# Magnetic Susceptibilities of $UO_2$–$Pr_2O_3$ Solid Solutions

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Magnetic susceptibilities of $Pr_yU_{1-y}O_{2+x}$ solid solutions ($y \leq 0.1$) with fluorite-type structure were measured from 4.2 K to room temperature. From the analysis of the magnetic susceptibility data, it was found that the oxidation state of uranium was tetravalent or pentavalent and that of praseodymium was trivalent. The susceptibilities of oxygen-stoichiometric solid solutions ($Pr_yU_{1-y}O_2$) increased with Pr concentration ($y$) in the whole temperature range measured, indicating the magnetic moment of $Pr^{3+}$ is larger than that of $U^{4+}$. The susceptibilities of solid solutions with low Pr concentrations ($y \leq 0.07$) increased with decreasing temperature down to ca. 31 K, and showed discontinuous change (susceptibility drop) at ca. 30–31 K ($T_d$ temperature). Below this temperature, after a little decrease, the magnetic susceptibilities increased again with decreasing temperature. This increase of susceptibility below $T_d$ temperature is considered to be due to the $U^{5+}$ ion formed in the solid solutions.   © 1988 Academic Press, Inc.

## Introduction

It is well known that a wide homogeneous region of solid solution having a fluorite-type structure exists in $UO_2$–$Pr_2O_3$–$O_2$ system. However, its magnetic properties have not been investigated yet. Two kinds of unpaired electrons, i.e., $5f$ electrons and $4f$ electrons, bear the paramagnetism of this solid solution. Both are $f$ electrons, but their magnetic behavior is not the same. Since the $4f$ electrons of rare-earth ions are effectively shielded from their environment by the completed $5s$ and $5p$ subshells, these ions, even if in a crystal lattice, behave almost as though they are "free ions." On the other hand, the $5f$ electrons of actinides are less effectively screened by the outer electron shells. The electric field term, $V$, in the Hamiltonian differs depending on the

type of compounds, but is often of comparable order of magnitude to the spin-orbit coupling constant, $\xi$, and to the interelectronic coupling constant, $e^2/r$. Therefore, the magnetic susceptibility data of actinide compounds are not capable of simple interpretation.

$UO_2$ is a paramagnetic compound with two unpaired $5f$ electrons and is in an antiferromagnetically ordered state below the Néel temperature, $T_N = 30.8$ K (*1–3*). The transition from paramagnetic to antiferromagnetic state is of the first order and the sharp step-like decline of the magnetic susceptibility is observed as the temperature is lowered through $T_N$ (*4–6*). Below $T_N$ the susceptibility is constant. When oxygen ions enter $UO_2$ lattice, the transition temperature is considerably lowered (for example, $T_N = 6$ K for $UO_{2.1}$ (*4, 5*)). If $UO_2$ is

magnetically diluted with diamagnetic $ThO_2$ or $ZrO_2$, the Néel temperature decreases linearly with decreasing uranium concentration (6–8).

Praseodymium sesquioxide, $Pr_2O_3$, is a paramagnetic compound with two unpaired $4f$ electrons per $Pr^{3+}$. The ground state is singlet and therefore $Pr_2O_3$ shows the Van Vleck paramagnetism at low temperatures. The $Pr_2O_3$ also has a range of nonstoichiometry with respect to oxygen. As oxygen ions enter into the $Pr_2O_3$ lattice, forming $Pr_2O_{3+x}$, the magnetic moment decreases with increasing oxygen amount ($x$) and the temperature-independent paramagnetic susceptibility disappears, i.e., the magnetic susceptibility increases with decreasing temperature. These phenomena were reasonably accounted for by assuming that a part of the $Pr^{3+}$ ions are oxidized to $Pr^{4+}$ state (9). In the temperature region from 4.2 K to room temperature, magnetic cooperative phenomena are not observed in the $Pr_2O_3$, $Pr_2O_{3+x}$, or $PrO_2$ (9). However, $PrO_2$ prepared at higher oxygen pressures (200–2000 atm.) has been reported to transform to antiferromagnetic state below 14 K (10).

In the present study, $Pr_yU_{1-y}O_{2+x}$ solid solutions with various $x$ and $y$ values of which the crystal structures are fluorite type (same as $UO_2$) were prepared and their magnetic susceptibilities were measured in a range from liquid helium temperature to room temperature. The effect of substitution of praseodymium for uranium on the magnetic properties of solid solutions was examined.

