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Magnetic Studies on (U, La)O_{2+x} Solid Solutions

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Magnetic susceptibilities of $La_yU_{1-y}O_{2+x}$ solid solutions with fluorite structure were measured from 4.2 K to room temperature. An antiferromagnetic transition was observed for the solid solutions with lanthanum concentration $0 \leq y \leq 0.3$ in both stoichiometric ($x = 0$) and hypostoichiometric oxygen range ($x < 0$). From comparison of the magnetic properties of solid solutions with different oxygen amounts ($x < 0$, $x = 0$, $x > 0$), both oxygen vacancies and interstitial oxygens were found to weaken the magnetic exchange interactions between uranium ions. The Néel temperature decreased with decreasing uranium concentration. The variation of the Néel temperature of (U, La)O_2 solid solutions with uranium concentration was different from that of (U, Th)O_2 solid solutions. The magnetic moment decreased with decreasing uranium concentration. Its rate was larger than that of (U, Th)O_2 solid solutions and was comparable with that of (U, Y)O_2 solid solutions. The oxidation state of uranium in the solid solutions was examined from the magnetic susceptibility data. The uranium ions were found to be in either the tetravalent or the pentavalent state. The effect of magnetic dilution was larger with La_2O_3 than with Y_2O_3 and/or Sc_2O_3. © 1987 Academic Press, Inc.

Introduction

Like other uranium dioxide–lanthanide sesquioxide solid solutions, a $La_yU_{1-y}O_{2+x}$ solid solution crystallizes in a cubic fluorite-type structure in certain ranges of y and x. Lanthanum ranks first in the series of lanthanide elements, and its trivalent ion has a closed-shell electron configuration; i.e., it is diamagnetic. However, the incorporation of La^{3+} in UO_2 (formation of the solid solution) causes an increase of the mean uranium valency through a charge neutrality condition, which is also accompanied by an increase of the unit cell size of the solid solution. The latter fact is in contrast to the case of (U, Y)O_2 or (U, Sc)O_2 solid solutions where the cubic lattice parameters decrease with decreasing uranium concentration. Therefore, by comparing the data of (U, La)O_2 solid solutions with those of (U, Y)O_2 or (U, Sc)O_2 solid solutions it is expected that some insight into the effect of the distance between uranium ions on the magnetic exchange interactions between them will be obtained. There is still another effect. Oxygen nonstoichiometry, the degree of which is given by x, results in not only a change of the uranium valency in the solid solution but also a weakening of the magnetic interaction. Deconvolution of these effects is necessary.

In spite of many investigations on the system La–U–O (*1*), only a few reports have been presented on the magnetic properties of this system. Kemmler-Sack *et al.* (*2*) measured the magnetic susceptibilities of $La_{0.5}U_{0.5}O_2$ and $La_{0.33}U_{0.67}O_{2.17}$ in the

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temperature range from 84 to 473 K and applied the Curie–Weiss law considering the contribution of temperature-independent paramagnetism. They discussed the relationship between the Curie constant obtained and the symmetry of ligands around the central uranium ion. On the other hand, Henrich (*3*) measured the magnetic susceptibility of $La_{0.5}U_{0.5}O_2$ in the temperature range from 4.2 K to room temperature and reported that the magnetic moment varied from 0.39 μ_B (at 4.2 K) to 1.41 μ_B (at room temperature). In both the investigations, the oxidation state of uranium was made a priori pentavalent, and no discussion was made on the effect of lanthanum concentration on the magnetic interactions between uranium ions. Also, the effect of excess oxygen at the interstitial sites in $La_{0.33}U_{0.67}O_{2.17}$ on the magnetic interactions has not been discussed.

In this study, we prepared the solid solutions with cubic fluorite structure, $La_yU_{1-y}O_{2+x}$, with various x and y values, and measured their magnetic susceptibilities from 4.2 K to room temperature. The effect of lanthanum concentration and oxygen nonstoichiometry on the magnetic interactions between uranium ions was examined. The magnetic parameters obtained were compared with those for (U, Y)O_2 (*4*), (U, Sc)O_2 (*5*), and (U, Th)O_2 (*6*) solid solutions.

Experimental

Sample Preparation

As the starting materials, UO_2 and La_2O_3 were used. Before use, UO_2 was reduced to stoichiometric composition in flowing hydrogen at 1000°C, and La_2O_3 was heated in air at 850°C to remove any moisture.

The UO_2 and La_2O_3 were weighed to the intended atom ratios of uranium and lanthanum. 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. In an induction furnace in flowing helium at 1400°C for 8 hr.

Condition II. In the same induction furnace in flowing helium at 1500°C for 40 hr.

