JOURNAL OF SOLID STATE CHEMISTRY 73, 388–397

Magnetic Susceptibilities of UO_2–Nd_2O_3 Solid Solutions

YUKIO HINATSU AND TAKEO FUJINO

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

Received July 1, 1987

Magnetic susceptibilities of $Nd_yU_{1-y}O_{2+x}$ solid solutions with fluorite-type structure were measured from 4.2 K to room temperature. The susceptibilities of oxygen-stoichiometric solid solutions ($Nd_yU_{1-y}O_2$) increased with Nd concentration, i.e., y value, in the whole temperature range measured. From the analysis of the magnetic susceptibility data, it was found that the oxidation state of uranium was tetravalent or pentavalent. The susceptibilities of solid solutions with low Nd concentrations ($y \leq 0.07$) increased with decreasing temperature down to ca. 31 K, and showed discontinuous change (susceptibility drop) at ca. 30–31 K (T_d temperature). Below this temperature, after a little decreasing, the magnetic susceptibilities increased again with decreasing temperature. This increase of susceptibility below T_d temperature is considered to be due to both U^{5+} ion and Nd^{3+} ion. The effective magnetic moment of $Nd_yU_{1-y}O_{2+x}$ solid solutions is discussed as a function of x and y. © 1988 Academic Press, Inc.

Introduction

The phase relations on UO_2–UO_3–Nd_2O_3 system have been extensively studied by several researchers (*1–4*). Hund and Peetz (*1*) indicated that solid solutions with fluorite structure were formed in air-sintered UO_2–Nd_2O_3 mixtures in the range from 25 to 65 mole% Nd_2O_3 at 1200°C. Lambertson and Mueller (*2*) found that the Nd^{3+} ion could be substituted extensively for the U^{4+} ion in the fluorite-type solid solutions formed by sintering in hydrogen atmosphere. Kolar *et al.* (*3*) studied the formation of the compounds in either air or hydrogen atmosphere by chemical, X-ray, and differential thermal analyses. Keller and Boroujerdi (*4*) examined in further detail the phase relation at $p(O_2) = 1$ atm and $1150°C \leq T \leq 1550°C$. As Nd^{3+} ion is substituted for U^{4+} ion in the face-centered cubic lattice, an oxygen deficiency must be created or some of the U^{4+} ion must be oxidized to a higher valence state to conserve the charge neutrality in the solid solutions. However, there have been no definite descriptions about the oxidation state of uranium.

As shown above, there have been several phase relation studies on this system, but no magnetic studies seem to have been reported yet. Although the electronic configuration of Nd^{3+} ([Xe]$4f^3$) is different from that of Pr^{3+} ([Xe]$4f^2$), the magnetic moment of Nd^{3+} is close to that of Pr^{3+} in a free ion state. Therefore, if magnetic data of $Nd_yU_{1-y}O_2$ solid solutions with fluorite structure are compared with those of $Pr_yU_{1-y}O_2$ solid solutions (*5*), the effect of the ground state of rare-earth ions (Nd^{3+} and Pr^{3+}) on the magnetic properties of solid solutions could be elucidated. The effect of interstitial oxygen will also be clarified by comparing the results of hyperstoi-

0022-4596/88 $3.00

Copyright © 1988 by Academic Press, Inc.
All rights of reproduction in any form reserved.

chiometric $Nd_yU_{1-y}O_{2+x}$ ($x > 0$) solid solutions with those of stoichiometric $Nd_yU_{1-y}O_2$ solid solutions.

In the present study, $Nd_yU_{1-y}O_{2+x}$ solid solutions with various x and y values of which the crystal structures are fluorite-type (same as UO_2) were prepared and their magnetic susceptibilities were measured in the range from 4.2 K to room temperature. The change of the magnetic properties of solid solutions is examined as a function of substituted Nd^{3+} for U^{4+} and/or the interstitial oxygens. The oxidation state of uranium in the solid solutions is discussed in terms of the magnetic susceptibility data.

Experimental

1. Sample Preparation

As starting materials, UO_2 and Nd_2O_3 were used. Before use, UO_2 was reduced to stoichiometric composition in a flow of hydrogen gas at 1000°C. Nd_2O_3 was heated in air at 850°C to remove any moisture.

The UO_2 and Nd_2O_3 were weighed to the intended atom ratios of uranium and neodymium ($Nd/(Nd+U) \leq 0.30$). After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated under either of the following three conditions:

Condition I: The reaction in an induction furnace in a flow of purified helium gas at 1400°C for 8 hr.

Condition II: The reaction in an SiC resistance furnace in a flow of unpurified helium gas at 1340°C for 150 hr. The partial pressure of oxygen in the helium gas used here was significantly higher than that of Condition I.

Condition III: The reaction in a muffle furnace with molybdenum silicide heating elements in air at 1600°C for 11 hr.

After cooling to room temperature, the samples were reground, pressed again to pellets, and heated under the same conditions as before to make the reaction complete. These procedures were repeated twice.