On the magnetic behavior of combined $5f$–$4f$ electronic systems, the magnetic properties of phosphide ($L_yU_{1-y}P$) and sulfide ($L_yU_{1-y}S$) solid solutions where $L = Pr$ and Nd have already been reported (11–13). Since UP (antiferromagnet with type I) and PrP (paramagnet with a singlet ground crystal-field state) show similar magnetic behavior to $UO_2$ and $Pr_2O_3$, respectively,

the magnetic properties of the present $Pr_yU_{1-y}O_2$ solid solutions were compared with those of the $Pr_yU_{1-y}P$ solid solutions.

## Experimental

### 1. Sample Preparation

As starting materials, $UO_2$ and $Pr_6O_{11}$ were used. Before use, $UO_2$ was reduced to stoichiometric composition in flowing hydrogen at 1000°C. $Pr_6O_{11}$ was reduced to a light-green sesquioxide composition in flowing hydrogen at 850°C.

The $UO_2$ and $Pr_2O_3$ were weighed to the intended atom ratios of uranium and praseodymium. 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 purified helium at 1400°C for 8 hr.

Condition II: The reaction in an SiC resistance furnace in a flow of unpurified helium at 1340°C for 150 hr. The partial pressure of oxygen in the helium gas used here was significantly higher than that of Condition I.

After cooling to room temperature, the samples were reground, pressed again to pellets, and heated 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 was performed using $CuK\alpha$ radiation with a Philips PW-1390 diffractometer equipped with curved graphite monochromator. The lattice parameter of the samples was determined by the Nelson–Riley extrapolation method (14) applied to the diffraction lines above 80° ($2\theta$).

*2.2. Determination of oxygen amount.* The oxygen-nonstoichiometry in the solid solutions was determined by the back-titra-

tion method (15, 16). 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 standard iron(II) ammonium sulfate solution with ferroin indicator. The oxygen amount was determined for predetermined Pr/U ratio.

### 3. 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 (17) (4.2–40 K) and an Au–Co vs Cu thermocouple (10 K to room temperature). Rapid thermal equilibrium was attained around the sample by introducing helium gas into the system up to ca. 10 mm Hg. To examine the field dependence, the magnetic susceptibilities were measured in each of the field strengths of 4700, 6900, 9000, and 10,600 G. To correct the magnetic susceptibilities for the samples, the measurements were also made on the blank quartz tube under the same conditions as in the case containing the samples. Details of the experimental procedure have been described elsewhere (7).

## Results and Discussion

### 1. Lattice Parameter and O/M Ratio

X-ray diffraction analysis showed that cubic solid solutions with fluorite structure were formed in single phase for all the specimens in this study. The composition and lattice parameter are listed in Table I. The O/M ratios for the solid solutions prepared under Condition I were close to two, where M indicates Pr + U. Similar behavior has

LATTICE PARAMETERS OF $Pr_yU_{1-y}O_{2+x}$ SOLID SOLUTIONS

| Solid solutions | Lattice parameter (Å) | Preparation condition |
|---|---|---|
| $Pr_{0.01}U_{0.99}O_{2.000}$ | 5.4731 | I |
| $Pr_{0.03}U_{0.97}O_{1.998}$ | 5.4713 | I |
| $Pr_{0.05}U_{0.95}O_{1.998}$ | 5.4708 | I |
| $Pr_{0.07}U_{0.93}O_{1.991}$ | 5.4710 | I |
| $Pr_{0.10}U_{0.90}O_{1.987}$ | 5.4710 | I |
| $Pr_{0.10}U_{0.90}O_{2.168}$ | 5.4520 | II |

already been reported in earlier works on this system (18) and on some rare-earth oxide–uranium oxide systems (19–22). The lattice parameter of these solid solutions did not appreciably change with Pr concentration from that of $UO_2$ (5.4704 Å). From these two facts, the change of magnetic susceptibility with Pr concentration for the solid solutions of Condition I is considered to reflect exclusively the effect of the substitution of the $Pr^{3+}$ ion for the $U^{4+}$ ion in the $UO_2$ lattice as a first approximation.