Condition III. In an SiC resistance furnace in flowing unpurified helium at 1310°C for 210 hr. The partial pressure of oxygen in the helium gas used here was significantly higher than the pressures of Conditions I and II.

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

Analysis

X-ray diffraction analysis. X-ray diffraction study was performed using Cu$K\alpha$ radiation using a Philips PW-1390 diffractometer with a curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson–Riley extrapolation method applied to the diffraction lines above 80° (2θ).

Determination of oxygen. 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. 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 the ferroin indicator. The oxygen amount was determined for predetermined La/U ratio.

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 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 (liquid He temperature ~ 40 K) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (*6*).

Results and Discussion

X-ray Diffraction and Oxygen Nonstoichiometry

X-ray diffraction analysis showed that cubic solid solutions with fluorite structure were formed for all the specimens in this study with the exception of the La/(La + U) = 0.1 specimen formed under Condition III which was a mixture of cubic solid solution and rhombohedral U_3O_8. The variation of lattice parameter of the solid solutions with lanthanum concentration, *y*, is shown in Fig. 1.

The determination of the amount of oxygen in the solid solutions by the back-titration method showed that the solid solutions prepared under Conditions I, II, and III were nearly oxygen stoichiometric, oxygen deficient, and oxygen excess, respectively. Figure 2 shows the variation of O/*M* ratio with lanthanum concentration, where *M* indicates La + U.

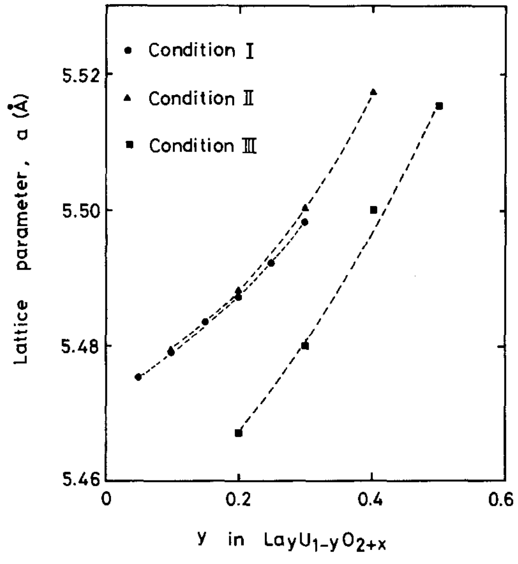

FIG. 1. Variation of lattice parameter with lanthanum concentration.

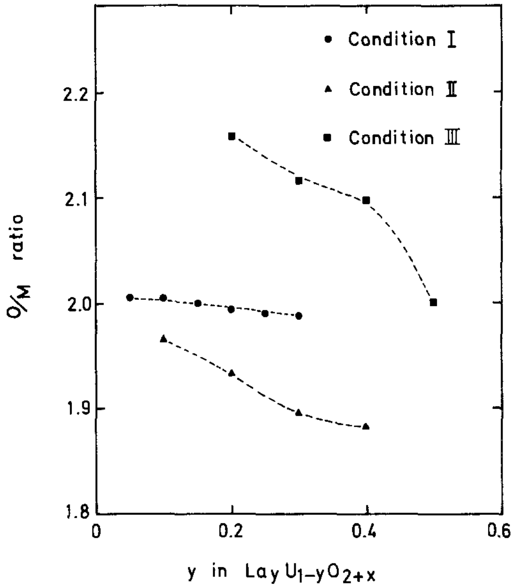

FIG. 2. Variation of O/*M* ratio with lanthanum concentration.

It has been reported by several researchers that in the La–U–O system the oxygen-stoichiometric solid solutions (O/*M* = 2) can be prepared under a variety of reaction conditions (partial pressure of oxygen, reaction temperature, etc.). However, the lattice parameter seems to vary with lanthanum concentration among the reports. According to Hill (*9*), the solid solutions prepared under a hydrogen atmosphere at 1750°C were oxygen stoichiometric and the lattice parameter increased with lanthanum concentration, where its derivative also increased with lanthanum concentration. Stadlbauer *et al.* (*10*) studied the relationship between the lattice parameter and the equilibrium oxygen pressure of oxygen-stoichiometric solid solution for various lanthanum concentrations. They report that the lattice parameter increased linearly with the lanthanum concentration. Tagawa *et al.* (*11*) reported the solid solutions prepared under hydrogen atmosphere at 1100°C to be oxygen stoichiometric, but the description of the lattice parameter is lacking. In the present study, oxygen-stoichiometric solid solutions were prepared under Condition I, i.e., oxygen pressure of ca. 1×10^{-1} Pa and a reaction temperature of 1400°C. The lattice parameter, a, did not increase linearly with lanthanum concentration, y, and the derivative $\partial a/\partial y$ increased with lanthanum concentration. This result is consistent with that obtained by Hill.

