Magnetic Susceptibilities of $Y_yU_{1-y}O_{2+x}$ Solid Solutions

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Magnetic susceptibilities of $Y_yU_{1-y}O_{2+x}$ solid solutions with fluorite structure were measured from 4.2 K to room temperature. An antiferromagnetic transition was observed even for the solid solutions in which the mean uranium valency is over +5. From the comparison of the susceptibility data of oxygen hyper- and hypostoichiometric solid solutions ($x \gtrless 0$) with those of stoichiometric solid solutions ($x = 0$), it was found that both oxygen interstitials and oxygen vacancies weaken the magnetic exchange interactions between uranium ions. With increasing yttrium and oxygen concentrations, the effective magnetic moment of uranium decreased, and the uranium ions were found to be oxidized from +4 to +6 through the +5 state. © 1991 Academic Press, Inc.

Introduction

Uranium dioxide (UO_2) is paramagnetic with two unpaired $5f$ electrons and becomes antiferromagnetically ordered below 30.8 K (*1*). Some metal oxides are known to dissolve in UO_2 at high temperatures, forming substitutional solid solutions (*2*). In an earlier paper (*3*), we prepared $Y_yU_{1-y}O_{2+x}$ ($y \leq 0.55$, $x \leq 0$) solid solutions and measured their magnetic susceptibilities in the temperature range of 4.2 K to room temperature to elucidate the substitution effect of yttrium for uranium. With increasing yttrium concentration, the effective magnetic moment of uranium decreased. From the analysis of the magnetic susceptibilities, some of the tetravalent uranium ions are oxidized not to +6, but to the +5 state. The paramagnetic–antiferromagnetic transition temperature, the Néel temperature, decreased with increasing yttrium concentration, which means that the uranium ions are magnetically diluted with diamagnetic yttrium ions.

In the present study, the magnetic susceptibility measurements were extended to the solid solutions with higher uranium oxidation state. One aim of this study is to elucidate the effect of oxygen nonstoichiometry on the magnetic properties of $Y_yU_{1-y}O_{2+x}$ solid solutions.

Experimental

1. Sample Preparation

As starting materials, uranium dioxide (UO_2), triuranium octoxide (U_3O_8), and yttrium sesquioxide (Y_2O_3) were used. Before use, UO_2 was reduced to stoichiometric composition in flowing hydrogen at 1000°C, U_3O_8 was oxidized in air at 850°C to form a stoichiometric compound, and Y_2O_3 was heated in air at 800°C to remove any moisture.

The UO_2, U_3O_8, and Y_2O_3 were weighed to form seemingly oxygen stoichiometric solid solutions, $Y_yU_{1-y}O_{2.00}$ ($y = 0.2 \sim 0.7$), as shown in the equation

$$(1 - 7y/4) \, UO_2 + y/4 \, U_3O_8 + y/2 \, Y_2O_3 \rightarrow Y_yU_{1-y}O_{2.00}. \quad (1)$$
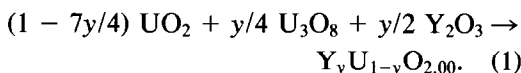
After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated under either of the following two conditions:

Condition I. The reaction in a flow of helium gas at 1300 °C for 80 hr. The approximate partial pressure of oxygen was 10 Pa.

Condition II. The reaction in air at 1400 °C for 40 hr. The yttrium concentration (y) was limited to 0.4 and 0.5.

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 on the solid solutions was performed using CuKα radiation on a Philips PW-1390 diffractometer with a curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson–Riley extrapolation method (4) applied to the diffraction lines above 80° (2θ).

2.2. Determination of oxygen amount. The oxygen nonstoichiometry in the solid solutions was determined by the cerium back-titration method (5, 6). A weighed amount of sample was dissolved in an excess of cerium(IV) sulfate solution, which was standardized in advance with stoichiometric UO_2. The remaining cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with the ferroin indicator. The oxygen amount was evaluated for each predetermined Y : U ratio.

3. Magnetic Susceptibility Measurement

Magnetic susceptibility was measured by a Faraday-type torsion balance in the temperature range from 4.2 K to room temperature. The apparatus was calibrated with Mn–Tutton's salt ($\chi_g = 10,980 \times 10^{-6}/(T + 0.7)$) used as a standard. The temperature of the sample was measured by a "normal" Ag vs Au–0.07 at% Fe thermocouple (4.2 $\sim$ 40 K) (7) and an Au–Co vs Cu thermocouple (10 K $\sim$ room temperature).

