

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

### II. Magnetic Susceptibilities of Solid Solutions with High Lanthanum and Oxygen Concentrations

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Magnetic susceptibilities of fluorite-type  $La_yU_{1-y}O_{2+x}$  solid solutions with various  $x$  and  $y$  values were measured from 1.8 K to room temperature. With increasing lanthanum and oxygen concentrations, the effective magnetic moment of uranium decreased, and the uranium ions were found to be oxidized from +4 to +5 to +6. The effect of lanthanum substitution for uranium and oxygen nonstoichiometry on the variation of effective magnetic moment and the Néel temperature was discussed. © 1991 Academic Press, Inc.

#### Introduction

Uranium dioxide ( $UO_2$ ) is a paramagnet with two unpaired  $5f$  electrons and becomes antiferromagnetically ordered below 30.8 K (1). Some metal oxides such as lanthanum sesquioxide are known to dissolve in the  $UO_2$  at high temperatures, forming substitutional solid solutions (2). In the preceding paper (3), we prepared solid solutions with the fluorite-type structure,  $La_yU_{1-y}O_{2+x}$ , with various  $x$  and  $y$  values in flowing helium atmospheres and measured their magnetic susceptibilities in the temperature range of 4.2 K to room temperature. With substituting lanthanum for uranium, the magnetic exchange interactions between uranium ions are weakened and some of the tetravalent uranium ions are oxidized not to the +6 state, but to the +5 state. The oxidation of uranium did not proceed beyond +5, even by further substitution of lanthanum for uranium.

In this study, the reaction was carried out

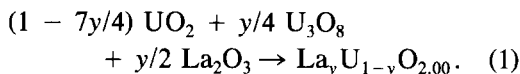
in air to prepare solid solutions in which the mean uranium valency is over +5. The oxidation state of uranium in the  $La_yU_{1-y}O_{2+x}$  solid solutions was elucidated through their magnetic susceptibility measurements, and the effect of oxygen nonstoichiometry on the magnetic properties of solid solutions was discussed.

#### Experimental

##### 1. Sample Preparation

As starting materials,  $UO_2$ ,  $U_3O_8$ , and  $La_2O_3$  were used. Before use,  $UO_2$  was reduced to stoichiometric composition in flowing hydrogen at 1000°C,  $U_3O_8$  was oxidized in air at 850°C to form stoichiometric compound, and  $La_2O_3$  was heated in air at 800°C to remove any moisture.

The  $UO_2$ ,  $U_3O_8$  and  $La_2O_3$  were weighed to form seemingly oxygen stoichiometric solid solutions,  $La_yU_{1-y}O_{2.00}$ , as shown in the following equation:



After being finely ground in an agate mortar, the mixtures were pressed into pellets and then heated under either of the following two conditions:

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

**Condition II:** The reaction in air at 1400°C for 40 hr. After cooling 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  $\text{CuK}\alpha$  radiation on a Philips PW-1390 diffractometer with a curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson-Riley extrapolation method (4) applied to the diffraction lines above  $80^\circ$  ( $2\theta$ ).

**2.2 Chemical Analysis.** The chemical analysis to determine  $x$  and  $y$  values in the  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  solid solutions was done by determining the amount of total uranium and  $\text{U}^{4+}$  by means of Ce(IV)-Fe(II) back titration method after being dissolved in an excess cerium(IV) sulfate solution (5, 6). The cerium(IV) sulfate solution was standardized in advance with stoichiometric  $\text{UO}_2$ . The remaining cerium(IV) was titrated against a standard iron(II) ammonium sulfate solution with the ferroin indicator. After the  $y$  value was ascertained to be unchanged by heating, only the  $x$  value was determined by the titration. The error in  $x$  is estimated to be less than  $\pm 0.003$ .