In Fig. 3 the mean valency of uranium in the solid solutions against lanthanum concentration is plotted. The uranium is seen to be oxidized with increasing lanthanum concentration for the solid solutions prepared under any of the three conditions. However, the mean valency of uranium remains +5 for $La_{0.50}U_{0.50}O_{2.001}$ prepared under Condition III. This fact suggests that the oxidized state of uranium is U^{5+} in the solid solutions. This will be discussed in a later section.

Magnetic Susceptibility

The temperature dependence of magnetic susceptibilities per mole of uranium for the solid solutions is shown in Figs. 4–6. An antiferromagnetic transition was found for the solid solutions prepared under Conditions I and II ($y \leq 0.3$) in the temperature range measured.

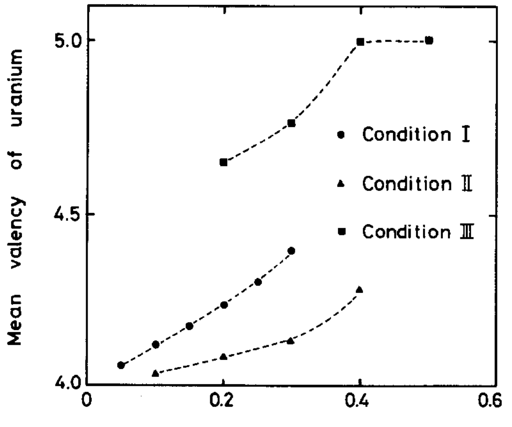

FIG. 3. Mean uranium valency against lanthanum concentration.

From the fact that the transition temperature decreases with increasing lanthanum concentration for the oxygen-stoichiometric solid solutions (Fig. 4), the magnetic dilution is found to proceed with lanthanum concentration. Below the transition temperature, the magnetic susceptibility decreased with decreasing temperature, which is normal to antiferromagnetism but contrasts the behavior found in UO_2 (*12–14*). The antiferromagnetic transition was not observed for the solid solutions with excess oxygens (Fig. 6). Hence, the excess oxygens located at the interstitial sites are considered to weaken the magnetic exchange interactions between the uranium ions significantly.

Oxidation State of Uranium

The oxidation state of uranium in the solid solutions can be elucidated from the magnetic susceptibility data.

In the case where U^{4+} ions are oxidized to the U^{6+} state, the ionic species in the solid solutions are expressed as

$$La_y^{3+}U_{1-x-1.5y}^{4+}U_{x+0.5y}^{6+}O_{2+x}^{2-}. \qquad (1)$$

This equation shows that only the U^{4+} ions contribute to the paramagnetic susceptibility of the solid solutions, because the U^{6+} ions are diamagnetic. Then, the ratio of U^{4+} ions in the two solid solutions with the same (total) uranium concentration will be proportional to the Curie constant in the paramagnetic temperature region where the Curie–Weiss law holds. For example, the Curie constants of $La_{0.20}U_{0.80}O_{1.994}$ and $La_{0.20}U_{0.80}O_{2.159}$ are 0.921 and 0.575, respectively. On the other hand, the ratios of U^{4+} ions (U^{4+}/U_{total}) which are given by $(1 - x - 1.5y)/(1 - y)$ are 0.883 and 0.676 for $La_{0.20}U_{0.80}O_{1.994}$ and $La_{0.20}U_{0.80}O_{2.159}$, re-

