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

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Magnetic susceptibilities of $Ca_yU_{1-y}O_{2+x}$ solid solutions with fluorite structure were measured from 4.2 K to room temperature. An antiferromagnetic transition was observed for all the solid solutions examined in this study ($y \leq 0.33$). The Néel temperature of the oxygen-hypostoichiometric solid solutions ($x < 0$) decreased with increasing calcium concentration, which shows that magnetic dilution proceeds with calcium concentration. The variation of the Néel temperature with uranium concentration was similar to that of $(U,Y)O_2$ solid solutions, but different from that of $(U,Th)O_2$ solid solutions. The effective magnetic moment decreased with increasing calcium concentration, which indicates the oxidation of uranium in the solid solutions. From the analysis of the magnetic susceptibility data, it was found that the oxidation state of uranium was either tetravalent or pentavalent. The Néel temperature of the hyperstoichiometric solid solutions ($x > 0$) did not change appreciably with calcium concentrations. From the comparison of the magnetic susceptibility data of the hypostoichiometric solid solutions with those of the hyperstoichiometric solid solutions, the effect of oxygen vacancies is more significant than that of interstitial oxygens on the decrease of magnetic interactions between uranium ions.

Introduction

Uranium dioxide (UO_2) has been by far the most intensively studied of the actinide oxides. Neutron diffraction analysis shows that UO_2 becomes antiferromagnetically ordered below 30.8 K. Its magnetic structure 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 in each plane are antiparallel to those of the neighboring planes (*1*). The crystal structure of UO_2 is cubic fluorite type and some metal oxides such as alkaline-earth oxides and rare-earth oxides are known to dissolve in UO_2 at high temperatures forming substitutional solid solutions. Although the physical, chemical, and/or thermodynamic properties of such solid solutions have been extensively investigated (*2*), studies on the magnetic properties are meager.

In the preceding papers, the magnetic properties of $(U, M)O_2$ solid solutions with fluorite structure have been examined, where M is a tetravalent or trivalent diamagnetic ion. From the magnetic studies on $(U, Th)O_2$ and $(U, Zr)O_2$ solid solutions, the substitution of Th^{4+} or Zr^{4+} for U^{4+} in UO_2 lattice caused a magnetic dilution, and the antiferromagnetic–paramagnetic transition temperature (the Néel temperature) has been found to decrease linearly with decreasing uranium concentration (*3–5*). In

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the case of (U, Y)O_2 or (U, La)O_2 solid solutions, however, the situation is a little more complicated (*6, 7*). The substitution of Y^{3+} or La^{3+} for U^{4+} in UO_2 lattice results in not only a magnetic dilution of UO_2, but also an oxidation of uranium ions to the pentavalent state in order to conserve the electrical neutrality in the solid solutions. The variation of the Néel temperature with uranium concentration is considerably different from those for (U, Th)O_2 and (U, Zr) O_2 solid solutions; a nonlinear dependence of the Néel temperature on uranium concentration has been found. Oxygen nonstoichiometry gives an additional effect on the magnetic properties by itself and through a valence state change of the uranium ions.

The magnetic studies on the compounds of Ca–U–O system were done only by Leroy and Triddot (*8*) and Brochu and Lucas (*9*). From the measurements of the magnetic susceptibility of $CaUO_{3.66}$, $CaUO_{3.50}$, and CaU_2O_6 in the temperature range from 77 to 680 K, Leroy and Triddot (*8*) assumed the existence of the UO_2^+ group with linear O–U–O bond in these compounds, but Keller (*10*) considered such a UO_2^+ group to be an incorrect form in the CaU_2O_6 with cubic fluorite structure. On the other hand, Brochu and Lucas (*9*) measured the magnetic susceptibility of CaU_2O_6 in the temperature range from 85 to 300 K, and obtained the magnetic moment of U^{5+} from the Curie–Weiss law relation.