## 3. Magnetic Susceptibility Measurement

Magnetic susceptibility was measured by a Faraday-type torsion balance in the tem-

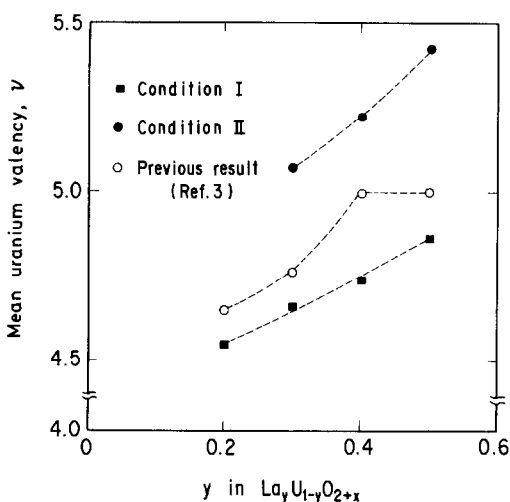


FIG. 1. Mean valency of uranium against lanthanum concentration.

perature range from 1.8 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 (1.8 ~40 K) (7) and an Au-Co vs. Cu thermocouple (10 K ~room temperature).

## Results and Discussion

### 1. Oxygen Nonstoichiometry

X-ray diffraction analysis showed that cubic solid solutions with the fluorite structure were formed in single phase for all of the solid solutions in this study. The composition and lattice parameter of the solid solutions prepared are listed in Table I together with those of the solid solutions previously reported (3).

Figure 1 shows the variation of mean valency of uranium ( $\nu$ ) in the solid solutions with lanthanum concentration ( $y$ ). In a flow of unpurified helium gas at 1310°C (previous experiment) (3), all of the uranium ions were oxidized to the +5 state for the  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  solid solutions with  $y = 0.4$ , and the

TABLE I  
MAGNETIC PARAMETERS OF  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  SOLID SOLUTIONS

Solid solution	Lattice parameter(Å)	Mean uranium valency	$\mu_{\text{eff}}$ ( $\mu_{\text{B}}$ )	$\theta$ (K)	$T_{\text{N}}$ (K)	Preparation condition
$\text{La}_{0.20}\text{U}_{0.80}\text{O}_{2.119}$	5.4712	4.55	2.26	-97.4	—	I
$\text{La}_{0.30}\text{U}_{0.70}\text{O}_{2.080}$	5.4846	4.66	2.10	-98.4	—	I
$\text{La}_{0.40}\text{U}_{0.60}\text{O}_{2.022}$	5.5033	4.74	1.94	-100.4	—	I
$\text{La}_{0.50}\text{U}_{0.50}\text{O}_{1.966}$	5.5192	4.86	1.65	-108.8	—	I
$\text{La}_{0.30}\text{U}_{0.70}\text{O}_{2.226}$	5.4769	5.07	1.65	-119.4	—	II
$\text{La}_{0.40}\text{U}_{0.60}\text{O}_{2.166}$	5.4970	5.22	1.43	-87.8	—	II
$\text{La}_{0.50}\text{U}_{0.50}\text{O}_{2.104}$	5.5108	5.42	1.21	-70.4	—	II
$\text{La}_{0.05}\text{U}_{0.95}\text{O}_{2.006}$	5.4755	4.07	2.97	-186.6	22.4	<sup>a</sup>
$\text{La}_{0.10}\text{U}_{0.90}\text{O}_{2.005}$	5.4790	4.12	2.89	-165.4	12.8	<sup>a</sup>
$\text{La}_{0.15}\text{U}_{0.85}\text{O}_{2.000}$	5.4836	4.18	2.80	-151.7	9.1	<sup>a</sup>
$\text{La}_{0.20}\text{U}_{0.80}\text{O}_{1.994}$	5.4873	4.24	2.71	-137.2	7.9	<sup>a</sup>
$\text{La}_{0.25}\text{U}_{0.75}\text{O}_{1.991}$	5.4923	4.31	2.54	-115.6	6.3	<sup>a</sup>
$\text{La}_{0.30}\text{U}_{0.70}\text{O}_{1.988}$	5.4983	4.39	2.49	-112.7	4.7	<sup>a</sup>
$\text{La}_{0.10}\text{U}_{0.90}\text{O}_{1.965}$	5.4780	4.03	2.86	-166.0	11.5	<sup>a</sup>
$\text{La}_{0.20}\text{U}_{0.80}\text{O}_{1.933}$	5.4881	4.08	2.66	-132.9	7.6	<sup>a</sup>
$\text{La}_{0.30}\text{U}_{0.70}\text{O}_{1.896}$	5.5003	4.13	2.54	-121.6	5.2	<sup>a</sup>
$\text{La}_{0.40}\text{U}_{0.60}\text{O}_{1.884}$	5.5174	4.28	2.38	-100.8	—	<sup>a</sup>
$\text{La}_{0.20}\text{U}_{0.80}\text{O}_{2.159}$	5.4672	4.65	2.14	-86.9	—	<sup>a</sup>
$\text{La}_{0.30}\text{U}_{0.70}\text{O}_{2.116}$	5.4800	4.76	1.96	-89.8	—	<sup>a</sup>
$\text{La}_{0.40}\text{U}_{0.60}\text{O}_{2.098}$	5.5003	4.99	1.66	-120.6	—	<sup>a</sup>
$\text{La}_{0.50}\text{U}_{0.50}\text{O}_{2.001}$	5.5153	5.00	1.65	-159.1	—	<sup>a</sup>

