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Studies on Magnetic Properties of UO_2–CeO_2 Solid Solutions

II. Effect of Oxygen Nonstoichiometry on Magnetic Susceptibilities of Solid Solutions

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Magnetic susceptibilities of $Ce_yU_{1-y}O_{2+x}$ ($x \gtreqless 0$) solid solutions with fluorite structure were measured from 4.2 K to room temperature. An antiferromagnetic transition was observed for the oxygen-stoichiometric ($x = 0$) and deficient ($x < 0$) solid solutions with y values less than 0.40. The Néel temperatures of oxygen-deficient solid solutions are lower than those of oxygen-stoichiometric solid solutions with the same y value, which indicates that the formation of oxygen vacancies results in weakening the magnetic interactions between uranium ions. From the analysis of magnetic susceptibility data, it was found that some cerium ions are reduced to trivalent state for oxygen-deficient solid solutions, while some uranium ions are oxidized to pentavalent state for oxygen-excessive solid solutions.

Introduction

It is well known that oxygen nonstoichiometry exerts a strong effect on the thermodynamic behavior of oxide nuclear fuels. In uranium–plutonium mixed oxide fuel, $(U, Pu)O_{2+x}$, uranium is oxidized to a higher oxidation state for oxygen-hyperstoichiometric compositions ($x > 0$), and plutonium is said to be reduced to the trivalent state for oxygen-hypostoichiometric compositions ($x < 0$) (*1*). Because of the similarity of cerium to plutonium in chemical properties, and because of the difficulty in handling of plutonium, $(U, Ce)O_2$ solid solutions have often been used as a substitute for $(U, Pu)O_2$ solid solutions.

Uranium dioxide is a paramagnetic compound with two unpaired $5f$ electrons and changes to the antiferromagnetic state below the Néel temperature, $T_N = 30.8$ K (*2*). The transition from paramagnetic to antiferromagnetic state is first order and a sharp step-like decline of the magnetic susceptibility has been observed as the temperature is lowered through T_N. On the other hand, cerium dioxide, CeO_2, is diamagnetic. Therefore, the effect of oxygen nonstoichiometry on UO_2 and CeO_2 is considered to be very large, because the Néel temperature of UO_{2+x} is considerably lowered with increasing x value (*3–5*) and because oxygen-substoichiometric CeO_{2-x} is paramagnetic. Then, from the magnetic susceptibility measurements, we can expect to obtain the information concerning the electronic states of uranium and cerium ions in $(U, Ce)O_2$ solid solutions.

In this study, we prepared the solid solutions with cubic fluorite structure, Ce_yU_{1-y}

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O_{2+x}, with various x and y values, and measured their magnetic susceptibilities from 4.2 K to room temperature. By comparing the results obtained here with those of oxygen-stoichiometric (U, Ce)O_2 solid solutions ($x = 0$) (*6*), the effect of oxygen nonstoichiometry on magnetic properties of the solid solutions was examined.

Experimental

1. Sample Preparation

UO_2 and CeO_2 were used as starting materials. Before use, UO_2 was reduced to the stoichiometric composition in flowing hydrogen at 1000°C, and CeO_2 was heated in air at 850°C to remove any moisture.

The UO_2 and CeO_2 were weighed to the intended atom ratios of uranium and cerium. After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated under one of the following three conditions:

Condition I. Reaction in an evacuated platinum ampoule with a volume of about 0.8 ml at 1500°C for >80 hr.

Condition II. Reaction in an induction furnace in flowing hydrogen at 1500°C for 50 hr.

Condition III. Reaction in the induction furnace in flowing unpurified helium at 1500°C for 50 hr.

After cooling to room temperature, the samples were crushed into powder, repressed, and reacted under the same conditions as before to make the reaction complete. These procedures were repeated twice.

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.

2.2. Determination of oxygen amount. Oxygen nonstoichiometry in the solid solutions was determined by the cerium back-titration method (*7, 8*). A weighed sample was dissolved in excess cerium(IV) sulfate solution. The cerium(IV) sulfate solution was standardized with stoichiometric UO_2. The excess cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with ferroin indicator. The amount of oxygen was determined for each predetermined Ce/U ratio.

3. Magnetic Susceptibility Measurement

Magnetic susceptibility was measured by a Faraday-type torsion balance in the temperature range from liquid helium temperature to room temperature. The apparatus was calibrated using 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 a "normal" Ag vs Au–0.07 at.% Fe thermocouple (4.2 to 40 K) and an Au–Co vs Cu thermocouple (10 K to room temperature). Details of the experimental procedure are described elsewhere (*9*).