2. Analysis

2.1. X-ray diffraction analysis. X-ray diffraction study was performed using Cu$K\alpha$ radiation with a Philips PW-1390 diffractometer equipped with curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson–Riley extrapolation method (*6*) 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 back-titration method (*7, 8*). The weighed amount of sample was dissolved in excess cerium(IV) sulfate solution. This cerium(IV) sulfate solution was standardized with stoichiometric UO_2. The excess cerium(IV) was titrated against standard iron(II) ammonium sulfate solution with ferroin indicator. The oxygen amount was determined for predetermined Nd/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 ($\chi_g = 10980 \times 10^{-6}/(T + 0.7)$) used as a standard. The temperature of the sample was measured by a "normal" Ag vs Au—0.07 at% Fe thermocouple (*9*) (4.2–40 K) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (*10*).

Results and Discussion

1. Lattice Parameter and Oxygen Nonstoichiometry

X-ray diffraction analysis showed that cubic solid solutions with fluorite-type structure were formed in single phase for all the specimens in this study with the exception of the Nd/(Nd + U) = 0.10 and 0.20 specimens formed under Condition III (in air). They were a mixture of cubic solid solution and orthorhombic α-U_3O_8. Figure 1 shows the variation of O/M ratio with Nd concentration, y, for the solid solutions prepared in this work (Conditions I, II, and III), where M indicates Nd + U. The O/M ratios for the solid solutions with $y \leq 0.10$ prepared under Condition I were close to two. Similar behavior has already been reported in earlier works on this system (*3*) and on some rare-earth oxide–uranium oxide systems (*11–14*). The solid solutions prepared under Conditions II and III showed hyperstoichiometry, i.e., the O/M ratios were larger than 2.

The variation of lattice parameter with y is indicated in Fig. 2. In spite of the substitution of Nd^{3+} of which the crystal radius is larger than that of U^{4+} (*15*), the lattice parameter of solid solutions prepared under Condition I decreased with increasing Nd concentration until $y = 0.20$. On the other hand, the lattice parameter of the solid solutions prepared under Condition II increased slightly with y. This difference is considered to arise from the enhanced oxidation of uranium in the solid solutions prepared under Condition II due to reaction with oxygen in higher oxygen pressure. The mean valency of uranium in the solid solutions against Nd concentration is shown in Fig. 3. The uranium ion is seen to be oxidized with increasing y for the solid solutions prepared under any of the three conditions. For the solid solutions with the same y value, the uranium ions were more oxidized under Condition II than under Condition I.

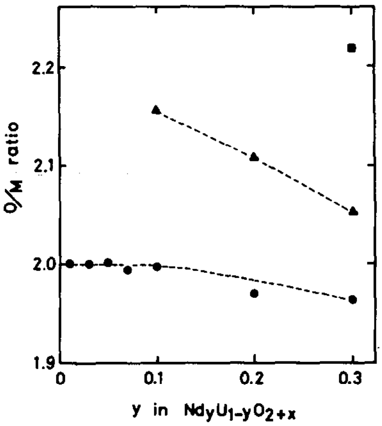

FIG. 1. Variation of O/M ratio with neodymium concentration. ●, Condition I; ▲, Condition II; ■, Condition III.

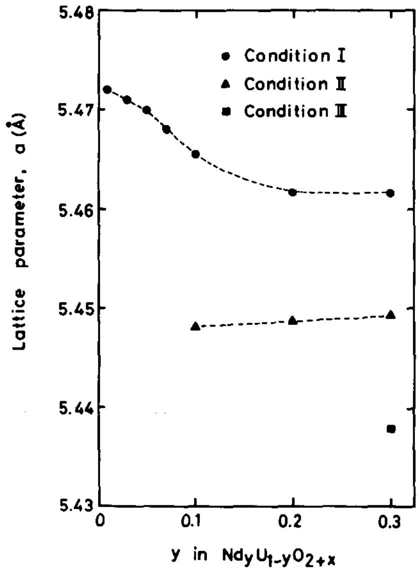

FIG. 2. Variation of lattice parameter with neodymium concentration.

2. *Magnetic Susceptibility*

For all specimens examined here, no field dependence of magnetic susceptibility was found. Figure 4 shows the temperature dependence of magnetic susceptibilities of $Nd_yU_{1-y}O_2$ solid solutions ($y \leq 0.1$) prepared under Condition I. Except for the lower temperature region ($T < 20$ K), the susceptibility behavior of the $Nd_yU_{1-y}O_2$ solid solutions is similar to that of the $Pr_yU_{1-y}O_2$ solid solutions (*5*). In the whole temperature range measured, the suscepti-