In the present study, $Ca_yU_{1-y}O_{2+x}$ solid solutions with various x and y values over which the crystal structures are fluorite type (same as UO_2) were prepared and their magnetic susceptibilities measured from 4.2 K to room temperature. The effect of calcium substitution and oxygen nonstoichiometry on the magnetic interactions between uranium ions was examined. From the analysis of magnetic susceptibility data, the oxidation state of uranium in the solid solutions is discussed.

Experimental

1. Sample Preparation

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

The UO_2, U_3O_8, and CaO were weighted to form seemingly oxygen stoichiometric solid solutions, $Ca_yU_{1-y}O_{2.00}$ (y = 0.05–0.33), as shown in the following equation.

$$(1-2.5y)UO_2 + 0.5yU_3O_8 + yCaO \rightarrow Ca_yU_{1-y}O_{2.00} \quad (1)$$

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 an induction furnace in a flow of helium gas at 1400°C for 15 hr. The partial pressure of oxygen was approximately 1×10^{-1} Pa.

Condition II: The reaction in an SiC resistance furnace in a flow of unpurified helium gas at 1400°C for 50 hr. The approximate partial pressure of oxygen was 10 Pa.

After cooling in the same atmosphere to room temperature, the samples were crushed into powder, re-pressed, 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. 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 the Nelson–Riley extrapolation method (*11*) 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 (*12, 13*). 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 a standard iron(II) ammonium sulfate solution with the ferroin indicator. The oxygen amount was determined for predetermined Ca/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 ($\chi_g = 10{,}980 \times 10^{-6}/(T + 0.7)$) as a standard. The temperature of the sample was measured by a "normal" Ag vs Au–0.07 at% Fe thermocouple (4.2–40 K) (*14*) and an Au–Co vs Cu thermocouple (10 K to room temperature). Details of the experimental procedure have been described elsewhere (*4*).

TABLE I

LATTICE PARAMETERS AND MAGNETIC PARAMETERS FOR $Ca_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS[a]

Solid solution	a (Å)	μ_{eff} (B.M.)	T_N (K)	Preparation condition
$Ca_{0.05}U_{0.95}O_{1.988}$	5.4613	2.96	24.1	I
$Ca_{0.10}U_{0.90}O_{1.984}$	5.4505	2.84	14.0	I
$Ca_{0.15}U_{0.85}O_{1.984}$	5.4430	2.77	11.8	I
$Ca_{0.20}U_{0.80}O_{1.985}$	5.4386	2.69	10.0	I
$Ca_{0.25}U_{0.75}O_{1.973}$	5.4339	2.57	8.0	I
$Ca_{0.30}U_{0.70}O_{1.960}$	5.4297	2.50	7.6	I
$Ca_{0.33}U_{0.67}O_{1.950}$	5.4270	2.47	7.4	I
$Ca_{0.10}U_{0.90}O_{2.065}$	5.4450	2.69	9.9	II
$Ca_{0.15}U_{0.85}O_{2.034}$	5.4353	2.66	9.0	II
$Ca_{0.20}U_{0.80}O_{2.030}$	5.4250	2.58	9.0	II
$Ca_{0.25}U_{0.75}O_{2.035}$	5.4133	2.42	8.6	II
$Ca_{0.30}U_{0.70}O_{2.039}$	5.4026	2.28	8.0	II
$Ca_{0.33}U_{0.67}O_{2.051}$	5.3940	2.09	8.0	II

[a] Estimated errors are $\Delta x = \pm 0.003$, $\Delta a = \pm 0.0005$ Å, $\Delta\mu_{eff} = \pm 0.01$ B.M., and $\Delta T_N = \pm 0.1$ K.

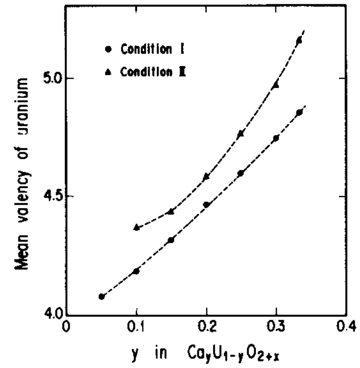

FIG. 1. Mean valency of uranium against calcium concentration.