### 2. Magnetic Susceptibility

For all the specimens examined, no field dependence of magnetic susceptibility was found. Figure 1 shows the temperature dependence of magnetic susceptibilities of $Pr_yU_{1-y}O_2$ solid solutions prepared under Condition I. In the whole temperature range measured, the susceptibility increases with Pr concentration ($y$). This shows that the effective magnetic moment of the $Pr^{3+}$ ion is larger than that of the $U^{4+}$ ion as will be described later. Figure 2 shows the reciprocal magnetic susceptibilities of $Pr_{0.10}U_{0.90}O_{1.987}$ and $Pr_{0.10}U_{0.90}O_{2.168}$ solid solutions. In the temperature region in which the Curie–Weiss law holds, the magnetic moments per mole of the $Pr_yU_{1-y}O_2$ solid solutions (Condition I), $\mu_{eff}$, were obtained from the inclination of the susceptibility vs temperature
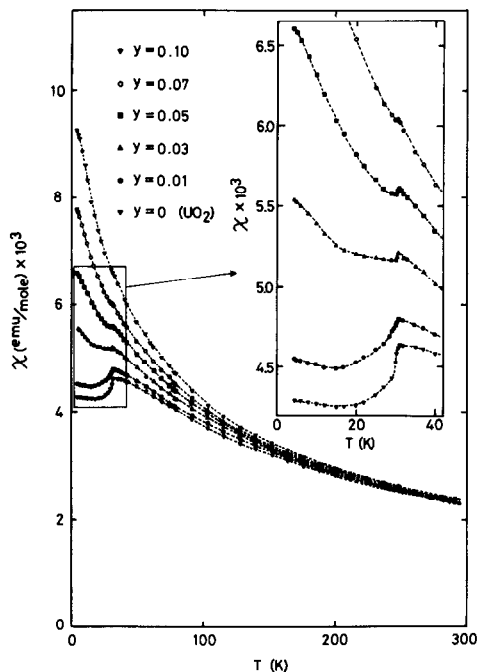
FIG. 1. Temperature dependence of magnetic susceptibilities of $Pr_yU_{1-y}O_2$ solid solutions prepared under Condition I.



FIG. 2. Temperature dependence of reciprocal magnetic susceptibilities of $Pr_{0.10}U_{0.90}O_{1.987}$ and $Pr_{0.10}U_{0.90}O_{2.168}$.

curves. The variation of $\mu_{eff}$ with Pr concentration is shown in Fig. 3.

## 3. Oxidation States of Uranium and Praseodymium

First, the oxidation states of uranium and praseodymium ions in the $Pr_yU_{1-y}O_{2+x}$ solid solutions will be considered. When the $U^{4+}$ ion is replaced by the $Pr^{3+}$ ion, the $U^{4+}$ or the $Pr^{3+}$ ion in the cyrstal is oxidized according to the charge neutrality condition. Since the Pr concentration of the present specimens is low, the case that both the $Pr^{3+}$ and the $U^{4+}$ ions are oxidized need not be considered. Let us discuss the following three cases:
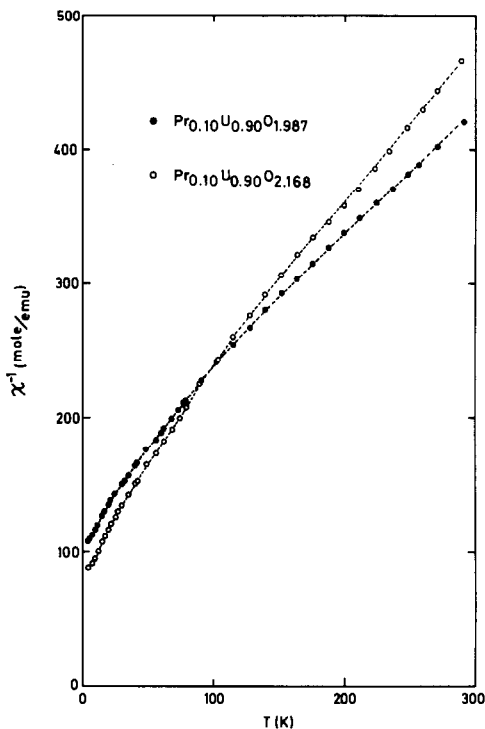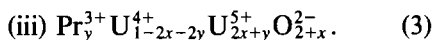
$$(i) \quad Pr_y^{4+}U_{1-y}^{4+}O_2^{2-} \tag{1}$$

$$(ii) \quad Pr_y^{3+}U_{1-x-1.5y}^{4+}U_{x+0.5y}^{6+}O_{2+x}^{2-} \tag{2}$$

$$(iii) \quad Pr_y^{3+}U_{1-2x-2y}^{4+}U_{2x+y}^{5+}O_{2+x}^{2-}. \tag{3}$$

If praseodymium ions exist as $Pr^{4+}$ in the solid solutions, the magnetic susceptibility per mole of $Pr_yU_{1-y}O_2$ solid solutions should decrease with increasing Pr concentration due to the smaller magnetic mo-
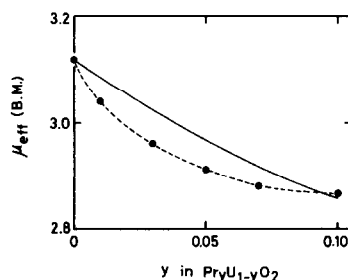


