

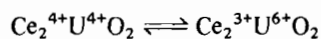
## Magnetic Studies on $\text{UO}_2$ – $\text{CeO}_2$ Solid Solutions\*

YUKIO HINATSU† and TAKEO FUJINO

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

Uranium dioxide ( $\text{UO}_2$ ) forms continuous solid solutions with cerium dioxide ( $\text{CeO}_2$ ). These solid solutions have a fluorite-type structure, and the lattice parameters obey Vegard's law [1, 2].

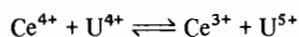
One of the interesting points is that some  $\text{UO}_2$ – $\text{CeO}_2$  solid solutions show a blue color known as 'cerium–uranium blue'. Hofmann and Höschele first reported the preparation of this 'cerium–uranium blue' having a composition near to  $\text{Ce}_2\text{UO}_6$  [3]. Because  $\text{UO}_2$  is brown and  $\text{CeO}_2$  is pale yellow, they ascribed the blue color of the mixed oxides as due to the oscillation of the valence:



Later researchers have revealed that the  $\text{Ce}_2\text{UO}_6$  composition is but one unexceptional example of solid solutions showing 'cerium–uranium blue' [1, 2]. Robin and Day [4] considered that the  $\text{U}^{6+}$  ion was not an appropriate form of the uranium ion in the cubic fluorite lattice, and they claimed the blue color to be due to the transfer of an electron between  $\text{Ce}^{4+}$  and  $\text{U}^{4+}$ :



From measurements of the optical absorption spectra of  $\text{UO}_2$ – $\text{CeO}_2$  solid solutions, Berman suggested the possibility of the resonance [5]:



Although there are many reports concerning the phase relation and thermodynamics of the uranium–cerium–oxygen system [6–8], its magnetic properties have not yet been reported. It is well known that  $\text{UO}_2$  is paramagnetic and changes to the antiferromagnetic state below  $T_N = 30.8$  K ( $T_N$  = the Néel temperature). According to a neutron diffraction study [9], the antiferromagnetism of  $\text{UO}_2$  is of type 1. Another fact is that this paramagnetic–antiferromagnetic transition is of the first-order [9]. On the other hand,  $\text{CeO}_2$  is diamagnetic.

From measurements of the magnetic susceptibility of  $(\text{U,Th})\text{O}_2$  or  $(\text{U,Zr})\text{O}_2$  solid solutions [10–12],

$\text{UO}_2$  was found to be magnetically diluted with diamagnetic  $\text{ThO}_2$  or  $\text{ZrO}_2$ , and the Néel temperature was found to decrease linearly with decreasing uranium concentration. Below the Néel temperatures, the magnetic susceptibilities attained constant values.

In the present study, nearly oxygen-stoichiometric  $(\text{U,Ce})\text{O}_2$  solid solutions were prepared and their magnetic susceptibilities were measured from liquid helium temperature to room temperature. The results were compared with those of  $(\text{U,Th})\text{O}_2$  and  $(\text{U,Zr})\text{O}_2$  solid solutions and the electronic state of uranium in the solid solutions was examined.

## Experimental

### Sample Preparation

$\text{UO}_2$  and  $\text{CeO}_2$  were used as starting materials. Before use,  $\text{UO}_2$  was reduced to stoichiometric composition in flowing hydrogen at 1000 °C, and  $\text{CeO}_2$  was heated in air at 850 °C to remove any moisture. After being finely ground in an agate mortar, the mixtures of  $\text{UO}_2$  and  $\text{CeO}_2$  were pressed into pellets and then sealed in evacuated platinum ampoules. The platinum ampoules were heated at 1500 °C for >80 h.

### Analysis

An X-ray diffraction study was performed using Cu  $K\alpha$  radiation with a Philips PW-1390 diffractometer equipped with curved graphite monochromator.

The oxygen-nonstoichiometry in the solid solutions was determined by the back-titration method [13, 14]. The weighed amount of sample was dissolved in excess cerium(IV) sulfate solution. The excess cerium(IV) was titrated against standard iron(II) ammonium sulfate solution with ferroin indicator. The oxygen amount was determined for predetermined Ce/U ratio.

### Magnetic Susceptibility Measurements

Magnetic susceptibility was measured by a Faraday-type torsion balance in the temperature range from liquid helium temperature to room temperature. The temperature of the sample was measured by a 'normal' Ag versus Au–0.07 at% Fe thermocouple [15] (4.2 K ~ 40 K) and an Au–Co versus Cu thermocouple (10 K ~ room temperature). Details of the experimental procedures have been described elsewhere [11].

## Results and Discussion

The X-ray diffraction analysis showed that cubic solid solutions with fluorite-type structure were

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†Author to whom correspondence should be addressed.

