5.2	[a]	−8.0	−4.7

[a] It is difficult to estimate $\chi(T \rightarrow 0)$.

The magnetic lattice for UO_2 is face-centered cubic; each U^{4+} ions has its twelve nearest neighbors along the face diagonals at distance $a_0/\sqrt{2}$, while the six next-nearest neighbors are along the cube edges at distance a_0. To obtain some knowledge of the exchange interactions, we use the molecular field approximation in which the interaction of the spins is isotropic. For face-centered cubic lattice with the first kind of magnetic ordering, the values of T_N and θ are expressed (*24*) as

$$T_N \simeq \tfrac{2}{3}S(S + 1)(-4J_1 + 6J_2), \qquad (3)$$

$$\theta \simeq \tfrac{2}{3}S(S + 1)(12J_1 + 6J_2), \qquad (4)$$

where J_1 and J_2 are the exchange interactions in (K) between nearest-neighbor spins and next-nearest-neighbor spins, respectively. By using these relations, one can make an estimate of J_1 and J_2 from the experimental values of T_N and θ. In Table I are listed the values of J_1 and J_2. The change of J_1 and J_2 is indicated in Fig. 6 as a function of ZrO_2 concentration. It is seen that J_1 decreases monotonically with increasing ZrO_2 concentration. From the significant decrease, it can be said that J_1 is a strong function of the number of nearest-neighbor magnetic ions. In contrast, the value of J_2 increases with ZrO_2 concentration. This means that the effect of an increase in the strength of magnetic coupling between next-nearest-neighbor uranium

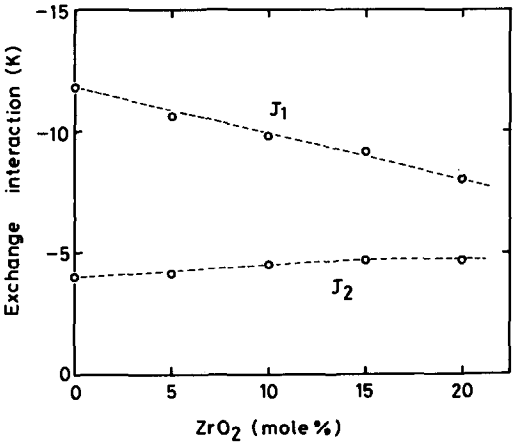

FIG. 6. Variation of J_1 and J_2 with composition.

ions due to smaller distance between them is larger than that of magnetic dilution with ZrO_2. If one may examine the system of which the lattice parameter increases with dilution, both J_1 and J_2 are expected to decrease monotonically. In fact in the case of $(U,Th)O_2$ solid solutions, both are observed to decrease (*8*). The facts described above suggest the following: The interaction between nearest-neighbor spins, J_1, is more affected by the magnetic properties of the nearest-neighbor metal ions than some variation (decrease) of lattice parameter. On the other hand, the interaction between next-nearest-neighbor spins, J_2, which is a superexchange interaction via oxygen ions, is predominantly affected by the distance of magnetic ion–oxygen ion–magnetic ion. In other words, the effect of magnetic dilution with ZrO_2 is not direct, but through oxygen ions on next-nearest-neighbor uranium ions. This is the reason that the effect of dilution with ZrO_2 is weaker than that from the change of lattice parameter.

In the molecular field approximation mentioned above, T_N is given as a linear combination of J_1 and J_2. With the dilution by ZrO_2, both J_1 and J_2 vary approximately linearly, which may cause a linear dependence of T_N with concentration of the U^{4+} ion in the solid solution.

In Fig. 5, the Weiss constant is also plotted against the mole% of ZrO_2. It decreases monotonically with increasing ZrO_2 concentration. Since the Weiss constant is generally indicative of the magnitude of the magnetic exchange interaction, it is read that the magnetic interaction is weakened as the concentration of ZrO_2 increases. In the region of UO_2–ZrO_2 solid solutions where we examined the magnetic properties, there exists an almost linear relation between the Weiss constant and the concentration of ZrO_2. This linearity can be shown in the same way as the case of UO_2–ThO_2 solid solutions (*8*) 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.

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