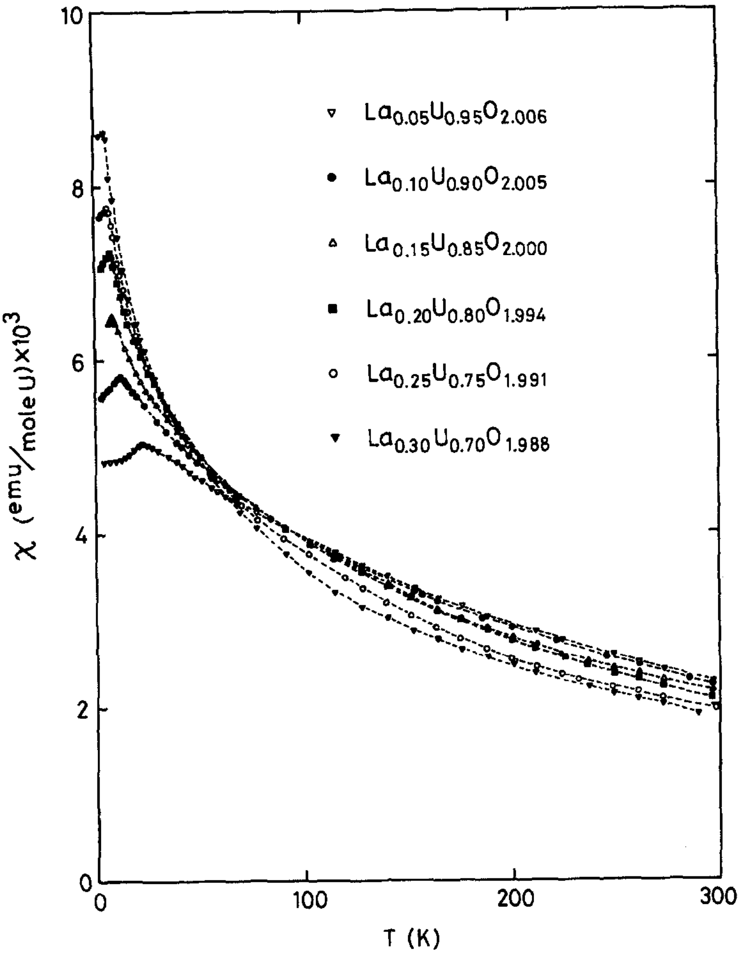

FIG. 4. Temperature dependence of magnetic susceptibilities of solid solutions prepared under Condition I.

spectively. The ratio of the Curie constant (0.921/0.575 = 1.60) is not near the ratio of U^{4+} ions (0.883/0.676 = 1.31) in the two solid solutions. From these results, it can be assumed that the uranium ions are not oxidized to the hexavalent state.

In the case where the oxidation of uranium proceeds from U^{4+} to U^{5+}, the ions in the solid solutions are

$$La_y^{3+}U_{1-2x-2y}^{4+}U_{2x+y}^{5+}O_{2+x}^{2-} \quad (2)$$

and both U^{4+} and U^{5+} ions contribute to the paramagnetism of the solid solutions.

For the magnetic susceptibilities of two solid solutions with the same y value but different x values (χ_1, χ_2), the following two equations hold:

$$\chi_1 = (1 - 2x_1 - 2y)\chi(U^{4+}) + (2x_1 + y)\chi(U^{5+}) \quad (3)$$

$$\chi_2 = (1 - 2x_2 - 2y)\chi(U^{4+}) + (2x_2 + y)\chi(U^{5+}), \quad (4)$$

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 these two equations, $\chi(U^{5+})$ is expressed as

$$\chi(U^{5+}) = \frac{[(1 - 2x_2 - 2y)\chi_1 - (1 - 2x_1 - 2y)\chi_2]}{2(1 - y)(x_1 - x_2)}. \quad (5)$$