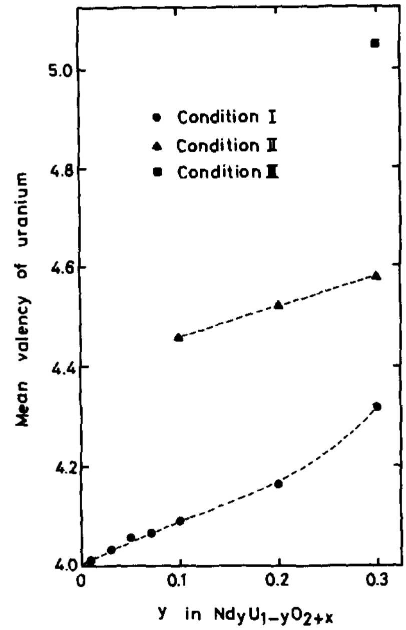

FIG. 3. Mean valency of uranium against neodymium concentration.

bility increases with Nd concentration (y). This fact reflects larger effective magnetic moment of Nd^{3+} than that of U^{4+} as will be described later. The magnetic susceptibility for the solid solutions with low Nd concentrations ($y \leq 0.07$) increases with decreasing temperature down to ca. 31 K, and shows discontinuous change at ca. 30–31 K (Fig. 4). This temperature will be referred to as T_d hereafter. Below this temperature, the susceptibility decreases but turns to increase again with decreasing temeprature. The temperature dependence of magnetic susceptibility in low-temperature region is shown in Fig. 5 more closely. For comparison, the data of $Pr_yU_{1-y}O_2$ solid solutions are also drawn in this figure as dot-dashed lines. The decline of magnetic susceptibility below T_d with decreasing temperature becomes less prominent with increasing Nd concentration. However, the T_d temperatures does not change irrespective of the Nd concentration. This behavior is different from $Th_yU_{1-y}O_2$ solid solutions in which the Néel temperature decreases linearly with decreasing uranium concentration (*10*, *16*). Neither $Y_yU_{1-y}O_2$ nor $La_yU_{1-y}O_2$ solid solutions (*17*, *18*) behave similarly. In these solid solutions where some uranium ions are oxidized to a higher valence state to maintain the electrical neutrality in the solids, the Néel temperature decreases with decreasing uranium concentration but the decrement becomes smaller with decreasing uranium concentration. Figures 6 and 7 show the temperature dependence of reciprocal magnetic susceptibilities of solid solutions with $y = 0.10$ and 0.20, respectively. In each case, the paramagnetic susceptibility is larger when the x value is larger below certain temperatures (Figs. 6 and 7). This result shows that the oxidation state of uranium in the solid solutions is either tetravalent or pentavalent, as will be described

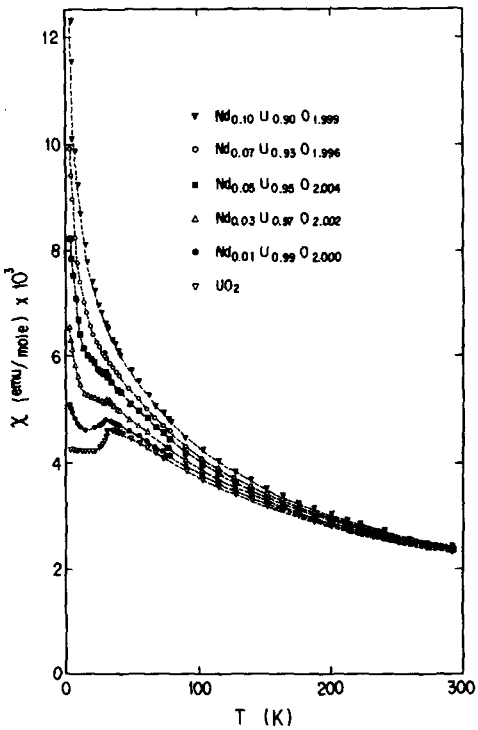

FIG. 4. Temperature dependence of magnetic susceptibilities of $Nd_yU_{1-y}O_2$ solid solutions ($y \leq 0.10$) prepared under Condition I.

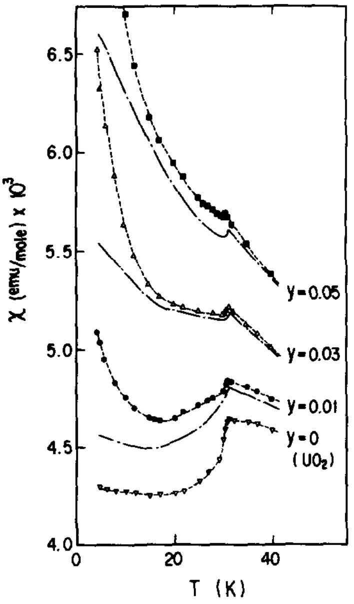

FIG. 5. Comparison of low-temperature magnetic susceptibilities of $Nd_yU_{1-y}O_2$ solid solutions with those of $Pr_yU_{1-y}O_2$ solid solutions. Dot-dashed lines represent the data of $Pr_yU_{1-y}O_2$ solid solutions.

later. Figure 8 shows the plot of reciprocal magnetic susceptibility against temperature for the solid solutions with $y = 0.30$. Above ca. 50 K, the magnetic susceptibility of the specimen with larger oxygen amount becomes smaller. In the temperature range in which the Curie–Weiss law holds, the effective magnetic moment per mole of $Nd_yU_{1-y}O_2$ solid solutions, μ_{eff}, were obtained from the slope of the reciprocal susceptibility vs temperature curves. The variations of μ_{eff} with Nd concentration is shown in Fig. 9.

