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

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Solid solutions $Mg_yU_{1-y}O_{2+x}$ with fluorite structure were prepared and their magnetic susceptibilities were measured from 4.2 K to room temperature. An antiferromagnetic transition was observed for the solid solutions examined in this study. Both the Néel temperature and the effective magnetic moment of uranium decreased with increasing magnesium concentration. The change in the magnetic properties of these solid solutions with x and y values was compared with that of $M_yU_{1-y}O_{2+x}$ solid solutions where $M = Ca^{2+}$, Y^{3+}, La^{3+}, or Th^{4+}. The substitution of Mg^{2+} for U^{4+} was found to oxidize uranium ions to the +5 state but not to the +6 state. The variation of the effective magnetic moment of uranium against mean uranium valency is quite similar to that for the solid solutions with $M = Ca^{2+}$, Y^{3+}, or La^{3+}.

Introduction

Uranium dioxide (UO_2) crystallizes in the well known fluorite structure in which U^{4+} ions order antiferromagnetically below 30.8 K (*1*). This UO_2 incorporates excess oxygen in the interstitial lattice positions. Some metal oxides such as alkaline earth oxides and rare earth oxides dissolve in the UO_2 at high temperatures forming substitutional solid solutions, $M_yU_{1-y}O_{2+x}$ (*2*), which show oxygen deficiency on one side of the stoichiometric composition and excess oxygen on the other (*3*). For the case of trivalent rare earth ions, oxygen stoichiometric solid solutions ($x = 0$) are formed and their magnetic properties have been examined to elucidate the behavior of 5*f* electrons in the solids. The substitution of M^{3+} for uranium results in not only a magnetic dilution of UO_2 but also an oxidation of uranium ions to the +5 state in order to preserve the electrical neutrality in the solid solutions (*4*). In the case of M^{2+}, the situation is more complicated, i.e., it is difficult to prepare oxygen stoichiometric solid solutions. Then, oxygen nonstoichiometry also affects the magnetic properties of solid solutions. In our earlier study, the magnetic properties of $Ca_yU_{1-y}O_{2+x}$ solid solutions were examined (*5*). In this study, we will extend the study to the $Mg_yU_{1-y}O_{2+x}$ solid solutions.

The magnetic properties of $Mg_yU_{1-y}O_{2+x}$ solid solutions were studied only by Kemmler-Sack *et al.* (*6*), who measured the magnetic susceptibility of $Mg_{0.33}U_{0.67}O_2$ (MgU_2O_6) in the temperature range of 78 to 473 K and found the susceptibility data followed the Langevin–Debye relation, $\chi = C/T + A$, where $C = 0.16$ and $A = 415 \times 10^{-6}$. However, the oxygen amount in the solid solution was not analyzed.

The solubility of magnesium oxide (MgO) in UO_2 is only a few mole percent, even at 2350°C in vacuum (*7*), because MgO has a rock salt structure which is not a related

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type to the fluorite structure of UO_2 and because the ionic radius of Mg^{2+} is considerably smaller than that of U^{4+}. However, it increases markedly when the solid solution is allowed to take up extra oxygen until a fluorite lattice having no vacant anion sites is formed. Fujino and Naito (*8*) reported the preparation of solid solutions with $0 < y < 0.33$ by the reaction of the mixtures of $MgUO_4$, MgU_3O_{10}, and/or UO_2 in a flow of helium gas at 1000 ~ 1100°C.

In this study, $Mg_yU_{1-y}O_{2+x}$ solid solutions with various x and y values over which the crystal structures are fluorite-type were prepared in a flow of helium gas, and their magnetic susceptibilities were measured from 4.2 K to room temperature. The results were compared with the magnetic properties of solid solutions, $M_yU_{1-y}O_{2+x}$, where $M = Ca^{2+}$, Y^{3+}, La^{3+}, or Th^{4+}, and the effects of magnesium substitution and oxygen nonstoichiometry on the magnetic properties of UO_2 were examined.

Experimental

1. Sample Preparation

As starting materials, UO_2, U_3O_8, and MgO 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 MgO was heated in air at 800°C to remove any moisture.

The UO_2, U_3O_8, and MgO were weighed to form seemingly oxygen stoichiometric solid solutions, $Mg_yU_{1-y}O_{2.00}$, as shown in the following equation:

$$(1 - 2.5y)\,UO_2 + 0.5y\,U_3O_8 + y\,MgO \rightarrow Mg_yU_{1-y}O_{2.00}. \quad (1)$$

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 1500°C for 15 hr. The partial pressure of oxygen was approximately 1×10^{-1} Pa; $y = 0.05, 0.10, 0.20, 0.30$.