Results and Discussion

1. Oxygen Nonstoichiometry

X-ray diffraction analysis showed that cubic solid solutions with the fluorite structure were formed as single phase for all the specimens in this study. The composition and lattice parameter of the solid solutions prepared are listed in Table I. The $Ca_yU_{1-y}O_{2+x}$ solid solutions prepared under Condition I have negative x values, i.e., they are oxygen hypostoichiometric. The oxygen/metal ratio, O/M, of the solid solutions with $y = 0.5$–0.20 does not change appreciably ($O/M \sim 1.98$), but the ratio for the solid solutions with $y \geq 0.25$ decreases with increasing calcium concentration. On the other hand, the solid solutions prepared under Condition II are all oxygen hyperstoichiometric ($x > 0$).

The variation of mean uranium valency with calcium concentration is shown in Fig. 1. The uranium ions are seen to be oxidized with increasing calcium concentration for the solid solutions prepared under any of these two conditions. For the solid solutions with the same y value, the uranium

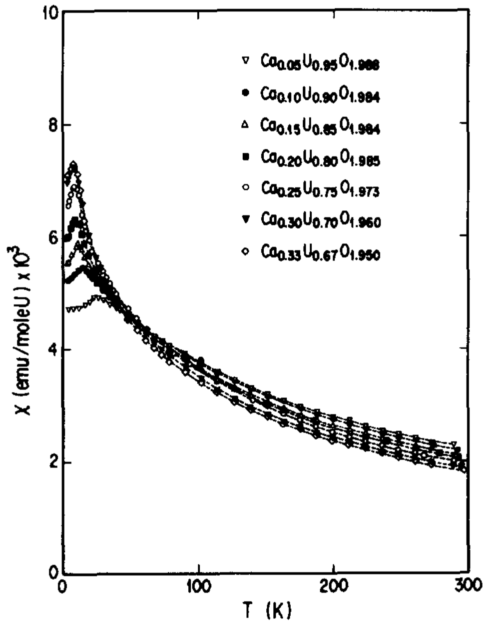

FIG. 2. Temperature dependence of magnetic susceptibilities of $Ca_yU_{1-y}O_{2+x}$ solid solutions under Condition I.

ions were more oxidized under Condition II than under Condition I.

2. *Magnetic Susceptibility*

The temperature dependence of magnetic susceptibilities per mole of uranium for the present solid solutions is shown in Figs. 2 and 3. An antiferromagnetic transition was found for all the solid solutions examined in this study. For the solid solutions prepared under Condition I (Fig. 2), the transition temperature (the Néel temperature) decreased with increasing calcium concentration, which indicates that the magnetic dilution proceeds with calcium concentration. Below the Néel temperature, the magnetic susceptibility decreases significantly with decreasing temperature and this decrease becomes more prominent for the solid solutions with higher calcium concentrations. This behavior is normal for the antiferromagnet and has been observed in the susceptibility of (U, Y)O_2 or (U, La)O_2 solid solutions (*6, 7*) but not in that of UO_2 (*15, 16*), (U, Th)O_2 solid solutions (*3, 4*), or (U, Zr)O_2 solid solutions (*5*). In the latter solid solutions, the magnetic susceptibilities attain constant values below the Néel temperatures. As will be discussed in the following section, some U^{4+} ions are oxidized to the U^{5+} state in the (U, Ca)O_2 solid solutions. Since the constant magnetic susceptibility has been found for the solid solutions in which the valence state of uranium is +4 only, the decrease of magnetic susceptibility below the Néel temperature may be due to the magnetic interactions between U^{5+}–U^{5+} ions or in some cases those between U^{5+}–U^{4+} ions. In the temperature region where the Curie–Weiss law holds (from liquid nitrogen temperature to room temperature), the susceptibility decreased with increasing calcium concentration, which is consistent with the increased amount of oxidized uranium (Fig. 1). On the other hand, the Néel temperature of the oxygen-hyper-