Results and Discussion

1. X-Ray Diffraction and Oxygen Nonstoichiometry

X-ray diffraction analysis showed that cubic solid solutions with the fluorite structure were formed in single phase for all specimens in this study. The determination of oxygen in the solid solutions by the cerium back-titration method showed that the solid solutions prepared under Conditions I, II, and III were nearly oxygen stoichiometric, oxygen deficient, and oxygen excessive, respectively. Several researchers have reported that an oxygen-deficient solid solution $Ce_yU_{1-y}O_{2+x}$ ($x < 0$) with $y > 0.35$ decomposes into two fluorite phases ($MO_{2.00} + MO_{2-x'}$, where M = Ce + U) below a certain temperature (*10–13*). To avoid phase separation, the specimens were rapidly cooled in the induction furnace after heating at 1500°C. In Table I are

TABLE I

MAGNETIC PARAMETERS OF $Ce_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS

Solid solution	μ_{eff} (BM)	T_N (K)	Preparation condition
$Ce_{0.10}U_{0.90}O_{1.996}$[a]	3.05	21.9	I
$Ce_{0.10}U_{0.90}O_{1.974}$	3.04	20.0	II
$Ce_{0.20}U_{0.80}O_{1.988}$[a]	3.01	17.0	I
$Ce_{0.20}U_{0.80}O_{1.967}$	3.01	13.0	II
$Ce_{0.30}U_{0.70}O_{1.987}$[a]	2.98	12.9	I
$Ce_{0.30}U_{0.70}O_{1.963}$	2.97	10.9	II
$Ce_{0.40}U_{0.60}O_{1.987}$[a]	2.92	—	I
$Ce_{0.40}U_{0.60}O_{1.946}$	2.91	—	II
$Ce_{0.40}U_{0.60}O_{2.157}$	2.47	—	III
$Ce_{0.50}U_{0.50}U_{1.990}$	2.95	—	I
$Ce_{0.50}U_{0.50}O_{2.033}$	2.70	—	III
$Ce_{0.50}U_{0.50}O_{2.075}$	2.51	—	III
$Ce_{0.50}U_{0.50}O_{2.112}$	2.18	—	III

[a] Data for these solid solutions are given in Ref. (*6*).

listed the solid solutions prepared in the present experiments together with magnetic data.

2. *Magnetic Susceptibility*

We already reported the magnetic susceptibilities of oxygen-stoichiometric $Ce_yU_{1-y}O_2$ solid solutions with $y \leq 0.40$ (*6*). An antiferromagnetic transition has been observed for the solid solutions with $y \leq 0.35$. The transition temperature (the Néel temperature) decreased with increasing cerium concentration (y). Below the Néel temperature, the magnetic susceptibility decreased with decreasing temperature and then increased again, which is different from the behavior found in $(U, Th)O_2$ (*9, 14*) or $(U, Th, Zr)O_2$ (*15*) solid solutions where the susceptibilities remain almost constant below the Néel temperatures.

The temperature dependence of magnetic susceptibilities per mole of uranium for the oxygen-deficient solid solutions prepared under Condition II is shown in Fig. 1. An antiferromagnetic transition has been observed for the solid solutions with $y \leq 0.3$, but the Néel temperatures are lower than those of the oxygen-stoichiometric solid solutions with the same y values (Table I). This is considered to be due to the formation of oxygen vacancies, because oxygen ions at the anion sites in the fluorite structure play an important role in transferring magnetic interactions between uranium ions. Experimentally, a lower Néel temperature has also been observed in oxygen-deficient $(U, La)O_{2+x}$ and $(U, Ca)O_{2+x}$ ($x < 0$) solid solutions (*16, 17*). The largest difference between oxygen-deficient and oxygen-stoichiometric solid solutions is in the temperature dependence of their magnetic susceptibilities below the Néel temperatures. The susceptibilities of oxygen-deficient solid solutions decrease with decreasing temperature and then maintain constant values; i.e., there is no increase of magnetic susceptibility with decreasing temperature as found in oxygen stoichio-