Condition II: The reaction in a flow of unpurified helium gas at 1260°C for 80 hr. The approximate partial pressure of oxygen was 10 Pa; $y = 0.05, 0.10, 0.15, \cdots, 0.30, 0.33$.

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. An 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 (*9*) 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 (*10, 11*). A weighed amount of sample was dissolved in an excess 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 Mg : U ratio. The error in x is estimated to be less than ±0.003.

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 ($\chi_g = 10980 \times 10^{-6}/(T + 0.7)$)

TABLE I

LATTICE PARAMETER AND MAGNETIC DATA FOR $Mg_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS

Solid solution	a (Å)	μ_{eff} (μ_B)	T_N (K)	Preparation condition
$Mg_{0.05}U_{0.95}O_{1.975}$	5.4602	3.03	26.6	I
$Mg_{0.10}U_{0.90}O_{1.932}$	5.4506	2.97	23.0	I
$Mg_{0.20}U_{0.80}O_{1.807}$	5.4485	2.94	20.8	I
$Mg_{0.10}U_{0.90}O_{2.006}$	5.4316	2.72	—	II
$Mg_{0.15}U_{0.85}O_{1.961}$	5.4152	2.66	10.8	II
$Mg_{0.20}U_{0.80}O_{1.927}$	5.3955	2.57	9.3	II
$Mg_{0.25}U_{0.75}O_{1.898}$	5.3778	2.44	8.4	II
$Mg_{0.30}U_{0.70}O_{1.859}$	5.3667	2.35	8.0	II
$Mg_{0.33}U_{0.67}O_{1.827}$	5.3624	2.31	7.8	II

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) (*12*) and an Au–Co vs. Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (*13*).

Results and Discussion

1. X-ray Diffraction and Oxygen Nonstoichiometry

X-ray diffraction analysis showed that cubic solid solutions with fluorite structure were formed as single phase for the specimens with $y = 0.05$, 0.10, and 0.20 under Condition I and for the specimens with $y = 0.10 \sim 0.33$ under Condition II. The specimen with $y = 0.30$ formed under Condition I was a mixture of cubic solid solution and cubic MgO, and the specimen with $y = 0.05$ formed under Condition II was a mixture of cubic solid solution and rhombohedral U_3O_8. The composition and lattice parameter of the solid solutions prepared are listed in Table I. The determination of oxygen amount in the solid solutions by the cerium back-titration method showed that except for the solid solution $Mg_{0.10}U_{0.90}O_{2.006}$ prepared under Condition II, the oxygen/metal ratios, O/M, of the solid solutions were less than two, i.e., they were oxygen hypostoichiometric.

The mean valency of uranium (ν) in the solid solutions was calculated assuming the valencies of magnesium and oxygen to be +2 and −2, respectively. Its variation against magnesium concentration (y) is shown in Fig. 1. The uranium ions in the solid solutions prepared under Condition II are seen to be oxidized with increasing magnesium concentration. On the other hand,

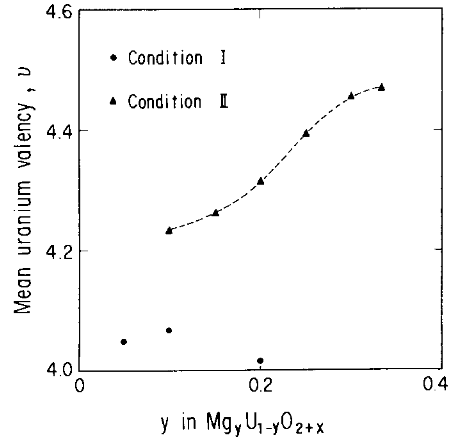

FIG. 1. Mean valency of uranium against magnesium concentration.

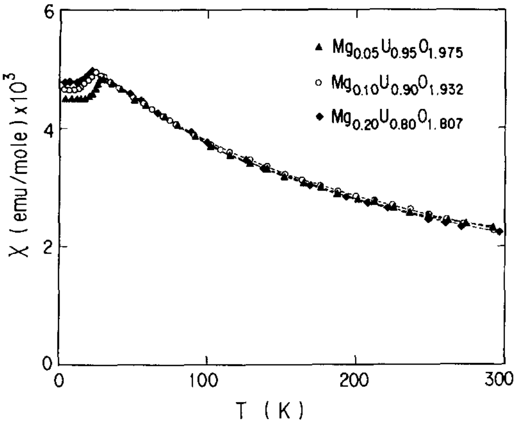

FIG. 2. Temperature dependence of magnetic susceptibilities of $Mg_yU_{1-y}O_{2+x}$ solid solutions prepared under Condition I.

the variation of mean uranium valency with y for the solid solutions prepared under Condition I is not straight. The reason for this is that the preparation conditions such as reaction temperature and partial pressure of oxygen are a little different from specimen to specimen.