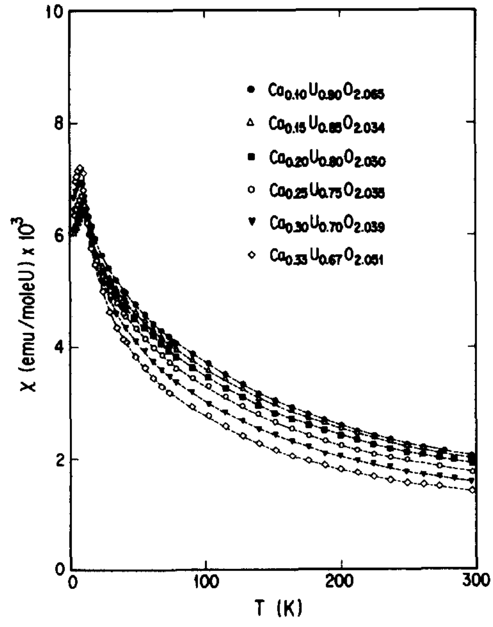

FIG. 3. Temperature dependence of magnetic susceptibilities of $Ca_yU_{1-y}O_{2+x}$ solid solutions under Condition II.

stoichiometric solid solutions prepared under Condition II did not change appreciably with calcium concentration (Fig. 3). The reason for this discrepancy will be discussed in a later section.

3. *Valence State of Uranium*

The oxidation state of uranium in the solid solutions will be discussed by analyzing the magnetic susceptibility data. The oxygen nonstoichiometry in the solid solutions affects the effective magnetic moment of uranium mainly through the change of the valence state of uranium. This effect will be analyzed for the solid solutions with the same y value but different x value.

If U^{4+} ions are assumed to be oxidized to the U^{6+} state by the substitution of Ca^{2+} for U^{4+} or by the incorporation of oxygen, the ionic species in the solid solutions are expressed as

$$Ca_y^{2+}U_{1-x-2y}^{4+}U_{x+y}^{6+}O_{2+x}^{2-}. \qquad (2)$$

This model shows that only the U^{4+} ions contribute to the paramagnetic susceptibility of the solid solutions, because the U^{6+} ions are diamagnetic. For the two solid solutions with the same calcium amount (y) but different oxygen amounts (x), the paramagnetic susceptibility of the solid solution with higher oxygen amount must be smaller than that of 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, for example, the magnetic susceptibility of $Ca_{0.10}U_{0.90}O_{2.065}$ is larger than that of $Ca_{0.10}U_{0.90}O_{1.984}$ below 100 K (see Fig. 4). The same results can be seen for a couple of solid solutions with $y = 0.15$ or 0.20. From these facts, we can conclude that the uranium ions are not oxidized as shown in Eq. (2).

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

$$Ca_y^{2+}U_{1-2x-3y}^{4+}U_{2x+2y}^{5+}O_{2+x}^{2-}, \qquad (3)$$

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

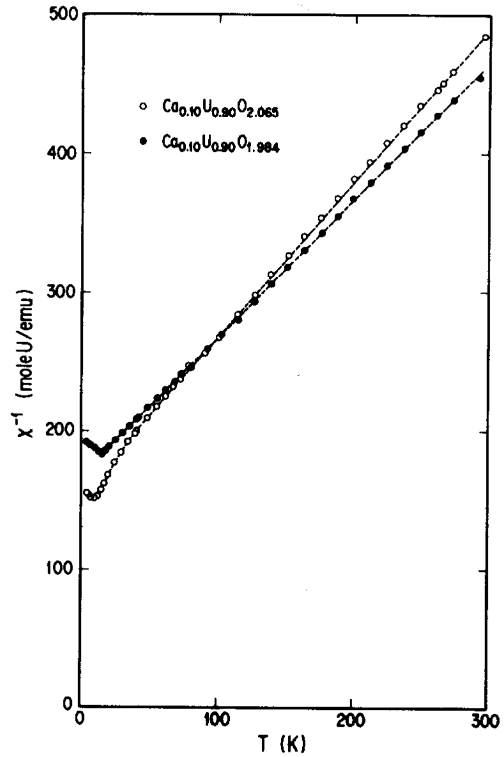

FIG. 4. Temperature dependence of reciprocal magnetic susceptibilities of $Ca_{0.10}U_{0.90}O_{1.984}$ and $Ca_{0.10}U_{0.90}O_{2.065}$.