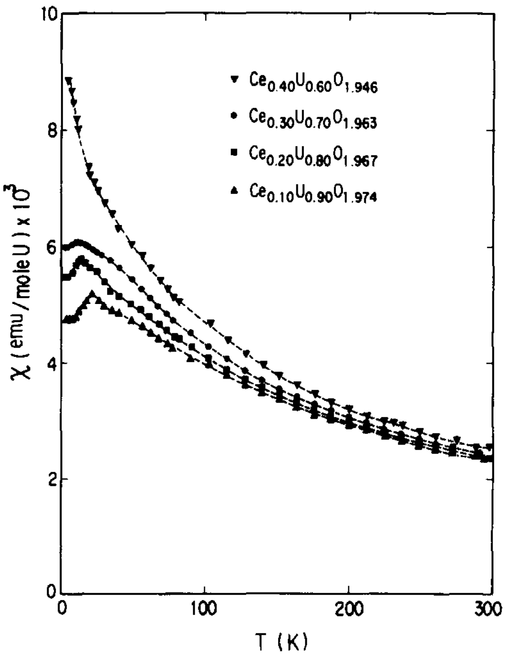

FIG. 1. Temperature dependence of magnetic susceptibilities per mole of uranium for the oxygen-deficient solid solutions prepared under Condition II.

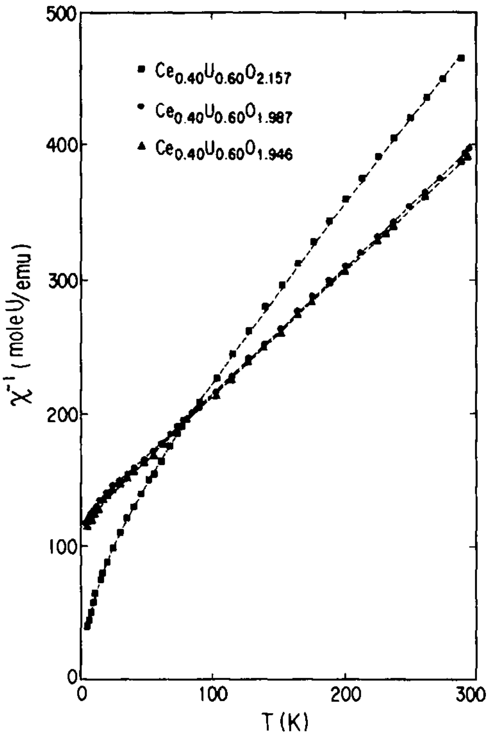

FIG. 2. Temperature dependence of inverse magnetic susceptibilities per mole of uranium for the solid solutions with $y = 0.40$.

metric solid solutions (*6*), which indicates that the charge transfer between uranium and cerium ions ($U^{4+} + Ce^{4+} \rightarrow U^{5+} + Ce^{3+}$) does not occur in oxygen-deficient solid solutions. Measurements of the oxygen potential–composition relationship of UO_{2+x} and CeO_{2-x} reveal that the Ce^{4+} ion is much more reducible than the U^{4+} ion (*18*); that is, in oxygen-deficient solid solutions, the oxidation state of uranium is +4 and the average state of the cerium ion is between +4 and +3. This is the same result as obtained by Murray *et al.* (*13*). Magnetic susceptibilities of (U, Th)O_2 and (U, Th, Zr)O_2 solid solutions, in which the uranium occurs only in the tetravalent state, attain constant values below T_N. The constant susceptibility found experimentally in oxygen-deficient solid solutions seems to show that the uranium is in the tetravalent state, and the effect of trivalent cerium ions on the low-temperature magnetic susceptibility is considerably smaller in this case.

Figure 2 shows the temperature dependence of inverse magnetic susceptibility of solid solutions with constant $y = 0.40$ but different x values. It is evident that the susceptibility of the hyperstoichiometric solid solution varies more with temperature. The temperature dependence of the magnetic susceptibility of the oxygen-deficient solid solution does not differ much from that of the oxygen-stoichiometric solid solution. The susceptibility of the oxygen-deficient solid solution is a little larger than that of the nearly oxygen-stoichiometric solid solution over the temperature range measured. This is considered to be due to the presence of a small amount of paramagnetic Ce^{3+} ions in the oxygen-deficient solid solution. From the slope of inverse magnetic susceptibility vs temperature curves in the paramagnetic range, the effective magnetic moments of uranium in the solid solutions are obtained and are summarized in Table I. The moment of uranium in the oxygen-hyperstoichiometric solid solution is lower than that in the stoichiometric solid solution, which indicates that uranium ions are oxidized from tetravalent to a higher oxidation state in the former solid solution. The fact that the (inverse) magnetic susceptibility vs temperature curves of oxygen-stoichiometric and hyperstoichiometric solid solutions intersect at ca. 80 K can be explained by assuming that uranium ions in the latter solid solution are in tetravalent and pentavalent states, as shown later. Figure 3 shows the temperature dependence of inverse magnetic susceptibility per mole of uranium for the solid solutions with $y = 0.50$. With increasing oxygen concentration (x), the susceptibility of the solid solution varies more with temperature. The effective magnetic moment of uranium decreases with increasing oxygen concentration, which is indicative of the existence of a greater number of U^{5+} in the crystal. In the next section, the oxidation state of uranium in the solid solutions will be discussed using the magnetic susceptibility data.