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 with the exception of $Mg_{0.10}U_{0.90}O_{2.006}$ prepared under Condition II. The transition temperature (the Néel temperature) decreased with increasing magnesium concentration, which indicates that the magnetic dilution proceeds with magnesium concentration. In the solid solutions prepared under Condition I, the magnetic susceptibilities become temperature-independent below the Néel temperatures (Fig. 2). Similar behavior has been observed in the susceptibilities of UO_2, $(U,Th)O_2$, or $(U,Zr)O_2$ solid solutions (*13–15*). On the other hand, the magnetic susceptibilities decrease significantly with decreasing temperature in the solid solutions prepared under Condition II, and this decrease becomes more prominent for the solid solutions with higher magnesium concentrations (Fig. 3). This behavior is normal for the antiferromagnet, and has been observed in the susceptibilities of $(U,Y)O_2$ or $(U,La)O_2$ solid solutions (*16, 17*). As will be discussed in the following section, some U^{4+} ions are oxidized to the U^{5+} state in the $(U,Mg)O_{2+x}$ solid solutions. So, the decrease of magnetic susceptibility with decreasing temperature below the Néel temperature is considered to be due to the magnetic interactions between U^{5+}–U^{5+} ions or in some cases those between U^{5+}–U^{4+} ions.

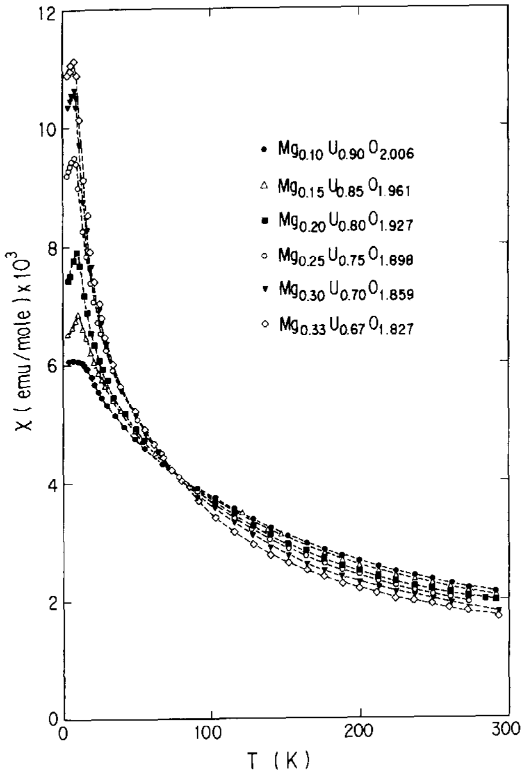

FIG. 3. Temperature dependence of magnetic susceptibilities of $Mg_yU_{1-y}O_{2+x}$ solid solutions prepared under Condition II.

3. *Oxidation State of Uranium*

The oxidation state of uranium in the solid solutions is 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 values.

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

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

This model shows that only the U^{4+} ions contribute to the paramagnetism of the solid solutions, because the U^{6+} ions generated by introduction of Mg^{2+} are diamagnetic. The excess oxygen is positioned interstitially. For the two solid solutions with the same magnesium 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 $Mg_{0.10}U_{0.90}O_{2.006}$ is larger than that of $Mg_{0.10}U_{0.90}O_{1.932}$ below 100 K. From these results, we can conclude that the uranium ions are not oxidized as shown in Eq. (1).