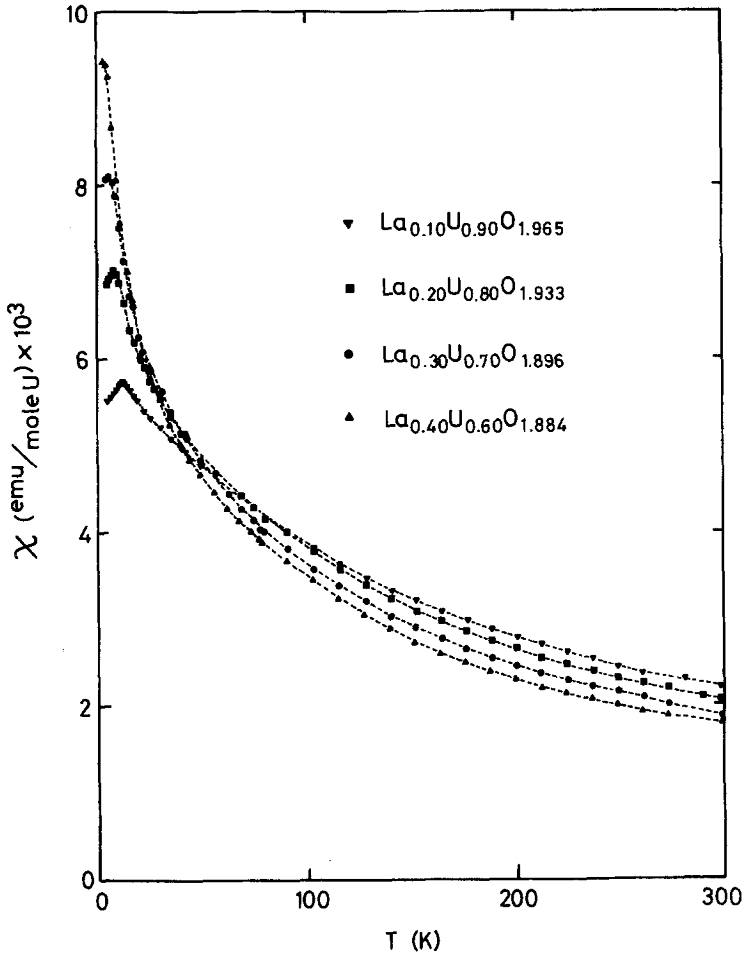

FIG. 5. Temperature dependence of magnetic susceptibilities of solid solutions prepared under Condition II.

When this model is applied to the two solid solutions, viz., $La_{0.20}U_{0.80}O_{1.994}$ and $La_{0.20}U_{0.80}O_{2.159}$, the reciprocal susceptibility of U^{5+} vs the temperature curve is obtained as shown in Fig. 7. The Curie–Weiss law is found to hold in the temperature range from 20 K to room temperature and its effective magnetic moment is 1.65 μ_B. This value is a little lower than the moment calculated by assuming that only the ground level of U^{5+} ion in a cubic crystalline field produced by eight oxygen ions contributes to the susceptibility (2.00 μ_B) (*5*, *15*), but is close to the value observed in the uranates of alkaline earth elements with fluorite structure MU_2O_6 (M = Ca, Sr or Ba) (1.6–1.8 μ_B), the uranium valency of which is +5 (*13*). Therefore, it is considered that the oxidation of U^{4+} proceeds by producing U^{5+} state in the $La_yU_{1-y}O_{2+x}$ solid solutions.

If the magnetic susceptibility of U^{5+} ion is eliminated from Eqs. (3) and (4), the susceptibility of U^{4+} ion is given as

$$\chi(U^{4+}) = \frac{(2x_1 + y)\chi_2 - (2x_2 + y)\chi_1}{2(1 - y)(x_1 - x_2)}. \quad (6)$$

Substituting the magnetic susceptibility data of $La_{0.20}U_{0.80}O_{1.994}$ and $La_{0.20}U_{0.80}O_{2.159}$ into Eq. (6), the susceptibility of U^{4+} ion is obtained. From the reciprocal susceptibility vs the temperature curve shown in Fig. 7, the magnetic moment of U^{4+} was obtained to be 2.96 μ_B. This value is between the moment of UO_2 (3.12 μ_B (*6, 17*), 3.2 μ_B (*15, 18*)) and that of UO_2 infinitely diluted with diamagnetic ThO_2, i.e., 2.83 μ_B (*17, 19*) or 2.79 μ_B (*6*). The magnetic moment obtained is in reasonable agreement with those of the compounds composed of U^{4+} ions, which also supports the above-mentioned oxidation model (Eq. (2)).

Néel Temperature

The paramagnetic–antiferromagnetic transition temperature, i.e., the Néel temperature, was plotted against uranium concentration in Fig. 8. For comparison, data for (U, Th)O_2 (*6*) and (U, Y)O_2 (*4*) solid solutions were also drawn. The variation of the Néel temperature for the present solid solutions with uranium concentration is similar to that for (U, Y)O_2 solid solutions, but considerably different from that for (U, Th)O_2 solid solutions where the Néel temperature decreases linearly with decreasing uranium concentration. The nonlinear dependence of Néel temperature on uranium concentration is understood as related to the formation of U^{5+} ions (*4*).