Results and Discussion

1. Oxygen Nonstoichiometry

X-ray diffraction analysis showed that under Condition I, the specimens with $y = 0.2 \sim 0.6$ formed cubic solid solutions with the fluorite structure in a single phase and that the specimen with $y = 0.7$ was a mixture of cubic solid solution phase and rhombohedral phase (8). Cubic solid solutions with the fluorite structure were formed for the $y = 0.4$ and 0.5 specimens under Condition II. The composition and lattice parameter of the solid solutions prepared are listed in Table I. Some data of the solid solutions prepared previously (3) are also included in Table I. Figure 1 shows the variation of the O/M ratio of the $Y_yU_{1-y}O_{2+x}$ solid solution as a function of yttrium concentration, y, where M indicates Y + U.
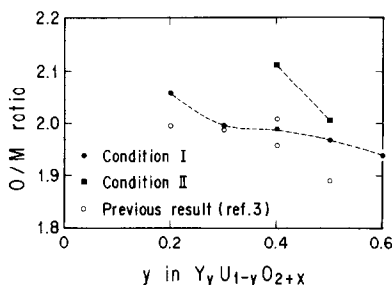

FIG. 1. Variation of O/M ratio with yttrium concentration.

TABLE I

MAGNETIC PARAMETERS OF $Y_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS[a]

Solid solution	Lattice parameter (Å)	Mean uranium valency	μ eff (μ_B)	T_N (K)	Preparation condition
$Y_{0.20}U_{0.80}O_{1.995}$	5.4228	4.24	2.73	12.9	b
$Y_{0.20}U_{0.80}O_{2.058}$	5.4181	4.40	2.47	8.4	I
$Y_{0.30}U_{0.70}O_{1.989}$	5.3978	4.40	2.44	10.1	b
$Y_{0.30}U_{0.70}O_{1.997}$	5.3966	4.42	2.39	10.0	I
$Y_{0.40}U_{0.60}O_{1.959}$	5.3740	4.53	2.19	8.1	b
$Y_{0.40}U_{0.60}O_{1.990}$	5.3716	4.63	2.11	8.8	I
$Y_{0.40}U_{0.60}O_{2.009}$	5.3700	4.70	2.01	6.7	b
$Y_{0.40}U_{0.60}O_{2.113}$	5.3646	5.04	1.63	5.4	II
$Y_{0.50}U_{0.50}O_{1.892}$	5.3590	4.57	1.92	5.4	b
$Y_{0.50}U_{0.50}O_{1.970}$	5.3505	4.88	1.71	6.6	I, b
$Y_{0.50}U_{0.50}O_{2.007}$	5.3481	5.03	1.66	6.7	II
$Y_{0.60}U_{0.40}O_{1.940}$	5.3285	5.20	1.41	—	I

[a] Estimated error in x is ± 0.003.

[b] These data are listed in Ref. (3).

In this study, we could prepare nearly oxygen stoichiometric solid solutions $Y_{0.30}U_{0.70}O_{1.997}$ and $Y_{0.40}U_{0.60}O_{1.990}$ under Condition I and $Y_{0.50}U_{0.50}O_{2.007}$ under Condition II.

The mean valency of uranium (ν) in the solid solutions was calculated assuming the valencies of yttrium and oxygen to be $+3$ and -2, respectively. Its variation against yttrium concentration is shown in Fig. 2. The uranium ions are seen to be oxidized with increasing yttrium concentration for the solid solutions prepared under Condition I. On the other hand, the mean uranium valencies were near $+5$ for the solid solutions prepared under Condition II (in air).

2. Magnetic Susceptibility

The temperature dependence of magnetic susceptibilities per mole of uranium for the solid solutions with $y = 0.2$, 0.4, and 0.5 is shown in Figs. 3, 4, and 5, respectively. For all the solid solutions, the antiferromagnetic transition was found to occur. With increasing oxygen concentration, the Néel temperatures of oxygen hyperstoichiometric solid solutions are lowered from the value of stoichiometric solid solution as shown in Figs. 3 and 4, which indicates that the interstitial oxygen weakens the magnetic exchange interaction between uranium ions. In the paramagnetic temperature range, the magnetic susceptibility decreases with increasing oxygen concentration. This means that some of the uranium
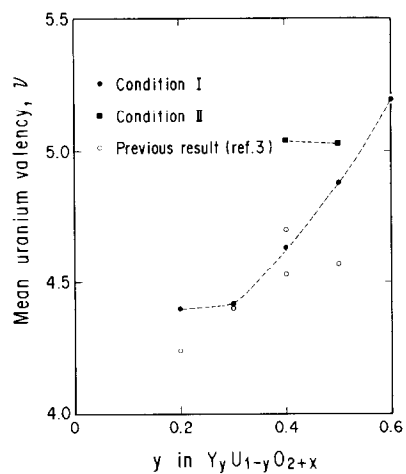