In the case where the oxidation of uranium proceeds from U^{4+} to U^{5+} by substitution of Mg^{2+} for U^{4+}, the ionic species in the solid solutions are

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

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,

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

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

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

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

When this model is applied to the two solid solutions, viz., $Mg_{0.10}U_{0.90}O_{1.932}$ and $Mg_{0.10}U_{0.90}O_{2.006}$, the susceptibility of U^{5+} is derived from Eq. (5). The effective magnetic moment of U^{5+} is calculated from the inclination of the reciprocal susceptibility vs. temperature curve and is obtained to be 1.67 μ_B. 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 Russell–Saunders' coupling scheme) splits into two levels, of which the lowest is quartet Γ_8 (in Bethe's notation) (*18*). If only this quartet level contributes to the paramagnetism of these solid solutions, its magnetic moment is calculated to be 2.00 μ_B (*19, 20*). The moment obtained from the present experiment is a little smaller than that calculated, but is very close to the magnetic moment of uranates of alkaline earth elements with fluorite structure, MU_2O_6 (M = Ca, Sr, or Ba) (1.68 ~ 1.82 μ_B) (*21*). These results indicate that there exist U^{4+} and U^{5+} ions in the $Mg_yU_{1-y}O_{2+x}$ solid solutions.

4. *Néel Temperature*

The variation of the Néel temperatures with uranium concentration is shown in Fig.

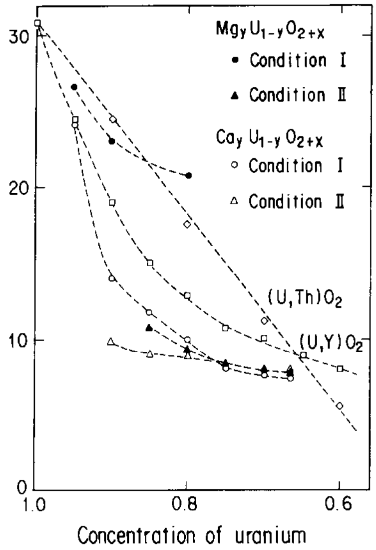

FIG. 4. Variation of Néel temperature with uranium concentration.

4. For comparison, the data for $Ca_yU_{1-y}O_{2+x}$, $Y_yU_{1-y}O_2$, and $Th_yU_{1-y}O_2$ solid solutions (*5*, *13*, *16*) are also shown. The Néel temperatures of solid solutions prepared under Condition I are decreased with decreasing uranium concentration, but the decrements are much smaller than those for $Ca_yU_{1-y}O_{2+x}$ solid solutions. The reason for this is that the oxidation of uranium did not proceed greatly with magnesium substitution (Fig. 1); that is, the oxygen concentration also decreased with decreasing uranium concentration. This effect is also found in the temperature dependence of magnetic susceptibilities in the lower temperature region, where the susceptibilities become temperature independent below the Néel temperature (Fig. 2). The Néel temperatures of solid solutions prepared under Condition II decrease with increasing magnesium concentration, indicating the magnetic dilution proceeds with magnesium substitution. The Néel temperatures of $Mg_yU_{1-y}O_{2+x}$ solid solutions are higher than those of $Ca_yU_{1-y}O_{2+x}$ solid solutions with the same y values, which indicates that the dilution effect of MgO on antiferromagnetic interactions between the uranium ions is smaller compared with that of CaO. This may be attributable to the fact that with increasing y value, the lattice parameter (therefore the distance between uranium ions) decreases much more in the magnesium solid solutions than in the calcium solid solutions. The same results have been found in the Néel temperatures of $Y_yU_{1-y}O_{2+x}$ and $La_yU_{1-y}O_{2+x}$ solid solutions (*16*, *17*). Surprisingly, no antiferromagnetic transition was observed in $Mg_{0.10}U_{0.90}O_{2.006}$ solid solution. One possible reason for this is that the interstitial oxygens hinder the magnetic exchange interactions between uranium ions.

5. *Magnetic Moment*

From the reciprocal susceptibility vs. temperature curves, the effective magnetic moments of uranium were obtained in the temperature region in which the Curie–Weiss law holds. The moments are listed in Table I. With increasing magnesium (y) or oxygen (x) concentrations, the moment decreased. The variation of magnetic moment with uranium concentration is shown in Fig. 5. For comparison, the data for $Th_yU_{1-y}O_2$, $Y_yU_{1-y}O_2$, and $Ca_yU_{1-y}O_{2+x}$ solid solutions (*5*, *13*, *16*) are also plotted in the same figure.