3. Oxidation State of Uranium

The oxidation state of uranium in the $Nd_yU_{1-y}O_{2+x}$ solid solutions can be elucidated from the magnetic susceptibility data. U^{4+} ions are oxidized to U^{5+} or U^{6+} by accommodation of Nd^{3+} ions in the crystal, and the same by accommodation of excess oxygen ions. In these cases, the following two models of ionic species are considered:

$$\text{(i)}\ Nd_y^{3+}U^{4+}_{1-x-1.5y}U^{6+}_{x+0.5y}O^{2-}_{2+x} \qquad (1)$$

$$\text{(ii)}\ Nd_y^{3+}U^{4+}_{1-2x-2y}U^{5+}_{2x+y}O^{2-}_{2+x} \qquad (2)$$

In the oxidation model (i) where the U^{6+} ions are formed, the paramagnetic ions are Nd^{3+} and U^{4+} only, since the U^{6+} ion is diamagnetic. For the two solid solutions with the same Nd amount (y) but different oxygen amounts (x), the paramagnetic susceptibility of the solid solution with higher oxygen amount must be smaller than that of the solid solution with lower oxygen amount, since the ratio U^{4+}/(total U) is smaller in the former solid solution. Experimental results, however, show that the magnetic susceptibility of $Nd_{0.10}U_{0.90}U_{2.157}$ is larger than that of $Nd_{0.10}U_{0.90}O_{1.999}$ below 90 K (Fig. 6). The same result is found for the solid solutions with $y = 0.20$, viz., $Nd_{0.20}U_{0.80}O_{2.110}$ and $Nd_{0.20}U_{0.80}O_{1.968}$ (Fig.

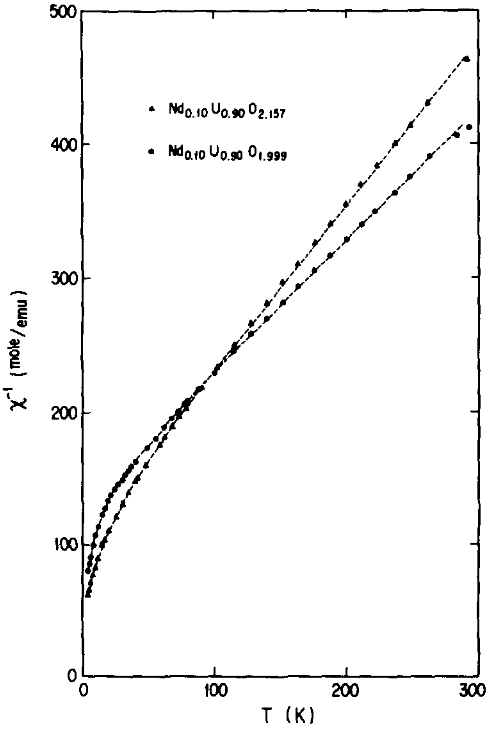

FIG. 6. Temperature dependence of reciprocal magnetic susceptibilities of $Nd_{0.10}U_{0.90}O_{1.999}$ and $Nd_{0.10}U_{0.90}O_{2.157}$.

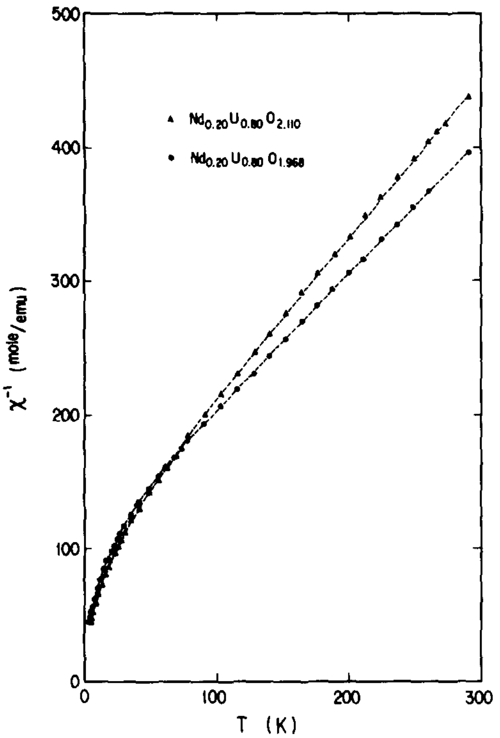

FIG. 7. Temperature dependence of reciprocal magnetic susceptibilities of $Nd_{0.20}U_{0.80}O_{1.968}$ and $Nd_{0.20}U_{0.80}O_{2.110}$.