FIG. 3. Variation of effective magnetic moment of $Pr_yU_{1-y}O_2$ solid solutions with Pr concentration. Solid line represents calculation result (see text).

ment of $Pr^{4+}$ compared with that of $U^{4+}$. Experimental results of the magnetic susceptibility for the samples prepared under Condition I (nearly oxygen-stoichiometric) showed the increase with Pr concentration in the whole temperature range, which indicates that model (i) can be excluded. Therefore, the $U^{4+}$ ions are oxidized by accommodation of praseodymium ions in the crystal to $U^{5+}$ or $U^{6+}$, and so by excess oxygen ions. In oxidation model (ii) where the $U^{6+}$ ions are formed, the paramagnetic ions are $Pr^{3+}$ and $U^{4+}$ only, since the $U^{6+}$ ion is diamagnetic. For the two solid solutions with the same Pr content ($y$) but with different oxygen contents ($x$), the paramagnetic susceptibility of solid solution with higher oxygen content must be smaller than that of solid solution with lower oxygen content, because the ratio of $U^{4+}$ ($1 - x - 1.5y$) is smaller in the former solid solution than in the latter solid solution. Experimental results, however, show that the magnetic susceptibility of $Pr_{0.10}U_{0.90}O_{2.168}$ is larger than that of $Pr_{0.10}U_{0.90}O_{1.987}$ below 100 K, and above this temperature the reverse situation holds (Fig. 2). The only possible explanation for this result is that the uranium ions are in the $U^{4+}$ or the $U^{5+}$ state. In this case, both the $U^{4+}$ and the $U^{5+}$ ions are paramagnetic (their temperature dependences of magnetic susceptibility differ from each other) and the ratio of $U^{4+}/U^{5+}$ changes with $x$ value of $Pr_y U_{1-y} O_{2+x}$.

When model (iii) is the case, there exist three kinds of paramagnetic ions in the solid solutions. If no magnetic interaction exists between paramagnetic ions, for the magnetic susceptibilities of two $Pr_y U_{1-y} O_{2+x}$ solid solutions with the same $y$ value but different $x$ values (to be referred to as $\chi(S.1)$ and $\chi(S.2)$), the following two equations hold,

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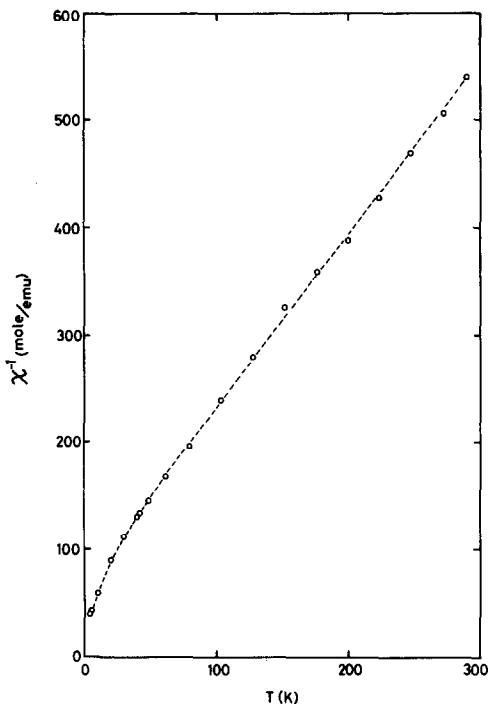


FIG. 4. Reciprocal susceptibility of $yPr^{3+} + (1 - y)U^{5+}$ vs temperature.

$$\chi(S.2) = y\chi(Pr^{3+})$$
$$+ (1 - 2x_2 - 2y)\chi(U^{4+})$$
$$+ (2x_2 + y)\chi(U^{5+}), \quad (5)$$

where $\chi(Pr^{3+})$, $\chi(U^{4+})$, and $\chi(U^{5+})$ are the magnetic susceptibilities of $Pr^{3+}$, $U^{4+}$, and $U^{5+}$, respectively. By eliminating $\chi(U^{4+})$ from Eqs. (4) and (5), Eq. (6) is obtained:

$$y\chi(Pr^{3+}) + (1 - y)\chi(U^{5+})$$
$$= \frac{1}{2(x_1 - x_2)} \{(1 - 2x_2 - 2y)\chi(S.1)$$
$$- (1 - 2x_1 - 2y)\chi(S.2)\}. \quad (6)$$