The Néel temperatures of (U, La)O_2 solid

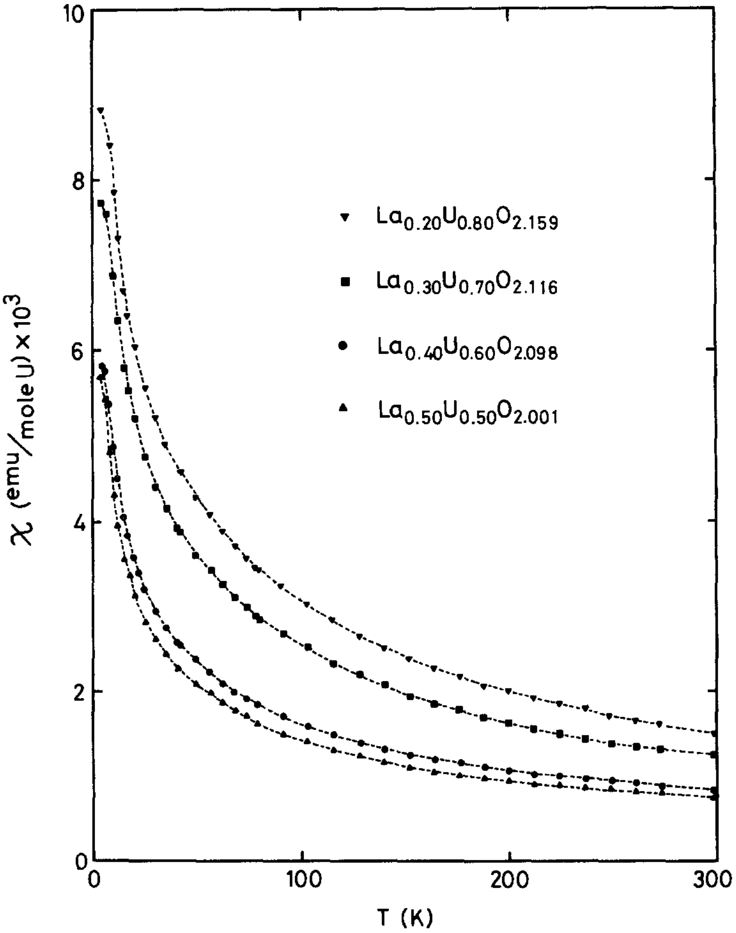

FIG. 6. Temperature dependence of magnetic susceptibilities of solid solutions prepared under Condition III.

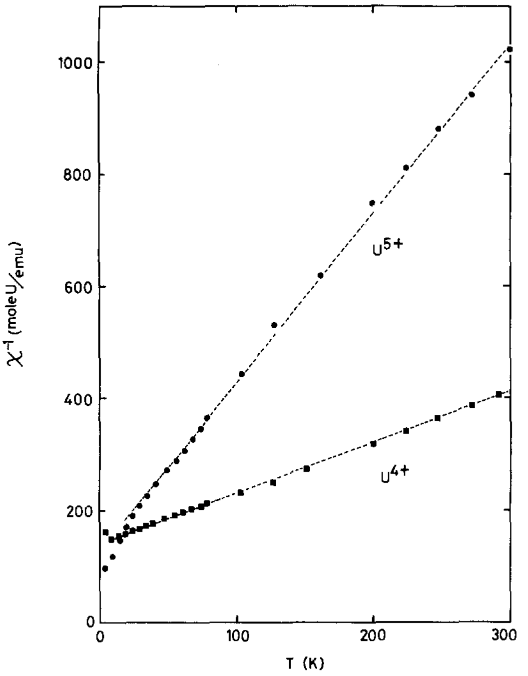

FIG. 7. Inverse magnetic susceptibilities of U^{5+} ion and U^{4+} ion vs temperature.

solutions are lower than those of the (U, Y)O_2 solid solutions with the same uranium concentrations. The lower temperatures indicate that the dilution effect of La_2O_3 on antiferromagnetic interactions between the uranium ions in the UO_2 lattice is larger compared with that of Y_2O_3. This difference may result from the fact that the distance between uranium ions increases with decreasing uranium concentration for (U, La)O_2 solid solutions while it decreases for (U, Y)O_2 solid solutions.

The Néel temperatures of (U, La)O_2 solid solutions are likely also to be lower than those of the (U, Sc)O_2 solid solutions with the same uranium concentrations. This is shown by the Néel temperatures 24.0 and 17.2 K for $Sc_{0.05}U_{0.95}O_{2.001}$ and $Sc_{0.10}U_{0.90}O_{1.998}$, respectively (*5*), although a very convincing conclusion cannot be drawn from the two data above for nearly oxygen-stoichiometric (U, Sc)O_2 solid solutions. The lower temperatures show that the mag-

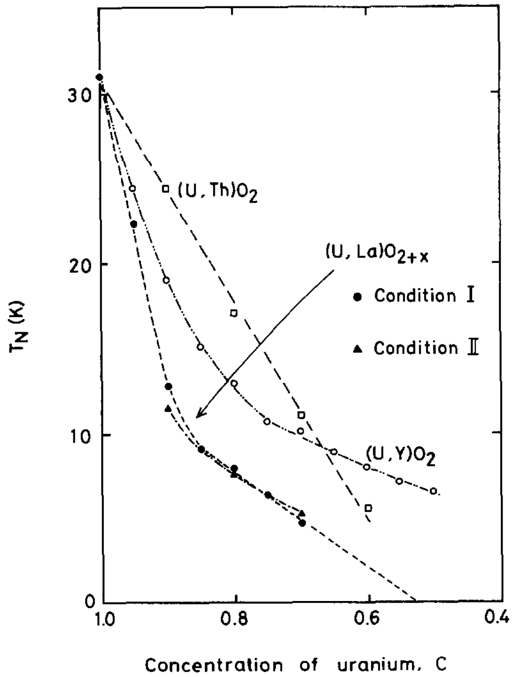

FIG. 8. Variation of Néel temperature with uranium concentration.