<sup>a</sup> These data have been reported in Ref. (3).

oxidation of uranium did not proceed beyond +5 by further lanthanum substitution for uranium. In this experiment, the uranium valency is over +5 even for the solid solution with  $y = 0.3$  heated in air (under Condition II) and the oxidation of uranium proceeds with increasing lanthanum concentration ( $y$ ). On the other hand, the mean uranium valency is less than +5 for the solid solutions prepared under Condition I (in a flow of helium at 1400°C) and it increases with lanthanum concentration.

## 2. Magnetic Susceptibility

Figure 2 shows the temperature dependence of magnetic susceptibilities of solid solutions prepared under Condition II (in air). We could no longer observe the magnetic exchange interactions between uranium ions down to 1.8 K. This result is con-

sistent with the previous result that when the mean uranium valency ( $\nu$ ) of the  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  solid solutions is over +4.4 or when the lanthanum concentration ( $y$ ) is over 0.3, there is no magnetic transition in the temperature range from 4.2 K to room temperature. The magnetic susceptibilities of solid solutions decrease with increasing lanthanum concentration, except at very low temperatures. This is due to the oxidation of uranium by the incorporation of lanthanum. Below 20 K, the susceptibility of  $\text{La}_{0.30}\text{U}_{0.70}\text{O}_{2.226}$  is smaller than that of  $\text{La}_{0.40}\text{U}_{0.60}\text{O}_{2.166}$ . The reason for this is that although the magnetic transition was not observed in the experimental temperature range, the antiferromagnetic interactions actually operated between uranium ions, which resulted in lowering the susceptibilities at low temperatures.

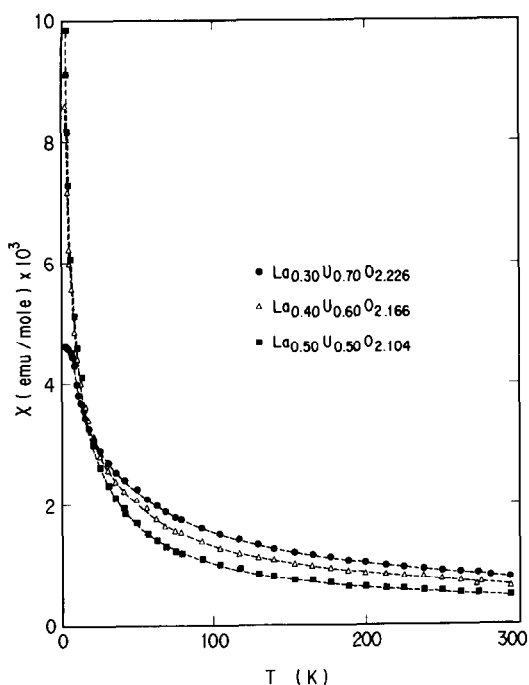


FIG. 2. Temperature dependence of magnetic susceptibilities of  $La_yU_{1-y}O_{2+x}$  solid solutions prepared under Condition II (in air).