3. Oxidation State of Uranium

When excess oxygen enters UO_2 lattice, some of the uranium ions in (U, Ce)O_{2+x} solid solutions ($x > 0$) are oxidized from tetravalent to higher oxidation state. The following two cases are considered for the ionic species in the solid solutions:

$$\text{(I)}\quad Ce_y^{4+}U_{1-x-y}^{4+}U_x^{6+}O_{2+x}^{2-} \tag{1}$$

$$\text{(II)}\quad Ce_y^{4+}U_{1-2x-y}^{4+}U_{2x}^{5+}O_{2+x}^{2-}. \tag{2}$$

In the oxidation model (I) where the U^{6+} ions are formed, the paramagnetic ions are U^{4+} only. If the two solid solutions with the same y value but different x values are compared, the magnetic susceptibility of the solid solution with a larger x value is smaller than that with a smaller x value, because the uranium ions in the former solid solution are more oxidized than those in the latter solid solution. Experimental results, however, show that the susceptibility of $Ce_{0.50}U_{0.50}O_{2.033}$ is larger than that of $Ce_{0.50}U_{0.50}O_{1.990}$ below ca. 80 K, that the susceptibility of $Ce_{0.50}U_{0.50}O_{2.075}$ is larger than that of $Ce_{0.50}U_{0.50}O_{2.033}$ below ca. 70 K, and that above these temperatures the reverse situation holds (see Fig. 3). These results indicate that the uranium ions are not oxidized as shown in model (I) and the only possible explanation for these results is that the uranium ions in the solid solutions are in the U^{4+} or U^{5+} state. In this case, both the U^{4+} and U^{5+} ions are paramagnetic (though the temperature dependences of their magnetic susceptibilities differ from each other) and the ratio of U^{4+}/U^{5+} changes with x in $Ce_yU_{1-y}O_{2+x}$.

Next, we consider the magnetic susceptibility of solid solution for model (II). For the magnetic susceptibility of two $Ce_yU_{1-y}O_{2+x}$ solid solutions with the same y value but different x values (to be referred to as $\chi(S.1)$ and $\chi(S.2)$), the following two equations hold, if no magnetic interactions exist between the uranium ions,

$$\chi(S.1) = (1 - 2x_1 - y)\chi(U^{4+}) + 2x_1\chi(U^{5+}) \tag{3}$$

$$\chi(S.2) = (1 - 2x_2 - y)\chi(U^{4+}) + 2x_2\chi(U^{5+}), \tag{4}$$

where $\chi(U^{4+})$ and $\chi(U^{5+})$ are the magnetic susceptibilities of U^{4+} and U^{5+}, respectively. By eliminating $\chi(U^{4+})$ from Eqs. (3) and (4), the following equation is obtained,

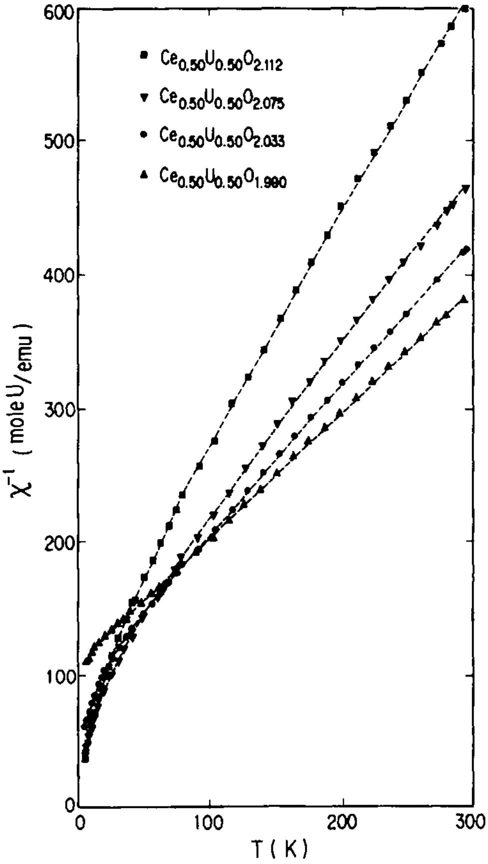

FIG. 3. Temperature dependence of inverse magnetic susceptibilities per mole of uranium for the solid solutions with $y = 0.50$.