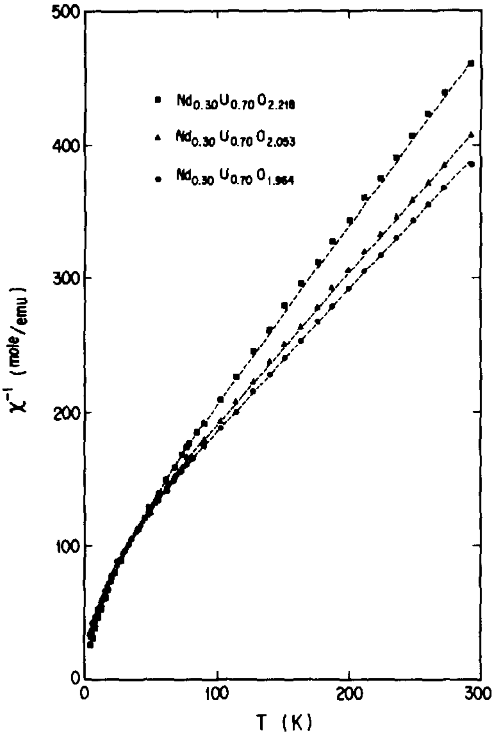

FIG. 8. Temperature dependence of reciprocal magnetic susceptibilities of $Nd_{0.30}U_{0.70}O_{1.964}$, $Nd_{0.30}U_{0.70}O_{2.053}$, and $Nd_{0.30}U_{70}O_{2.218}$.

7). From these facts, we can conclude that the uranium ions are not oxidized as shown in model (i).

When model (ii) is the case, there exist three kinds of paramagnetic ions in the solid solutions. For the magnetic susceptibilities of two $Nd_yU_{1-y}O_{2+x}$ 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,

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

$$\chi(S.2) = y\chi(Nd^{3+}) + (1 - 2x_2 - 2y)\chi(U^{4+}) + (2x_2 + y)\chi(U^{5+}), \quad (4)$$

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

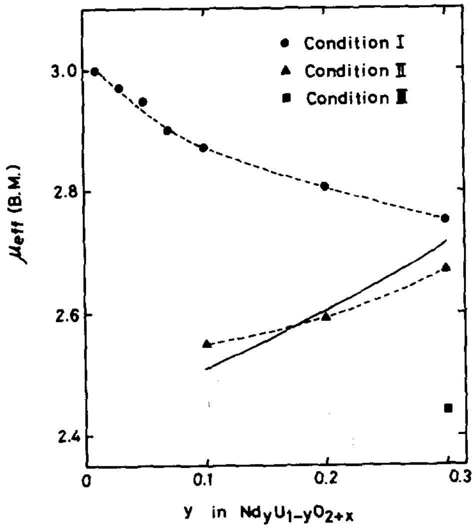

FIG. 9. Variation of effective magnetic moment of $Nd_yU_{1-y}O_{2+x}$ solid solutions with neodymium concentration. Solid line represents the calculation result (see text).

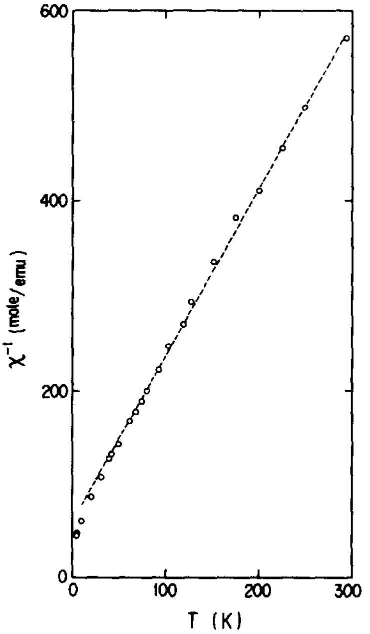

FIG. 10. Reciprocal susceptibility of $y\mathrm{Nd}^{3+} + (1 - y)\mathrm{U}^{5+}$ vs temperature.

tion is obtained,

$$
\begin{aligned}
&y\chi(\mathrm{Nd}^{3+}) + (1 - y)\chi(\mathrm{U}^{5+}) \\
&\quad = \frac{1}{2(x_1 - x_2)}\{(1 - 2x_2 - 2y)\chi(\mathrm{S.1}) \\
&\qquad - (1 - 2x_1 - 2y)\chi(\mathrm{S.2})\}. \quad (5)
\end{aligned}
$$

Equation (5) gives the magnetic susceptibility of solid solution containing Nd^{3+} and U^{5+} ions with a ratio $y/(1 - y)$. Applying this model to the two solid solutions, viz., $\mathrm{Nd_{0.10}U_{0.90}O_{1.999}}$ and $\mathrm{Nd_{0.10}U_{0.90}O_{2.157}}$, the reciprocal susceptibility of $y\mathrm{Nd}^{3+} + (1 - y)$ U^{5+} vs temperature curve is obtained as shown in Fig. 10. The moment is 2.13 B.M. Since the theoretical value of the magnetic moment of Nd^{3+} is 3.62 B.M.,[1] the moment of U^{5+} is calculated to be 1.89 B.M. 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 Russel–Saunders coupling scheme) splits into two levels, of which the lowest is quarter Γ_8 (in Bethe's notation) (*19*). If this quartet level contributes to the paramagnetism of these solid solutions, their magnetic moment is calculated to be 2.00 B.M. (*20, 21*). This value is close to the value obtained above: model (ii) is reasonable.