The magnetic moment of uranium reflects its oxidation state. First, the case of solid solutions prepared under Condition II will be considered. The effective magnetic moment of uranium decreases with increasing magnesium concentration, which corresponds to the increase of mean uranium valency as shown in Fig. 1. At the same y values, the magnetic moments of $Mg_yU_{1-y}O_{2+x}$ ($x \lesssim 0$) solid solutions prepared under Condition II are smaller than those of $Y_yU_{1-y}O_2$ solid solutions, which is attributable to the higher oxidation state of uranium in the former solid solutions than in the latter solid solutions. The effective magnetic mo-

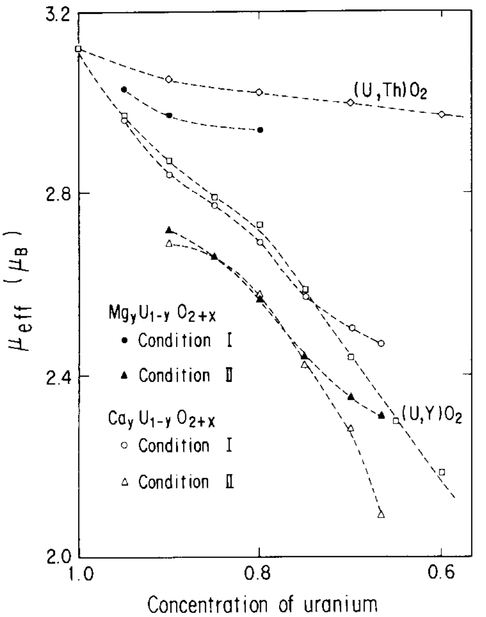

FIG. 5. Variation of effective magnetic moment of uranium with uranium concentration.

ments of solid solutions prepared under Condition I are larger than those of solid solutions prepared under Condition II. This result is caused by the less oxidized uranium (formation of the higher oxygen vacancies) in the former solid solutions than in the latter solid solutions (Fig. 1). Although the mean valency of uranium in $Mg_{0.20}U_{0.80}O_{1.807}$ ($\nu = +4.02$) is smaller than that in $Mg_{0.10}U_{0.90}O_{1.932}$ ($\nu = +4.07$), the moment of the former solid solution is smaller than that of the latter solid solution. The reason for this is the decrease of magnetic exchange interactions with decreasing uranium concentration. This effect is seen more clearly in the decrease of magnetic moment of $Th_yU_{1-y}O_2$ solid solutions with decreasing uranium concentration (*13*) (Fig. 5).

The variation of the effective magnetic moment of uranium against the mean uranium valency is shown in Fig. 6. For comparison, the moments of $Ca_yU_{1-y}O_{2+x}$ and $Y_yU_{1-y}O_2$ solid solutions are also drawn. The data of latter solid solutions are connected by dashed line. Both the moments of $Mg_yU_{1-y}O_{2+x}$ and $Ca_yU_{1-y}O_{2+x}$ prepared under Condition II follow this dashed line. This result means that the magnetic moment of uranium is insensitive to the kind of substitutional atom for uranium, i.e., it is determined mainly by the oxygen coordination around the uranium atom. From Fig. 6, the moment of uranium of which the mean valency is +5 is 1.67 μ_B, which is in accord with the moment obtained from Eq. (5). The moments of oxygen deficient solid solutions prepared under Condition I deviate a little downward from this dashed line. In the fluorite-type structure, each uranium ion is octa-coordinated by the eight oxygen ions. In the oxygen deficient solid solutions, some of these oxygen atoms remove from their regular sites, forming the oxygen vacancies. Therefore, it is considered that the lack of

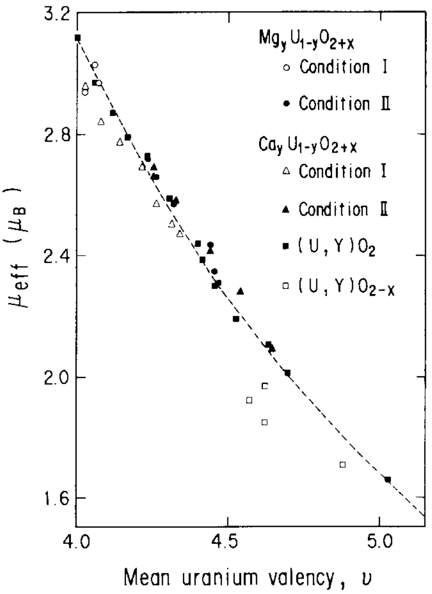

FIG. 6. Variation of effective magnetic moment of uranium with mean uranium valency.

oxygen atoms (formation of oxygen vacancies) in these solid solutions affects significantly the moments of uranium. The same deviation from this dashed line has been also found in the moments of oxygen hypostoichiometric solid solutions, $Y_yU_{1-y}O_{2-x}$ (*22*) (Fig. 6).

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