TABLE I. Lattice Parameters, Néel Temperatures and Magnetic Moments of (U,Ce)O<sub>2</sub> Solid Solutions

Solid solutions	<i>a</i> (Å)	<i>T</i> (K)	$\mu_{\text{eff}}$ (BM)
Ce <sub>0.05</sub> U <sub>0.95</sub> O <sub>2.000</sub>	5.4670	26.4	3.07
Ce <sub>0.10</sub> U <sub>0.90</sub> O <sub>1.996</sub>	5.4647	21.9	3.04
Ce <sub>0.15</sub> U <sub>0.85</sub> O <sub>2.008</sub>	5.4620	18.9	3.03
Ce <sub>0.20</sub> U <sub>0.80</sub> O <sub>1.998</sub>	5.4585	17.0	3.01
Ce <sub>0.25</sub> U <sub>0.75</sub> O <sub>1.993</sub>	5.4570	15.0	2.99
Ce <sub>0.30</sub> U <sub>0.70</sub> O <sub>1.987</sub>	5.4536	12.9	2.97
Ce <sub>0.35</sub> U <sub>0.65</sub> O <sub>2.006</sub>	5.4508	7.1	2.96
Ce <sub>0.40</sub> U <sub>0.60</sub> O <sub>1.951</sub>	5.4490		2.97

formed in a single phase for all the samples in this study. The lattice parameters of the solid solutions are listed in Table I.

The O/M ratios of the solid solutions determined by the cerium back-titration method were close to two.

#### Magnetic Susceptibility

The temperature dependence of inverse-magnetic susceptibilities per mole of uranium for the present solid solutions is shown in Fig. 1. An antiferromagnetic transition can be observed for the solid solutions with  $y \leq 0.35$ . The Néel temperature,  $T_N$ , decreases with increasing cerium concentration ( $y$ ). From these results, UO<sub>2</sub> is deduced to be magnetically diluted mainly with diamagnetic Ce<sup>4+</sup> ions, since if all the cerium ions were in the 3+ state (paramagnetic state), the decrease of  $T_N$  (which is the indication of the magnetic dilution of UO<sub>2</sub>) would no longer be observed.

A consistent result can be drawn from the magnitude and the dependence of the paramagnetic susceptibility on cerium concentration. Figure 1 shows that the inverse-magnetic susceptibility of uranium decreases with increasing cerium concentration over the paramagnetic temperature range examined. This behavior is the same as that found in (U,Th)O<sub>2</sub> [11] or (U,Zr)O<sub>2</sub> [12] solid solutions, and is different from that found in (U,Y)O<sub>2</sub> [16] or (U,La)O<sub>2</sub> [17] solid solutions. The susceptibility per mole of uranium for the (U,Y)O<sub>2</sub> or (U,La)O<sub>2</sub> solid solutions decreased with increasing concentration of diamagnetic diluents in the temperature range in which the Curie–Weiss law holds. This indicates that with an increasing amount of trivalent diluents, the amount of uranium ions oxidized from the tetravalent to the pentavalent state increases, which results in the decrease in the magnetic moment (magnetic susceptibility) of uranium overall.

Below the transition temperature, the magnetic susceptibility decreased first with decreasing temperature and then increased again, which is different from

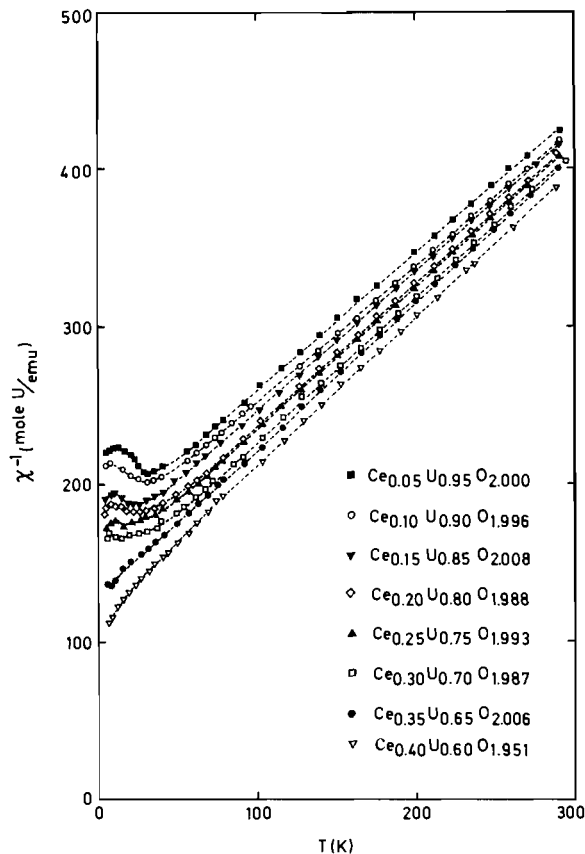


Fig. 1. Temperature dependence of inverse-magnetic susceptibilities per mole of uranium for (U,Ce)O<sub>2</sub> solid solutions.