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:

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

$$\chi_2 = (1 - 2x_2 - 3y)\chi(U^{4+}) + (2x_2 + 2y)\chi(U^{5+}), \qquad (5)$$

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. (4) and (5), $\chi(U^{5+})$ is expressed as

$$\chi(U^{5+}) = \frac{[(1 - 2x_2 - 3y)\chi_1 - (1 - 2x_1 - 3y)\chi_2]}{2(1 - y)(x_1 - x_2)}. \qquad (6)$$

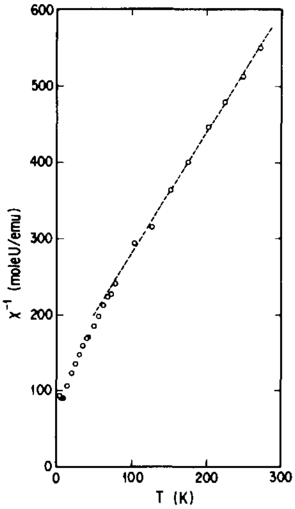

FIG. 5. Reciprocal magnetic susceptibility of U^{5+} ion vs temperature.

When this model is applied to the two solid solutions, viz., $Ca_{0.10}U_{0.90}O_{1.984}$ and $Ca_{0.10}U_{0.90}O_{2.065}$, the reciprocal susceptibility of U^{5+} vs temperature curve is obtained as shown in Fig. 5. The Curie–Weiss law is found to hold in the temperature range from 60 K to room temperature and its effective magnetic moment was obtained to be 2.27 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 quartet Γ_8 (in Bethe's notation) (*17*). If only this quartet level contributes to the paramagnetism of these solid solutions, their magnetic moment is calculated to be 2.00 B.M. (*18, 19*). The moment obtained from the present experiment is a little larger than that calculated and is lower than that of the U^{5+} in free ion state (2.54 B.M.). The mean valency of uranium in $Ca_{0.30}U_{0.70}O_{2.039}$ is near +5 (Fig. 1), and the effective magnetic moment is 2.28 B.M. from experiment. Therefore, the moment obtained above is considered to be reasonably due to U^{5+} ion. Since the moment of $Ca_{0.10}U_{0.90}U_{1.984}$ is 2.84 B.M., the effective magnetic moment of U^{4+} is calculated to be 2.96 B.M. This value is between the moment of UO_2 (3.12–3.20 B.M.) (*4, 18, 20, 21*) and that of UO_2 infinitely diluted with diamagnetic ThO_2 (2.79–2.83 B.M.) (*4, 20, 22*). The magnetic moment obtained is in reasonable agreement with those of the compounds composed of U^{4+} ions. As the result of above considerations, we may conclude that there exist U^{4+} and U^{5+} ions in the $Ca_yU_{1-y}O_{2+x}$ solid solutions.

4. *Néel Temperature*

The paramagnetic–antiferromagnetic transition temperature, i.e., the Néel temperature, is plotted against uranium concentration in Fig. 6. For comparison, the data for (U, Th)O_2 (*4*), (U, Y)O_2 (*6*), and (U, La)O_2 (*7*) solid solutions are also drawn. The decreasing trend of the Néel temperature with uranium concentration for the solid solutions prepared under Condition I is similar to those for (U, Y)O_2 and (U, La)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

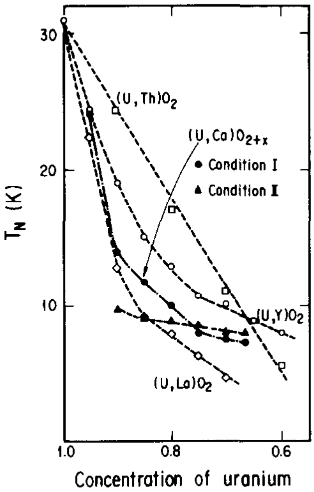

FIG. 6. Variation of Néel temperature with uranium concentration.

concentration. The nonlinear dependence of the Néel temperature on uranium concentration is understood as related to the formation of U^{5+} ions (*6*).