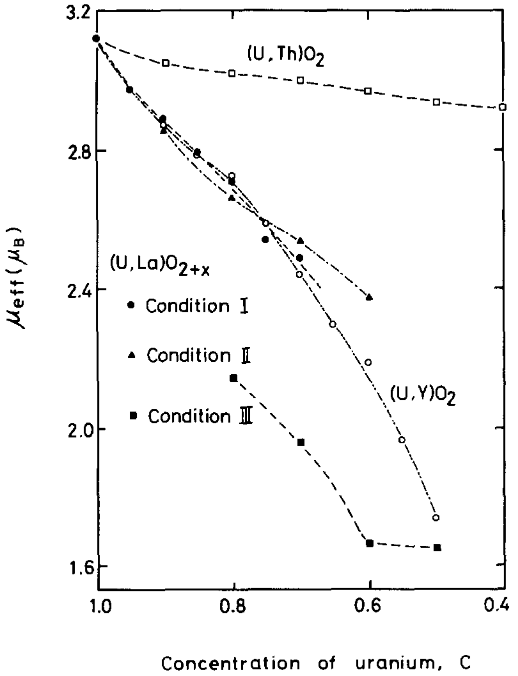

FIG. 9. Variation of magnetic moment with uranium concentration.

netic dilution effect of La_2O_3 is also larger than that of Sc_2O_3.

By extrapolating the curve of T_N versus C (= $1 - y$) to $T_N = 0$ K in Fig. 8, the critical concentration, C_0, at which the antiferromagnetism disappears for (U, La)O_2 solid solutions was estimated to be $C_0 = 0.53$.

As already mentioned, the antiferromagnetic transition was not observed in the temperature range measured for the solid solutions having excess oxygens, which indicates that the excess oxygens located at the interstitial sites weaken the magnetic interactions between uranium ions to a larger extent. On the other hand, if the Néel temperatures of $La_{0.10}U_{0.90}O_{1.965}$ and $La_{0.20}U_{0.80}O_{1.933}$ are compared with those of $La_{0.10}U_{0.90}O_{2.005}$ and $La_{0.20}U_{0.80}O_{2.001}$, respectively, oxygen vacancies are found also to weaken the magnetic interactions between uranium ions. From these facts, it is seen that it is the oxygen ions at the regular anion sites in the fluorite lattice that play an important role in transferring the magnetic interactions between uranium ions, which reversely shows that these magnetic exchange interactions are of the superexchange type of interaction via oxygen ions.

The Néel temperature of $La_{0.30}U_{0.70}O_{1.988}$ is slightly lower than that of $La_{0.30}U_{0.70}O_{1.896}$. In the $y = 0.3$ solid solutions, the oxygen nonstoichiometry has much larger effect on the increase of U^{5+} than in the $y = 0.1$ or 0.2 solid solutions. The ratios of U^{5+}/U^{4+} are 0.65 and 0.15, for $La_{0.30}U_{0.70}O_{1.988}$ and $La_{0.30}U_{0.70}O_{1.896}$, respectively. Therefore, it is considered that the increased U^{5+} ions influence the magnitudes of the magnetic interactions, as contrasted with the $y = 0.1$ or 0.2 cases.

Magnetic Moment

From the reciprocal susceptibility vs temperature curves, the effective magnetic moments were obtained in the temperature region in which the Curie–Weiss law holds. The variation of magnetic moment with uranium concentration is shown in Fig. 9. For comparison, the data for (U, Th)O_2 (*6*) and (U, Y)O_2 (*4*) solid solutions are also plotted. The magnetic moment decreased with decreasing uranium concentration for the solid solutions prepared under any of the three conditions.

First, the case of nearly oxygen-stoichiometric solid solutions prepared under Condition I will be considered. The magnetic moment decreased with decreasing uranium concentration. Its slope is much steeper than that of (U, Th)O_2 solid solutions and is comparable with that of (U, Y)O_2 solid solutions. Earlier discussion (*6*) on the decrease of magnetic moment in the (U, Th)O_2 solid solutions led to a conclusion that the decrease in the magnetic interactions with adjacent uranium ions is responsible for the phenomenon. On the other hand, the decrease of magnetic moment in the (U, Y)O_2 solid solutions is due to the formation of U^{5+} ion which gives a lower magnetic moment than U^{4+} ion (*4*). The data for (U, La)O_2 solid solutions are similar to those for (U, Y)O_2 solid solutions. The decrease of magnetic moment in the (U, La)O_2 solid solutions can be attributed to the oxidation of U^{4+} to U^{5+}.