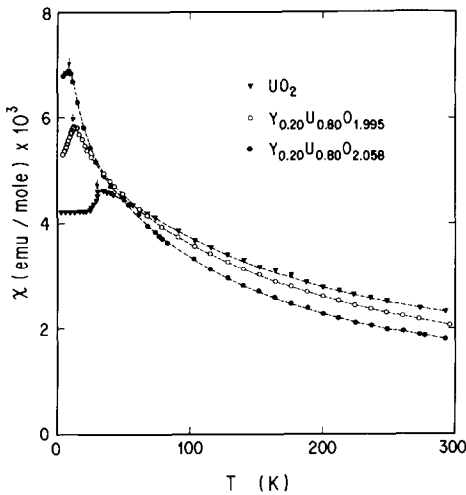FIG. 2. Mean valency of uranium against yttrium concentration.

FIG. 3. Temperature dependence of magnetic susceptibilities of $Y_yU_{1-y}O_{2+x}$ solid solutions with $y = 0.20$. Arrows show the Néel temperatures.

ions are oxidized by the incorporation of interstitial oxygens.

The effect of oxygen vacancies is seen in the magnetic susceptibilities of Fig. 5. With decreasing oxygen concentration, the mag-
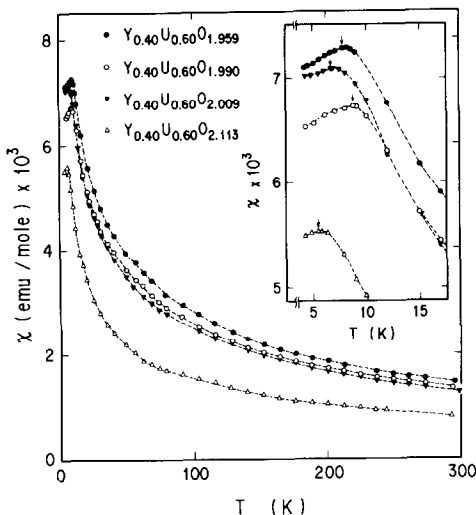

FIG. 4. Temperature dependence of magnetic susceptibilities of $Y_yU_{1-y}O_{2+x}$ solid solutions with $y = 0.40$. Arrows show the Néel temperatures.

netic susceptibility of the solid solutions increases. This result is caused by the less oxidized uranium in the solid solution by the formation of oxygen vacancies. The Néel temperature decreased with increasing oxygen vacancies. This result indicates that the formation of oxygen vacancies weakens the magnetic exchange interaction between uranium ions.

3. Valence State of Uranium

The oxidation state of uranium in the solid solutions can be elucidated from the magnetic susceptibility data. As a consequence of the substitution of Y^{3+} for U^{4+} and oxygen nonstoichiometry, some of the U^{4+} ions are oxidized. There are two possibilities, i.e., U^{5+} or U^{6+}. In the preceding paper (3), it was quantitatively elucidated that the U^{4+} ions are oxidized to the U^{5+} state, not to the U^{6+} state. For example, consider two solid solutions $Y_{0.20}U_{0.80}O_{1.995}$ and $Y_{0.20}U_{0.80}O_{2.058}$. Some of the uranium ions in the $Y_{0.20}U_{0.80}O_{1.995}$ are oxidized to the U^{5+} state as a result of the substitution of Y^{3+} for U^{4+} in the UO_2 lattice. In the $Y_{0.20}U_{0.80}O_{2.058}$, a larger number of uranium ions take on the U^{5+} state than in the $Y_{0.20}U_{0.80}O_{1.995}$ as a result of the incorporation of interstitial oxygens. Thus, it is expected that in the paramagnetic temperature range, the magnetic susceptibility of $Y_{0.20}U_{0.80}O_{1.995}$ is smaller than that of UO_2, and that the susceptibility of $Y_{0.20}U_{0.80}O_{2.058}$ is furthermore smaller than that of $Y_{0.20}U_{0.80}O_{1.995}$, which is consistent with the experimental results shown in Fig. 3.