If no magnetic interaction exists between three kinds of paramagnetic ions, the magnetic moment per mole of $\mathrm{Nd}_y\mathrm{U}_{1-y}\mathrm{O}_{2+x}$ solid solution (μ_{eff}) is expressed as

$$
\begin{aligned}
\mu_{\mathrm{eff}}^2 &= y\mu_{\mathrm{eff}}^2(\mathrm{Nd}^{3+}) \\
&\quad + (1 - 2x - 2y)\mu_{\mathrm{eff}}^2(\mathrm{U}^{4+}) \\
&\qquad + (2x + y)\mu_{\mathrm{eff}}^2(\mathrm{U}^{5+}), \quad (6)
\end{aligned}
$$

where $\mu_{\mathrm{eff}}(\mathrm{Nd}^{3+})$, $\mu_{\mathrm{eff}}(\mathrm{U}^{4+})$, and $\mu_{\mathrm{eff}}(\mathrm{U}^{5+})$ are the magnetic moments per mole of Nd^{3+}, U^{4+}, and U^{5+}, respectively. For oxygen-stoichiometric $\mathrm{Nd_{0.10}U_{0.90}O_{1.999}}$, by substituting the values obtained for μ_{eff}, $\mu_{\mathrm{eff}}(\mathrm{Nd}^{3+})$, and $\mu_{\mathrm{eff}}(\mathrm{U}^{5+})$ in Eq. (6), the magnetic moment of U^{4+} is calculated to be 2.86 B.M. This value is between the moment of $\mathrm{UO_2}$ (3.12–3.20 B.M.) (*10, 20, 22, 23*) and that of $\mathrm{UO_2}$ infinitely diluted with diamagnetic $\mathrm{ThO_2}$, i.e., 2.79–2.83 B.M. (*10, 22, 24*). Therefore, the magnetic moment obtained above is found to be reasonable as the value of the compounds composed of U^{4+} ions, which also supports the oxidation model (ii).

The mean valency of uranium for $\mathrm{Nd_{0.30}U_{0.70}O_{2.218}}$ is close to +5 as shown in Fig. 3. Since the effective magnetic moment of this solid solution is found to be 2.44 B.M. from experiment, the magnetic moment per uranium is calculated to be 1.70 B.M., which is a reasonable value for the moment of pentavalent uranium. This fact also supports the model of ionic species described by Eq. (2).

When a U^{4+} ion is replaced by a Nd^{3+} ion, another U^{4+} ion is oxidized to U^{5+} according to the model (ii), and the magnetic

---

[1] This value, p, is calculated from the relation $p = g_J\sqrt{J(J + 1)}$, where g_J is the Lande's splitting factor and J is the total angular momentum.

susceptibility of stoichiometric $Nd_yU_{1-y}O_2$ solid solutions should increase with Nd concentration. This is true as shown in Fig. 4 in the temperature range of this experiment. Similar behavior has been found in the magnetic susceptibility of $Pr_yU_{1-y}O_2$ solid solutions (*5*). The reason for the increase of magnetic susceptibility with y is considered to be the same for both $Nd_yU_{1-y}O_2$ and $Pr_yU_{1-y}O_2$ solid solutions (*5*). In the case that no magnetic interaction exists between paramagnetic ions, the susceptibility of stoichiometric $Nd_yU_{1-y}O_2$ solid solution is given by the following equation ($x = 0$ in Eq. (3)),

$$\chi(Nd_yU_{1-y}O_2) = y\chi(Nd^{3+}) + (1 - 2y)\chi(U^{4+}) + y\chi(U^{5+}). \quad (7)$$

The magnetic susceptibility of U^{4+} ion in UO_2 is expressed by the equation $\chi(U^{4+}) = 1.22/(T + 220)$ in the temperature range in which the Curie–Weiss law holds (*17*). Since the Weiss constant of U^{4+} is much larger than those of U^{5+}[2] and Nd^{3+},[3] the decrement of magnetic susceptibility due to the decrease of the U^{4+} ratio with increasing y, i.e., $-2y\chi(U^{4+}) = -2y \cdot 1.22/(T + 220)$ in Eq. (7), is small in this temperature range. This smaller effect could explain the increase in the magnetic susceptibility of solid solutions with Nd concentration.