The behavior of the magnetic moment with varying uranium concentration for the oxygen-deficient solid solutions is peculiar. The solid solutions $La_{0.10}U_{0.90}O_{1.965}$ and $La_{0.20}U_{0.80}O_{1.933}$ have smaller magnetic moments than the oxygen-stoichiometric solid solutions with the same uranium concentration, but in the case of solid solutions with $U/(U + La) = 0.7$, the magnetic moment of a nearly oxygen-stoichiometric solid solution ($La_{0.30}U_{0.70}O_{1.988}$) is smaller than that of an oxygen-deficient solid solution ($La_{0.30}U_{0.70}O_{1.896}$). This behavior is understandable by assuming the same mechanism as in the analysis of the Néel temperature. The smaller magnetic moment of oxygen-deficient solid solutions, in the case of U/(U +

La) = 0.8 and 0.9, is because the magnetic exchange interactions are weaker compared with those in the oxygen-stoichiometric solid solutions. The fact that the solid solution with weaker magnetic interaction has a smaller magnetic moment is found experimentally in (U, Th)O_2 solid solutions (*6*). When the concentration of uranium is lowered to 0.7, the effect of the increased U^{5+} ion which has smaller magnetic moment than U^{4+} ion is considered to be sufficiently large on the magnetic moment of the solid solution, and consequently, the oxygen-stoichiometric solid solution in which the oxidation of uranium proceeds more than in oxygen-deficient solid solution had smaller magnetic moment.

The next is for the case of the oxygen-excess solid solutions (prepared under Condition III). Compared with the oxygen-stoichiometric solid solutions, the magnetic moment of the oxygen-excess solid solutions is smaller, which indicates that the larger number of uranium was oxidized to U^{5+} state by excess oxygen. With decreasing uranium concentration, the magnetic moment decreased, but it did not decrease between $C = 0.6$ and 0.5. The magnetic moment was 1.65 μ_B for both $La_{0.40}U_{0.60}O_{2.098}$ and $La_{0.50}U_{0.50}O_{2.001}$. The mean valencies of uranium are both closely near to 5+ (Fig. 3). Therefore, this value of the magnetic moment would be solely that of the U^{5+} ion at the cation sites in fluorite structure, and is in good agreement with the moment of U^{5+} obtained in under Oxidation State of Uranium. Furthermore it is near to the magnetic moment of uranates of alkaline earth elements with fluorite structure, MU_2O_6 (M = Ca, Sr or Ba) (1.6–1.8 μ_B) (*16*).

Weiss Constant

In Fig. 10, the Weiss constant is plotted against the uranium concentration for nearly oxygen-stoichiometric solid solutions. For comparison, the data of (U, Y)O_2 solid solutions (*4*) are also drawn. The Weiss constant should be a measure of the magnitude of the magnetic exchange interaction. The Weiss constant of (U, La)O_2 solid solutions is smaller than that of (U, Y)O_2 solid solutions. The result can be related to the fact that the Néel temperature of the former solid solutions is lower than that of the latter solid solutions. The Weiss constant of (U, Th)O_2 solid solutions decreases linearly with decreasing uranium concentration, which is explained well by a model that the exchange interaction for any one U^{4+} ion is proportional to the number of nearest- and/or next-nearest-neighbor U^{4+} ions (*6*). With decreasing uranium concentration, the Weiss constant of (U, La)O_2 solid solutions deviates more from the linear relation obtained by the above model (solid straight line in Fig. 10), which corresponds to the formation of increased number of U^{5+} ions in the solid solutions.

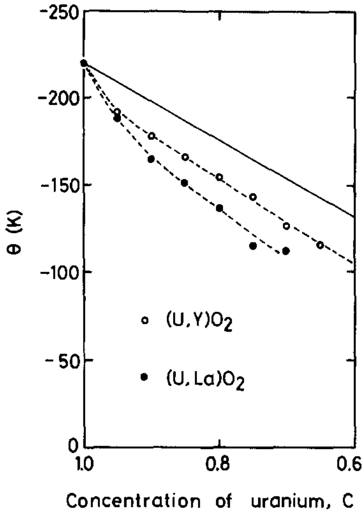

FIG. 10. Variation of Weiss constant with uranium concentration. The solid line represents the theoretical value calculated by assuming that the exchange interaction for any one U^{4+} ion is proportional to the number of nearest- and next-nearest-neighbor U^{4+} ions.

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