The mean uranium valency in $Y_{0.60}U_{0.40}O_{1.940}$ is $+5.20$. So, some of the uranium ions are oxidized to the hexavalent state. The effective magnetic moment of uranium in $Y_{0.60}U_{0.40}O_{1.940}$ is 1.41 μ_B from this experiment. If the oxidation state of uranium is U^{4+} or U^{6+}, i.e., $Y_{0.60}^{3+}U_{0.16}^{4+}U_{0.24}^{6+}O_{1.940}^{2-}$, the effective magnetic moment of U^{4+} is calculated to be 2.22 μ_B because of the diamagnetism of U^{6+}. This value is far be-
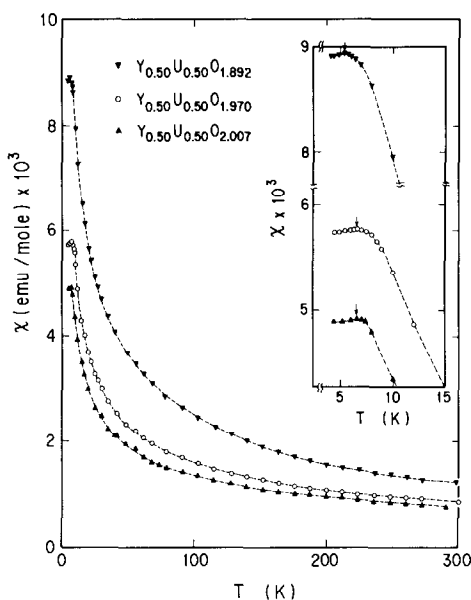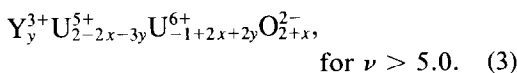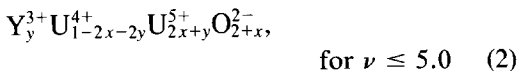
FIG. 5. Temperature dependence of magnetic susceptibilities of $Y_yU_{1-y}O_{2+x}$ solid solutions with $y = 0.50$. Arrows show the Néel temperatures.

uranium in the $Y_yU_{1-y}O_2$ solid solutions by the magnetic susceptibility measurements.

4. Magnetic Moment

From the slope of the reciprocal susceptibility vs temperature curves, the effective magnetic moments were obtained in the temperature region in which the Curie–Weiss law holds. The moments are listed in Table I. The magnetic moment decreases with oxidation of uranium. The variation of magnetic moment of uranium with its mean valency is shown in Fig. 6. The magnetic moments of uranium in the oxygen stoichiometric solid solutions are shown by closed circles and they are connected by the dashed line. The effective magnetic moment of the U^{5+} ion is the value of $La_{0.5}U_{0.5}O_{2.001}$ (open circle) of which the mean uranium valency is very close to $+5$ (16). This dashed line is not straight, but convex downward; i.e., the magnetic moment of the oxygen stoichiometric solid so-

low the moment of UO_2 (3.12 ~ 3.20 μ_B) (9–12) or UO_2 diluted in ThO_2 (2.79 ~ 2.83 μ_B) (9, 12, 13). For the case in which the oxidation state of uranium is U^{5+} or U^{6+} ($Y_{0.60}^{3+}U_{0.32}^{5+}U_{0.08}^{6+}O_{1.940}^{2-}$), the moment of U^{5+} is calculated to be 1.57 μ_B. This value is very near to the magnetic moment found experimentally in the uranates of alkaline earth elements with fluorite structure, MU_2O_6 (M = Ca, Sr, or Ba) (14).

Now the ionic species in the $Y_yU_{1-y}O_{2+x}$ solid solutions are

$$Y_y^{3+}U_{1-2x-2y}^{4+}U_{2x+y}^{5+}O_{2+x}^{2-},$$
$$\text{for } \nu \le 5.0 \quad (2)$$

$$Y_y^{3+}U_{2-2x-3y}^{5+}U_{-1+2x+2y}^{6+}O_{2+x}^{2-},$$
$$\text{for } \nu > 5.0. \quad (3)$$