4. Low-Temperature Magnetic Susceptibility

The largest difference in magnetic behavior between $Nd_yU_{1-y}O_2$ and $Pr_yU_{1-y}O_2$ solid solutions (*5*) is in the temperature dependence of magnetic susceptibility at low temperatures ($T < T_d$) (Fig. 5). With increasing Nd concentration, the increase of magnetic susceptibility becomes pronounced. Similar behavior has been found in the magnetic susceptibility vs temperature curve of $Pr_yU_{1-y}O_2$ solid solutions, and we discussed the origin of this increase as due to the U^{5+} ion formed in the solid solutions to maintain charge neutrality (*5*). The U^{5+} ion is a Kramers' ion with one unpaired electron. Below the antiferromagnetic–paramagnetic transition temperature (T_N), UO_2 (*27, 28*), $(U,Th)O_2$ (*10, 16*), and $(U,Zr)O_2$ (*29*) show constant magnetic susceptibilities. As mentioned above, the ion species of uranium and the oxidation state of rare-earth element in $Nd_yU_{1-y}O_2$ solid solutions are the same as those in $Pr_yU_{1-y}O_2$ solid solutions. Despite that, the increase of magnetic susceptibility below T_d temperature is more striking for the $Nd_yU_{1-y}O_2$ solid solutions than for the $Pr_yU_{1-y}O_2$ solid solutions. Therefore, these phenomena are considered to be not due to the effect of U^{4+}, but due to the effect of U^{5+} and Nd^{3+}. Both U^{5+} and Nd^{3+} ions are Kramers' ions with odd unpaired electrons and their ratios in total metal amount both increase with Nd concentration.

It may be useful to compare these magnetic behavior with those of other combined 5*f*–4*f* electronic systems. The magnetic properties of phosphide ($Ln_yU_{1-y}P$) and sulfide ($Ln_yU_{1-y}S$) solid solutions (*Ln* being Pr or Nd) have been reported (*30–32*). The Néel temperature of $Nd_yU_{1-y}P$ solid solutions decreases with increasing y (*30, 32*). This is reasonable because UP and NdP are type-I antiferromagnetic with Néel temperatures 125 and 11 K, respectively (*33, 34*). On the other hand, it is difficult to explain the magnetic behavior of $Nd_yU_{1-y}O_2$ solid solutions from composite UO_2 and Nd_2O_3, since UO_2 transforms to antiferromagnetic state below 30.8 K (*35*) but Nd_2O_3 is paramagnetic down to 4.2 K (*36*).

---

[2] The susceptibility of U^{5+} ion in fluorite structure is given, for example, by the equation $\chi = 0.42/(T + 111)$ for SrU_2O_6 (*25*).

[3] Several data for the Weiss constant of Nd^{3+} ion are given in (*26*).

5. *Magnetic Moment*

From Fig. 9, the effective magnetic moment for the solid solutions prepared under Condition I is found to decrease with increasing Nd concentration. On the other hand, the moment for the solid solutions prepared under Condition II increases. For the solid solutions with the same y value but different x values, the effective magnetic moment decreases with increasing x value, which is caused from the increased mean valency of uranium due to uptake of oxygen (Fig. 3). First, we will discuss the decrease of magnetic moment for the case of Condition I. The magnitude of the moment is comparable to that of $Pr_yU_{1-y}O_2$ solid solutions ($0 \leq y \leq 0.1$) (*5*). Since the effective magnetic moment of Nd^{3+} (3.62 B.M.) is close to that of Pr^{3+} (3.58 B.M.) (see footnote 1) the origin for the decrease of magnetic moment of $Nd_yU_{1-y}O_2$ solid solutions is considered to be the same as that for $Pr_yU_{1-y}O_2$ solid solutions, that is, this decrease is due to both the oxidation of uranium and the decrease of magnetic moment of tetravalent uranium with increasing Nd concentration. It is difficult to evaluate the magnetic moments of $Nd_yU_{1-y}O_{2+x}$ ($x < 0$) solid solutions with $y \geq 0.2$, because the assumption that the uranium ion is surrounded by eight oxygen ions is no longer valid for considerably oxygen-deficient solid solutions.

Let us evaluate the effective magnetic moment of oxygen hyperstoichiometric solid solutions, and discuss the increase of the moment with y for $Nd_yU_{1-y}O_{2+x}$ prepared under Condition II. As a first approximation, we treat the central uranium ion to be surrounded by the nearest-neighbor eight oxygen ions located at the coners of a cube. Since the magnetic exchange interactions are not found in these solid solutions (Figs. 6–8), we can take the moment 2.80 B.M., as the effective magnetic moment of U^{4+}, $\mu_{eff}(U^{4+})$. The effective magnetic moment of U^{5+}, $\mu_{eff}(U^{5+})$, is calculated to be 1.70 B.M. from the data of $Nd_{0.30}U_{0.70}O_{2.218}$ of which the mean uranium valency is closely near to +5. The magnetic moment of Nd^{3+} ion, $\mu_{eff}(Nd^{3+})$, is 3.62 B.M. By substituting the values obtained for $\mu_{eff}(U^{4+})$, $\mu_{eff}(U^{5+})$, and $\mu_{eff}(Nd^{3+})$ in Eq. (6), the effective magnetic moment per mole of $Nd_yU_{1-y}O_{2+x}$ solid solution, μ_{eff}, is obtained as follows,

$$\mu_{eff} = \sqrt{7.84 - 9.90x + 0.31y}. \qquad (8)$$

For the solid solutions prepared under Condition II, μ_{eff} is found to increase with Nd concentration (y) (solid line in Fig. 9), which corresponds to the experimental results. However, the agreement between calculated and found values is not good. This is considered to be ascribed to a small change in the crystal field by interstitial oxygens, which may result in the excursion of magnetic moments of $\mu_{eff}(U^{4+})$ and $\mu_{eff}(U^{5+})$ in Eq. (6).