When the concentration of oxygen vacancies is as low as 0.8 at%, the effect of such oxygen vacancies on the magnetic interactions between uranium ions may be negligibly small (*19*). Since the solid solutions with $y \leq 0.20$ prepared under Condition I contain the vacancies lower than 0.8 at% (Table I), the comparison of the magnetic data of these solid solutions can be made meaningfully with those of (U, Y)O_2 and (U, La)O_2 solid solutions. As seen from Fig. 6, the Néel temperatures of oxygen-hypostoichiometric (U, Ca)O_{2-x} solid solutions are lower than those of the (U, Y)O_2 solid solutions and higher than those of the (U, La)O_2 solid solutions at the same uranium concentrations. This result indicates that the effect of magnetic dilution with calcium on the antiferromagnetic interactions is between those with yttrium and lanthanum. The above intermediate interactions may result from the fact that the distance between uranium ions in the (U, Ca) O_{2-x} solid solutions is between those in (U, Y)O_2 and (U, La)O_2 solid solutions.

The Néel temperatures of the solid solutions prepared under Condition II (which are oxygen hyperstoichiometric) does not change appreciably with calcium concentration. When the Néel temperatures of these solid solutions are compared with those of the solid solutions prepared under Condition I ($y \leq 0.20$), the excess oxygens located at the interstitial sites in UO_2 lattice can be found to weaken the magnetic interactions between uranium ions to a larger extent. The same results have been found in the magnetic susceptibilities of UO_{2+x} (*15, 16*), (U, Sc)O_{2+x} (*19*), and (U, La)O_{2+x} (*7*) solid solutions. For the solid solutions with $y = 0.25$–0.33 prepared under Condition I, the concentration of oxygen vacancies is too large to neglect such effect on the magnetic interactions between uranium ions. They contribute significantly in weakening the magnetic exchange interactions between uranium ions (*6, 7*). The Néel temperatures of these solid solutions are lower than those of the oxygen-hyperstoichiometric solid solutions prepared under Condition II with the same calcium concentrations. Since the concentrations of oxygen vacancies (Condition I) are comparable to those of interstitial oxygens (Condition II) for the solid solutions with $y = 0.30$ and 0.33, it may be said that the effect of oxygen vacancies is much larger than that of interstitial oxygens on the decrease of magnetic interactions between uranium ions.

5. *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 moments are listed in Table I. The variation of magnetic moment with uranium concentration is shown in Fig. 7. For comparison, the data for (U, Th)O_2 (*4*) and (U, Y)O_2 (*6*) solid solutions are also plotted in the same figure.

First, the case of the solid solutions prepared under Condition I will be considered. The magnetic moment decreases with de-

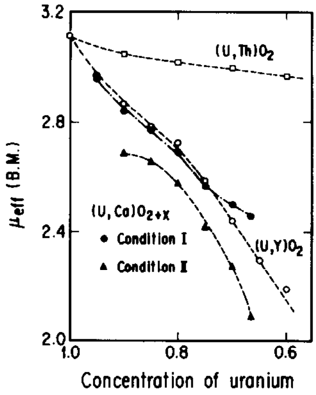

FIG. 7. Variation of effective magnetic moment with uranium concentration.