This result indicates that with increasing yttrium (y) and oxygen (x) concentrations, uranium ions are oxidized from $+4$ to $+5$, and then to $+6$. Miyake et al. (15) also showed qualitatively the oxidation state of
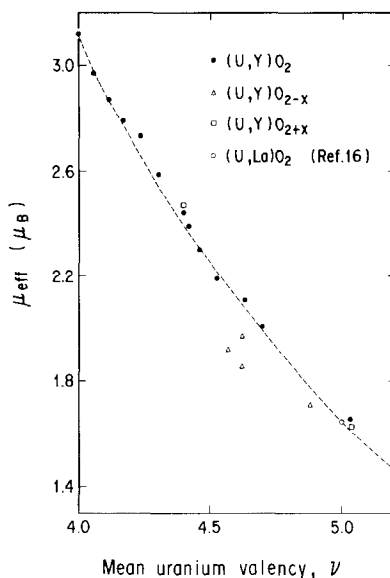

FIG. 6. Variation of effective magnetic moment of uranium with the mean valency. For the oxygen stoichiometric solid solutions, in addition to the data listed in Table I, previous results (Ref. (3)) are also included.

lution is lower than the arithmetic mean value of the individual magnetic moments of U^{4+} and U^{5+}. The reason for this is that the effective magnetic moment of U^{4+} in UO_2 actually decreases with magnetic dilution from 3.12 to 2.79 μ_B (12). The data points shown by open triangles depart from this dashed line. This is due to the oxygen deficiency of these solid solutions. The magnetic moments of uranium for the oxygen excess solid solutions (shown by open squares) also depart from this dashed line. The magnetic moments of oxygen-deficient solid solutions deviate more greatly from the dashed line (oxygen stoichiometric solid solutions) than those of oxygen excess solid solutions. In the fluorite-type structure, each uranium atom is octacoordinated by eight oxygen atoms. For oxygen-deficient solid solutions, some of these oxygen atoms move from their regular sites, forming the oxygen vacancies. On the other hand, for oxygen excess solid solutions, the excess oxygen atoms exist at the interstitial site, that is, outside the coordination sphere of eight oxygen atoms. Therefore, it is considered that the lack of oxygen atoms (formation of oxygen vacancies) significantly affects the magnetic moment of uranium.

5. Néel Temperature

With substitution of yttrium for uranium, the magnetic interaction between uranium ions weakens. At the same time, the oxidation of uranium proceeds accompanying oxygen sublattice imperfections. In this study, the solid solutions with the same y value but different x values were prepared. The Néel temperatures are also listed in Table I. The effective magnetic moment decreases with increasing oxygen concentration, which is due to the oxidation of uranium. However, the variation of Néel temperature is not straightforward. With increasing oxygen concentration, the Néel temperature is lowered from $Y_{0.40}U_{0.60}O_{1.990}$ to $Y_{0.40}U_{0.60}O_{2.009}$ to $Y_{0.40}U_{0.60}O_{2.113}$. This

result shows that the incorporation of interstitial oxygens weakens the magnetic interaction between uranium ions through the oxidation of uranium. The experimental result that the Néel temperature of $Y_{0.20}U_{0.80}O_{2.058}$ is lower than that of $Y_{0.20}U_{0.80}O_{1.995}$ is due to the same reason. The Néel temperature of $Y_{0.40}U_{0.60}O_{1.959}$ is lower than that of $Y_{0.40}U_{0.60}O_{1.990}$, indicating that the formation of oxygen vacancies also weakens the magnetic interaction between uranium ions, because this interaction is of the superexchange type of interaction via oxygen ions. The same situation holds for $Y_{0.50}U_{0.50}O_{1.892}$ and $Y_{0.50}U_{0.50}O_{1.970}$ solid solutions. Therefore, both oxygen vacancies and oxygen interstitials weaken the magnetic exchange interactions between uranium ions, which results in a lowering of the Néel temperature of the solid solutions.

Both the solid solutions $Y_{0.40}U_{0.60}O_{2.113}$ and $Y_{0.50}U_{0.50}O_{2.007}$ prepared in air (Condition II), the mean uranium valencies of which are over +5, still show antiferromagnetic transitions at 5 $\sim$ 6 K. This result is quite different from the magnetic properties of $La_yU_{1-y}O_{2+x}$ solid solutions: in the latter, when the mean uranium valency (v) is over +4.4 or the lanthanum concentration (y) is over 0.3, there is no magnetic transition down to 4.2 K (16). This comparison indicates that the magnetic dilution effect of La_2O_3 is much stronger than that of Y_2O_3.

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