References

1. F. Hund and U. Peetz, *Z. Anorg. Allg. Chem.* **271,** 6 (1952).
2. W. A. Lambertson and M. H. Mueller, ANL-5312 (1954).
3. D. Kolar, J. H. Handwerk, and R. J. Beals, ANL-6631 (1962).
4. C. Keller and A. Boroujerdi, *J. Inorg. Nucl. Chem.* **34,** 1187 (1972).
5. Y. Hinatsu and T. Fujino, *J. Solid State Chem.*, in press.
6. L. V. Azaroff, *in* "Elements of X-ray Crystallography," p. 479, McGraw–Hill, New York (1968).
7. S. R. Dharwadkar and M. S. Chandrasekharaiah, *Anal. Chem. Acta* **45,** 545 (1969).
8. T. Fujino and T. Yamashita, *Fresenius' Z. Anal. Chem.* **314,** 156 (1983).
9. L. L. Sparks and R. L. Powell, *J. Res. Nat. Bur. Stand. U.S.* **A76,** 263 (1972).
10. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **60,** 195 (1985).
11. D. C. Hill, *J. Amer. Ceram. Soc.* **45,** 258 (1962).
12. S. F. Bartram, E. F. Junke, and E. A. Aitken, *J. Amer. Ceram. Soc.* **47,** 171 (1964).
13. R. J. Beals and J. H. Handwerk, *J. Amer. Ceram. Soc.* **48,** 271 (1965).

14. T. YAMASHITA, T. FUJINO, AND H. TAGAWA, *J. Nucl. Mater.* **132,** 192 (1985).
15. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
16. J. B. COMLY, *J. Appl. Phys.* **39,** 716 (1968).
17. Y. HINATSU AND T. FUJINO, *J. Solid State Chem.* **66,** 332 (1987).
18. Y. HINATSU AND T. FUJINO, *J. Solid State Chem.* **68,** 255 (1987).
19. K. R. LEA, M. J. M. LEASK, AND W. P. WOLF, *J. Phys. Chem. Solids* **23,** 1381 (1962).
20. S. NASU, *Japan. J. Appl. Phys.* **5,** 1001 (1966).
21. Y. HINATSU AND T. FUJINO, *J. Solid State Chem.* **62,** 342 (1986).
22. E. SLOWINSKI AND N. ELLIOTT, *Acta Crystallogr.* **5,** 768 (1952).
23. J. K. DAWSON AND M. K. LISTER, *J. Chem. Soc.,* 5041 (1952).
24. C. A. HUTCHISON, JR., AND G. A. CANDELA, *J. Chem. Phys.* **27,** 707 (1957).
25. R. BROCHU AND J. LUCAS, *Bull. Soc. Chim. France,* 4764 (1967).
26. "Theory and Applications of Molecular Paramagnetism" (E. A. Boudreaux and L. N. Mulay, Eds.), Wiley–Interscience, New York (1976).
27. A. ARROTT AND J. E. GOLDMAN, *Phys. Rev.* **108,** 948 (1957).
28. M. J. M. LEASK, L. E. ROBERTS, A. J. WALTER, AND W. P. WOLF, *J. Chem. Soc.,* 4788 (1963).
29. Y. HINATSU AND T. FUJINO, *J. Solid State Chem.* **60,** 244 (1985).
30. R. TROĆ, R. NIEDZIELSKI, J. LECIEJEWICZ, AND A. MURASIK, *in* "Rare Earths and Actinides" (D. Corner and B. K. Tanner, Eds.), p. 196, The Institute of Physics, Conf. Series No. 37, Bristol and London (1978).
31. R. TROĆ, R. NIEDZIELSKI, J. LECIEJEWICZ, AND A. MURASIK, *J. Magn. Magn. Mater.* **15–18,** 1251 (1980).
32. R. TROĆ, *Physica* **102B,** 233 (1980).
33. N. A. CURRY, *Proc. Phys. Soc.* **89,** 427 (1966).
34. P. SCHOBINGER-PAPAMOUTELLOS, P. FISHER, O. VOGT, AND E. KALDIS, *J. Phys. C* **6,** 725 (1973).
35. B. C. FRAZER, G. SHIRANE, D. E. COX, AND C. E. OLSEN, *Phys. Rev.* **140,** A1448 (1965).
36. P. CARO, J. DEROUET, L. BEAURY, AND E. SOULIE, *J. Chem. Phys.* **70,** 2542 (1979).