creasing uranium concentration, and the decrement is much larger than that in the (U, Th)O_2 solid solutions and is comparable to that in the (U, Y)O_2 solid solutions. The reason for the decrease of magnetic moment in the (U, Th)O_2 solid solutions has been discussed in terms of the decrease in the magnetic interactions with adjacent uranium ions (*4*). 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*). Since the mean valency of uranium increases with calcium concentration (Fig. 1), this decrease of magnetic moment is considered to be mainly due to the oxidation of U^{4+} to U^{5+} in the solid solutions. The substitution of one Ca^{2+} ion for U^{4+} ion in UO_2 lattice results in the oxidation of two U^{4+} ions to the U^{5+} state in the (U, Ca)O_2 solid solutions, not one U^{4+} ion as found in the (U, Y)O_2 solid solutions. The number of U^{5+} ions is twice as many in the (U, Ca)O_2 solid solutions as in the (U, Y)O_2 solid solutions, and therefore the effective magnetic moment of the former solid solutions is expected to be lower than that of the latter solid solutions. Experimental results, however, show that the magnitude of the effective magnetic moment of (U, Ca)O_{2-x} solid solutions (Condition I) is comparable to that of (U, Y)O_2 solid solutions. The reason for the large magnetic moment is not clear at the present stage, but it may be the case that in the (U, Ca)O_{2-x} solid solutions the crystalline field distorts slightly from cubic symmetry, which could affect the magnetic moments. Since calcium valency (+2) is more apart from uranium valency (+4) than yttrium valency (+3) is, the distortion of oxygen atoms from the regular positions with cubic symmetry is possible.

The next is for the case of the oxygen-excess solid solutions (prepared under Condition II). The effective magnetic moment of uranium decreases with increasing calcium concentration, which corresponds to the increase of mean uranium valency as shown in Fig. 1. Compared with the results of the solid solutions prepared under Condition I, the magnetic moment is smaller for Condition II specimens. The oxidized U^{5+} ion produced in large number by excess oxygens is no doubt responsible for such smaller moments.

References

1. B. C. Frazer, G. Shirane, D. E. Cox, and C. E. Olsen, *Phys. Rev. A* **140,** 1148 (1965).
2. "Gmelin's Handbuch der Anorganischen Chemie," System-Nr55, U, Teil C3, Springer-Verlag, New York/Berlin (1975).
3. J. B. Comly, *J. Appl. Phys.* **39,** 716 (1968).
4. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **60,** 195 (1985).
5. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **60,** 224 (1985).
6. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **66,** 332 (1987).
7. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **68,** 255 (1987).
8. J. M. Leroy and G. Triddot, *C. R. Acad. Sci. Paris, Ser. C* **262,** 1376 (1966).
9. R. Brochu and J. Lucas, *Bull. Soc. Chim. Fr.*, 4764 (1967).
10. "Gmelin's Handbuch der Anorganischen Chemie," p. 90, System-Nr55, U, Teil C3, Springer-Verlag, New York/Berlin (1975).
11. L. V. Azaroff, *in* "Elements of X-ray Crystallography," p. 479, McGraw–Hill, New York (1968).
12. S. R. Dharwadkar and M. S. Chandrasekharaih, *Anal. Chim. Acta* **45,** 545 (1969).
13. T. Fujino and T. Yamashita, *Fresenius' Z. Anal. Chem.* **314,** 156 (1983).
14. L. L. Sparks and R. L. Powell, *J. Res. Natl. Bur. Stand. Sect. A* **76,** 263 (1972).
15. A. Arrott and J. E. Goldman, *Phys. Rev.* **108,** 948 (1957).
16. M. J. M. Leask, L. E. J. Roberts, A. J. Walter and W. P. Wolf, *J. Chem. Soc.*, 4788 (1967).
17. K. R. Lea, M. J. M. Leask, and W. P. Wolf, *J. Phys. Chem. Solids* **23,** 1381 (1962).
18. S. Nasu, *Japan. J. Appl. Phys.* **5,** 1001 (1966).
19. Y. Hinatsu and T. Fujino, *J. Solid State Chem.* **62,** 342 (1986).
20. E. Slowinski and N. Elliott, *Acta Crystallogr.* **5,** 768 (1952).
21. J. K. Dawson and M. W. Lister, *J. Chem. Soc.*, 5041 (1952).
22. C. A. Hutchison, Jr. and G. A. Candela, *J. Chem. Phys.* **27,** 707 (1957).