The effect of oxygen nonstoichiometry on the magnetic susceptibilities of  $La_yU_{1-y}O_{2+x}$  solid solutions with  $y = 0.30$  is shown in their temperature dependences (Fig. 3). With increasing oxygen concentration ( $x$ ), the susceptibility decreases, which is due to the oxidation of uranium. The antiferromagnetic transition was found at 4.7 K in  $La_{0.30}U_{0.70}O_{1.988}$ . No magnetic excess solid solutions ( $x = 0.080, 0.116, \text{ and } 0.226$ ), which indicates that the interstitial oxygens weaken the magnetic exchange interactions through oxidation of uranium. Since this interaction is of the superexchange type of interaction via oxygen ions, the oxygen vacancies also weaken the magnetic interaction between uranium ions, which is found experimentally in the  $La_yU_{1-y}O_{2+x}$  solid solutions with  $y = 0.1$  and  $0.2$  (3). The Néel temperature of  $La_{0.30}U_{0.70}O_{1.896}$  is slightly higher than that

of  $La_{0.30}U_{0.70}O_{1.988}$  (Table I). The reason for this is that in the  $y = 0.3$  solid solutions the lanthanum substitution for uranium has much larger effect on the increase of  $U^{5+}$  than in the  $y = 0.1$  or  $0.2$  solid solutions; that is, in the  $La_{0.30}U_{0.70}O_{1.988}$  solid solution, a larger number of  $U^{5+}$  ions influence the magnitude of the magnetic interactions.

### 3. Oxidation State of Uranium

As a consequence of the substitution of  $La^{3+}$  for  $U^{4+}$  and oxygen nonstoichiometry, some of the  $U^{4+}$  ions are oxidized. In the preceding paper (3), it was quantitatively elucidated that the  $U^{4+}$  ions are oxidized to the  $U^{5+}$  state, not to the  $U^{6+}$  state; that is, the ionic species in the solid solutions are expressed as  $La_y^{3+}U_{1-2x-2y}^{4+}U_{2x+y}^{5+}O_{2+x}^{2-}$ .

The mean uranium valencies of solid solutions prepared in air (Condition II) are over

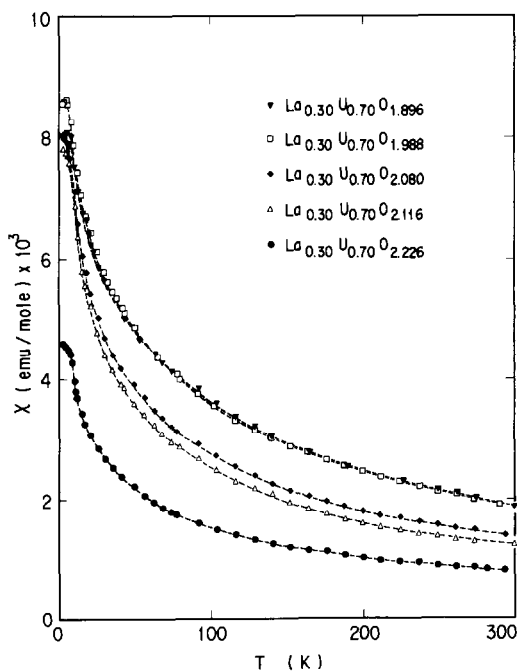
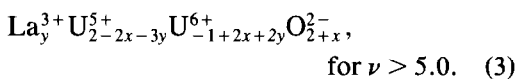
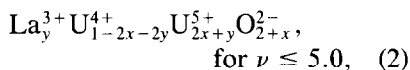


FIG. 3. Temperature dependence of magnetic susceptibilities of  $Y_yU_{1-y}O_{2+x}$  solid solutions with  $y = 0.30$ .