the behaviour found in (U,Th)O<sub>2</sub> [10,11] or (U,Zr)O<sub>2</sub> [12] solid solutions, where the magnetic susceptibilities attained respective constant values below the Néel temperatures. For comparison, the magnetic susceptibility data of Ce<sub>0.10</sub>U<sub>0.90</sub>O<sub>1.996</sub>, Ce<sub>0.20</sub>U<sub>0.80</sub>O<sub>1.988</sub>, Th<sub>0.10</sub>U<sub>0.90</sub>O<sub>2.000</sub> and Th<sub>0.20</sub>U<sub>0.80</sub>O<sub>2.000</sub> are depicted together in Fig. 2. The behavior found in (U,Ce)O<sub>2</sub> solid solutions also contrasts that in (U,Y)O<sub>2</sub> [16] or (U,La)O<sub>2</sub> [17] solid solutions, where the magnetic susceptibilities monotonously decreased with decreasing temperature. A similar magnetic susceptibility *versus* temperature curve is found for the Np<sub>y</sub>U<sub>1-y</sub>O<sub>2</sub> solid solutions ( $y = 0.15$  and  $0.25$ ) [18]. In the susceptibility curve for Np<sub>0.15</sub>U<sub>0.85</sub>O<sub>2</sub>, a sharp maximum is observed at 27 K. Below *ca.* 14 K, the susceptibility increases again with decreasing temperature.

#### Magnetic Moment

From the inclination of the reciprocal susceptibility *versus* temperature curves, the effective magnetic moments were obtained in the temperature region where the Curie–Weiss law holds. They are listed in Table I. The magnetic moment decreases with decreasing uranium concentration. The decrease

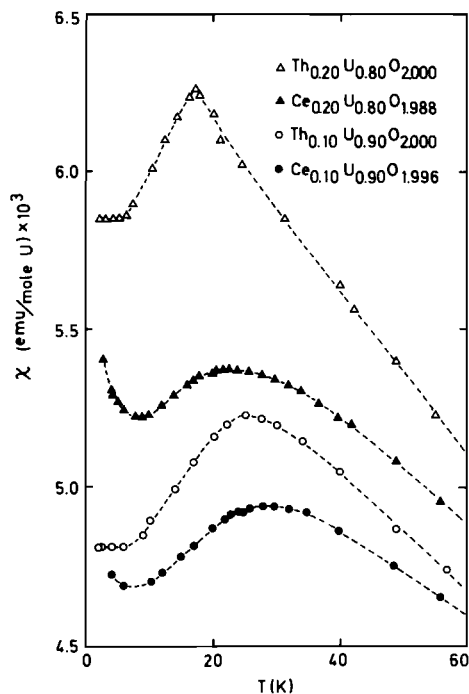


Fig. 2. Magnetic susceptibilities of  $L_{0.10}U_{0.90}O_2$  and  $L_{0.20}U_{0.80}O_2$  ( $L = \text{Ce}$  or  $\text{Th}$ ) solid solutions.

with  $(\text{U,Ce})O_2$  is comparable with that of  $(\text{U,Th})O_2$  solid solutions [11], and is less than that of  $(\text{U,Y})O_2$  or  $(\text{U,La})O_2$  solid solutions [16, 17]. As discussed earlier [11], the decrease in magnetic moment in the  $(\text{U,Th})O_2$  solid solutions is responsible for the decrease in the magnetic interactions between the adjacent uranium ions. On the other hand, the decrease in magnetic moment in the  $(\text{U,Y})O_2$  or  $(\text{U,La})O_2$  solid solutions is due to the formation of the  $U^{5+}$  ion which gives a lower magnetic moment than the  $U^{4+}$  ion [16, 17]. From the similarity of the magnetic moments of  $(\text{U,Ce})O_2$  solid solutions to that of  $(\text{U,Th})O_2$  solid solutions, the slight decrease in the magnetic moment of  $(\text{U,Ce})O_2$  solid solutions with decreasing uranium concentration is considered to be mainly due to the decrease in the magnetic interactions between the adjacent uranium ions. The fact that the Néel temperature decreases with decreasing uranium concentration supports this conclusion.