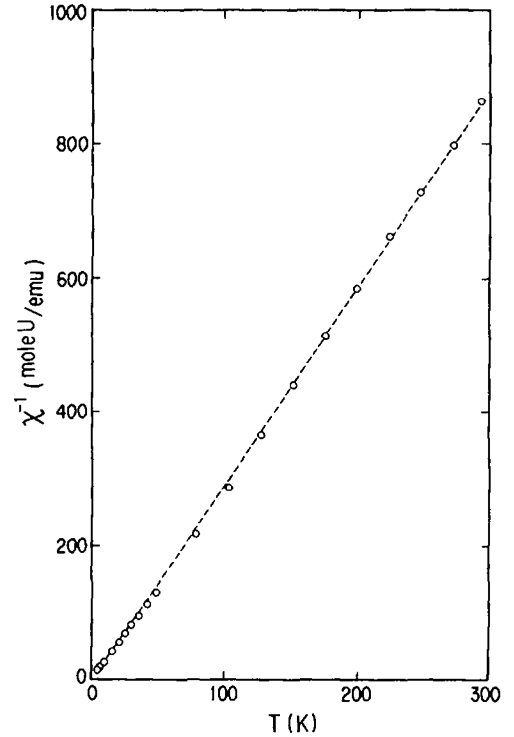

FIG. 4. Inverse magnetic susceptibility of the U^{5+} ion vs temperature.

$$\chi(U^{5+}) = \frac{1}{2(x_1 - x_2)(1 - y)} \times [(1 - 2x_2 - y)\chi(S.1) - (1 - 2x_1 - y)\chi(S.2)], \quad (5)$$

where $\chi(S.1)$ and $\chi(S.2)$ are given as magnetic susceptibilities per mole of $Ce_yU_{1-y}O_{2+x}$, not per mole of uranium as given in Figs. 1 to 3. Applying this model to the two solid solutions, viz. $Ce_{0.50}U_{0.50}O_{2.033}$ and $Ce_{0.50}U_{0.50}O_{2.075}$, the following equation is obtained,

$$\chi(U^{5+}) = 10.33\chi(S.2) - 8.33\chi(S.1). \quad (6)$$

The inverse magnetic susceptibility of the U^{5+} ion vs the temperature curve is shown in Fig. 4. The Curie–Weiss law is found to hold in the temperature range measured, and its effective magnetic moment is 1.65 BM. In the case that a U^{5+} ion is in the crystalline field produced by eight oxygen ions in cubic symmetry, the ground state $^2F_{5/2}$ (in the Russell–Saunders coupling scheme) splits into two levels, of which the lowest is quartet Γ_8 (in Bethe's notation) (*19*). If only this quartet level contributes to the paramagnetism of these solid solutions, the magnetic moment is calculated to be 2.00 BM (*20, 21*). The moment obtained from the present experiment is a little lower than that calculated, but is close to the value observed in the uranates of alkaline earth elements with the fluorite structure MU_2O_6 (M = Ca, Sr, or Ba) (*22*). The moment obtained is reasonable for the U^{5+} ion. Since the effective magnetic moment of the uranium ion in $Ce_{0.50}U_{0.50}O_{2.033}$ solid solution is 2.70 BM from experiment (Table I), and since the moment obtained for the U^{5+} ion is 1.65 BM, the moment of the U^{4+} ion is 2.83 BM. This value is between the moment of UO_2 (3.12–3.20 BM) (*9, 20, 23, 24*) and that of UO_2 infinitely diluted with diamagnetic ThO_2 (2.79–2.83 BM) (*9, 23, 24*); i.e., the moment obtained for the U^{4+} ion is reasonable. Therefore, it is concluded that some U^{4+} ions are oxidized to U^{5+} by the accommodation of excess oxygens: Model (II) is valid.

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