+5. So, some of the uranium ions are oxidized to the hexavalent state. The effective magnetic moment of uranium in the solid solutions,  $\text{La}_{0.30}\text{U}_{0.70}\text{O}_{2.226}$ ,  $\text{La}_{0.40}\text{U}_{0.60}\text{O}_{2.166}$ , and  $\text{La}_{0.50}\text{U}_{0.50}\text{O}_{2.104}$ , are listed in Table I. If the oxidation state of uranium is  $\text{U}^{4+}$  or  $\text{U}^{6+}$ , i.e.,  $\text{La}_y^{3+}\text{U}_{1-x-1.5y}^{4+}\text{U}_{x+0.5y}^{6+}\text{O}_{2+x}^{2-}$ , the effective magnetic moments of  $\text{U}^{4+}$  are calculated to be 2.42, 2.29, and 2.24  $\mu_B$ , respectively, because of the diamagnetism of  $\text{U}^{6+}$ . These values are far below the moment of  $\text{U}^{4+}$  in  $\text{UO}_2$  (3.12 ~ 3.20  $\mu_B$ ) (8-11) or  $\text{U}^{4+}$  in  $\text{ThO}_2$  (2.79 ~ 2.83  $\mu_B$ ) (8, 11, 12). For the case that the oxidation state of uranium is  $\text{U}^{5+}$  or  $\text{U}^{6+}$  ( $\text{La}_y^{3+}\text{U}_{2-2x-3y}^{5+}\text{U}_{-1+2x+2y}^{6+}\text{O}_{2+x}^{2-}$ ), the moments of  $\text{U}^{5+}$  are calculated to be 1.71, 1.62, and 1.58  $\mu_B$ , respectively. These values are very near to the magnetic moment found experimentally in the uranates of alkaline earth elements with fluorite structure,  $\text{MU}_2\text{O}_6$  ( $M = \text{Ca}, \text{Sr}, \text{or Ba}$ ) (13), and the moments of  $\text{La}_{0.40}\text{U}_{0.60}\text{O}_{2.098}$  and  $\text{La}_{0.50}\text{U}_{0.50}\text{O}_{2.001}$ , in which the mean uranium valencies are very close to +5.

Now the ionic species in the  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  solid solutions are given as follows:



This result indicates that with increasing lanthanum ( $y$ ) and oxygen ( $x$ ) concentrations, uranium ions are oxidized from +4 to +5 to +6.

#### 4. Magnetic Moment

The effective magnetic moments obtained from the slope of the reciprocal susceptibility vs. temperature curves are listed in Table I together with those of solid solutions previously reported (3), and they decrease with increasing oxygen and lanthanum concentrations, which is the result of oxidation of uranium. The variation of magnetic moment

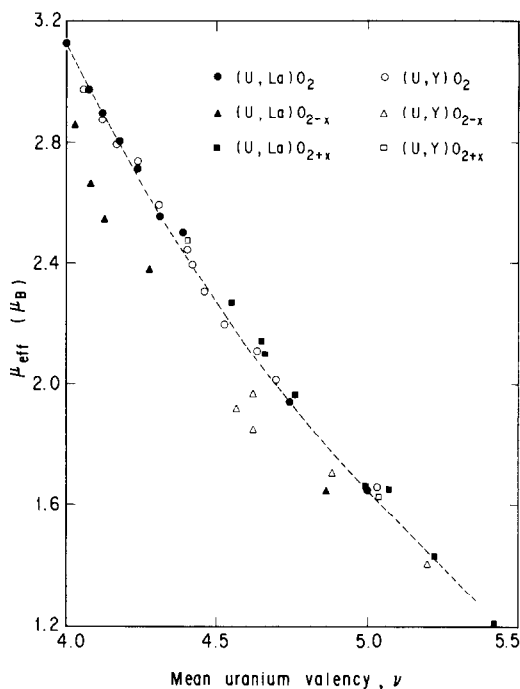


Fig. 4. Variation of effective magnetic moment of uranium with the mean valency.

of uranium with its mean valency is shown in Fig. 4. The magnetic moments of uranium in the oxygen stoichiometric solid solutions are shown by closed circles and they are connected by the dashed line. This dashed line is not straight, but convex downwards; i.e., the magnetic moment of oxygen stoichiometric solid solution is lower than the arithmetic mean value of the individual magnetic moments of  $\text{U}^{4+}$  and  $\text{U}^{5+}$ . The reason for this is that the effective magnetic moment of  $\text{U}^{4+}$  in  $\text{UO}_2$  actually decreases with magnetic dilution from 3.12 to 2.79  $\mu_B$  (11). The data points shown by closed triangles depart from this dashed line. This is due to the oxygen deficiency of these solid solutions. The departure of the magnetic moments of uranium from this dashed line for the oxygen excess solid solutions (shown by closed squares) is not great compared with