#### Néel Temperature

The Néel temperature was plotted against the uranium concentration, as shown in Fig. 3. It decreases gradually with decreasing uranium concentration ( $C$ ) down to  $C = 0.70$ . Below that concentration it decreases more rapidly ( $T_N = 7.1$  K for  $U_{0.65}\text{-}Ce_{0.35}O_2$ ) until  $C = 0.60$ , at which no antiferromagnetic transition is observed in the experimental temperature range (Fig. 1). For comparison, the data for  $(\text{U,Th})O_2$  [11],  $(\text{U,Zr})O_2$  [12] and  $(\text{U,Y})O_2$  [16]

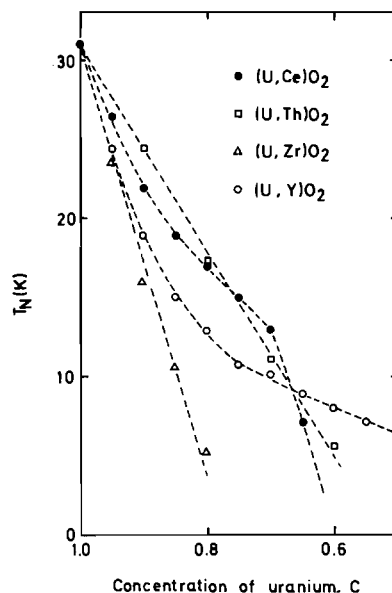


Fig. 3. Variation of Néel temperature with uranium concentration.

solid solutions are also drawn in Fig. 3. In  $(\text{U,Th})O_2$  and  $(\text{U,Zr})O_2$  solid solutions, the Néel temperature decreases linearly with decreasing uranium concentration. This behavior is qualitatively in accord with the theoretical prediction, except for behavior around the critical concentration at which the antiferromagnetism disappears [19–24]. The non-linear dependence of the Néel temperatures on uranium concentration found for  $(\text{U,Y})O_2$  and  $(\text{U,La})O_2$  solid solutions is understood to be related to the formation of  $U^{5+}$  ions [16, 17]. Although the magnetic susceptibility vs. temperature curve of  $Np_yU_{1-y}O_2$  solid solutions ( $y = 0.15$  and  $0.25$ ) is similar to that of  $Ce_yU_{1-y}O_2$  solid solutions, the electronic state of neptunium in  $Np_yU_{1-y}O_2$  solid solutions is different from that of cerium in  $Ce_yU_{1-y}O_2$  solid solutions. From the Mössbauer measurements, the oxidation state of neptunium remains tetravalent; that is, the electronic configuration is  $[\text{Rn}]5f^3$  [18]. When the oxidation state of cerium remains tetravalent, the electronic configuration is  $[\text{Xe}]4f^0$ , *i.e.*, it is diamagnetic. From both the results of the non-linear dependence of Néel temperature on uranium concentration and the increase in magnetic susceptibility below  $T_N$ , which will be discussed later, we consider that in the  $(\text{U,Ce})O_2$  solid solutions, the transfer of electrons is considered to occur to some extent between uranium and cerium ions; *i.e.*, part of the uranium ions are oxidized and the corresponding amount of the cerium ions are reduced. In this case, the oxidation states of uranium and cerium are pentavalent and trivalent, respectively [4], *i.e.*



If this charge transfer proceeds completely (all the  $Ce^{4+}$  ions are reduced to  $Ce^{3+}$  state), the so-called magnetic dilution should not occur because of the paramagnetism of the  $Ce^{3+}$  ion, as mentioned above. Therefore, it is considered that the charge-transfer reaction described by the above equation takes place partly between uranium and cerium ions. The rapid decrease in the Néel temperature of  $(U,Ce)O_2$  solid solutions below  $C = 0.70$  has been considered to be, as one possibility, due to the occurrence of the charge transfer to a larger extent in this concentration range [25].

The magnetic susceptibility of  $(U,Ce)O_2$  solid solutions increases with decreasing temperature at very low temperatures below  $T_N$  and this trend becomes more conspicuous as the cerium concentration increases. This increase in magnetic susceptibility is supposed to be due to the increased amount of  $Ce^{3+}$  ions, and not to be due to the  $U^{5+}$  ions, because the magnetic interactions between  $U^{5+}-U^{5+}$  ions, or in some cases those between  $U^{5+}-U^{4+}$  ions, in fluorite structure diminish the magnetic susceptibility below  $T_N$ , as shown in the case of  $(U,Y)O_2$  [15] or  $(U,La)O_2$  [16] solid solutions. The  $Ce^{3+}$  ion is a Kramers' ion, having one unpaired 4f electron and its ratio in the cerium ions is likely to increase with cerium concentration.

We have discussed above that some uranium ions in the  $(U,Ce)O_2$  solid solutions are oxidized to the pentavalent state. However, this effect is not reflected in the decrease in the magnetic moment of uranium. Details of this point will be described in a subsequent paper [25].

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