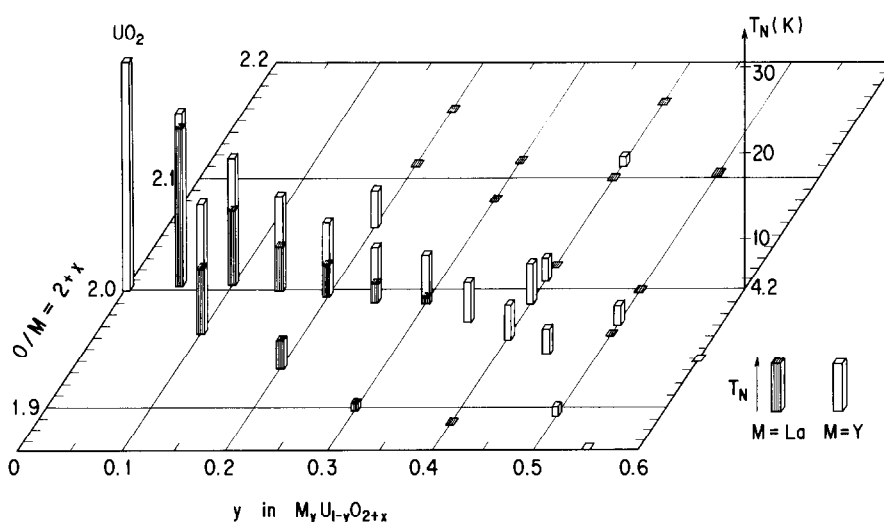


FIG. 5. Variation of Néel temperatures of  $M_y U_{1-y} O_{2+x}$  solid solutions ( $M = \text{La}, \text{Y}$ ) with  $x$  and  $y$  values.

that for the oxygen deficient solid solutions. In this fluorite-type structure, each uranium atom is octa-coordinated by the eight oxygen atoms. For oxygen deficient solid solutions, some of these oxygen atoms are missing from their regular sites, forming the oxygen vacancies. On the other hand, for oxygen excess solid solutions, the excess oxygen atoms exist at the interstitial site, that is, outside of the coordination sphere by eight oxygen atoms. Therefore, it is considered that the lack of oxygen atoms (formation of oxygen vacancies) affects significantly the magnetic moment of uranium. In Fig. 4, the magnetic moments of  $Y_y U_{1-y} O_{2+x}$  solid solutions are also shown. The magnetic moments of oxygen stoichiometric ( $x = 0$ ), hypostoichiometric ( $x < 0$ ), and hyperstoichiometric ( $x > 0$ )  $Y_y U_{1-y} O_{2+x}$  solid solutions (14) are shown by open circles, open triangles, and open squares, respectively. The same situation with the case of  $La_y U_{1-y} O_{2+x}$  solid solutions was found. The magnetic moments of oxygen stoichiometric  $Y_y U_{1-y} O_{2+x}$  solid solutions also follow the same dashed line. On the other

hand, the moments of oxygen hypostoichiometric solid solutions deviate greatly from this dashed line. This result indicates that the main factor which determines the magnetic moment of uranium in this crystal is the oxygen crystal field around the uranium ions.

### 5. Néel Temperature

With substitution of lanthanum for uranium, the magnetic interaction between uranium ions weakens. At the same time, the oxidation of uranium proceeds, accompanying oxygen sublattice imperfections. The variation of Néel temperatures of  $La_y U_{1-y} O_{2+x}$  solid solutions with  $x$  and  $y$  values are drawn in Fig. 5. This figure shows that not only the substitution of lanthanum for uranium but also oxygen sublattice imperfections (oxygen vacancies and oxygen interstitials) weaken the magnetic interactions between uranium ions. The Néel temperatures of  $Y_y U_{1-y} O_{2+x}$  solid solutions (14) are also drawn in this figure. The magnetic dilution effect of  $La_2 O_3$  is much stronger than that of  $Y_2 O_3$ . One reason for this is that the

distance between uranium ions increases with  $y$  value for  $\text{La}_y\text{U}_{1-y}\text{O}_{2+x}$  solid solutions while it decreases with increasing  $y$  value for  $\text{Y}_y\text{U}_{1-y}\text{O}_{2+x}$  solid solutions.

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