The magnetic susceptibility of the solid solution containing the $Pr^{3+}$ and the $U^{5+}$ ions with a ratio $y/(1 - y)$ is to be obtained from Eq. (6). Applying this model to the two solid solutions, viz. $Pr_{0.10}U_{0.90}O_{1.987}$ and $Pr_{0.10}U_{0.90}O_{2.168}$, the reciprocal susceptibility of $yPr^{3+} + (1 - y)U^{5+}$ vs temperature curve is obtained as shown in Fig. 4. The

moment is 2.19 BM. Since the theoretical value of the magnetic moment of $Pr^{3+}$ is 3.58 BM,[1] the moment of $U^{5+}$ is calculated to be 1.98 BM.

The stoichiometric uranium dioxide has a cubic fluorite structure. In the nonstoichiometric solid solutions also, a uranium ion at the center of a cube can be considered to be surrounded by eight oxygen ions located at the corners of the cube, as a first approximation. The ground state of $U^{5+}$ ion with one unpaired electron is $^2F_{5/2}$. In the crystalline field with cubic symmetry, this multiplet state splits into two states, doublet state $\Gamma_7$ and quartet state $\Gamma_8$ (23). The ground state is $\Gamma_8$ and its wave functions are

$$\sqrt{\frac{5}{6}}\left|\pm\frac{5}{2}\right\rangle + \sqrt{\frac{1}{6}}\left|\mp\frac{3}{2}\right\rangle, \left|\pm\frac{1}{2}\right\rangle. \quad (7)$$

If only this quartet state contributes to the paramagnetism, the magnetic susceptibility of the solid solutions is calculated as

$$\chi = \frac{Ng^2\beta^2}{kT} \cdot \frac{65}{36}, \quad (8)$$

and the effective magnetic moment is calculated to be 2.00 BM. This value is very close to the value obtained experimentally.

If no magnetic interaction exists between three kinds of paramagnetic ions, the magnetic moment per mole of $Pr_yU_{1-y}O_{2+x}$ solid solution ($\mu_{eff}$) is expressed as shown in the following equation:

$$\begin{aligned}\mu_{eff}^2 = &\, y\mu_{eff}^2(Pr^{3+}) \\ &+ (1 - 2x - 2y)\mu_{eff}^2(U^{4+}) \\ &+ (2x + y)\mu_{eff}^2(U^{5+}), \quad (9)\end{aligned}$$

where $\mu_{eff}(Pr^{3+})$, $\mu_{eff}(U^{4+})$, and $\mu_{eff}(U^{5+})$ are the magnetic moments per mole of $Pr^{3+}$, $U^{4+}$, and $U^{5+}$, respectively. For $Pr_{0.10}U_{0.90}O_{1.987}$, by substituting the values obtained for $\mu_{eff}$, $\mu_{eff}(Pr^{3+})$, and $\mu_{eff}(U^{5+})$ in Eq. (9), the magnetic moment of $U^{4+}$ is cal-

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[1] This value, $p$, is calculated from the relation $p = g_J\sqrt{J(J + 1)}$, where $g_J$ is the Lande's splitting factor and $J$ is the total angular momentum.

culated to be 2.84 BM. This value is between the moment of $UO_2$, 3.12 BM (7, 24) or 3.2 BM (25, 26), and that of $UO_2$ infinitely diluted with diamagnetic $ThO_2$, i.e., 2.83 BM (24, 27) or 2.79 BM (7). The magnetic moment obtained is found to be in reasonable agreement with those of the compounds composed of the $U^{4+}$ ions, which also supports oxidation model (iii).

## 4. Magnetic Susceptibility in The Low-Temperature Region

The magnetic susceptibility for the solid solutions with low Pr concentrations ($y \leq 0.07$) increases with decreasing temperature down to ca. 31 K and shows discontinuous change at ca. 30–31 K (Fig. 1). This temperature will be referred to as $T_d$ hereafter. Below this temperature, after a little decrease, the susceptibility increases again with decreasing temperature. In the inset of Fig. 1, the temperature dependence of magnetic susceptibility in the low-temperature region is magnified. The decline of magnetic susceptibility with decreasing temperature becomes prominent with decreasing Pr concentration, but the $T_d$ temperatures are constant irrespective of the Pr concentration. This magnetic susceptibility change of $Pr_yU_{1-y}O_2$ solid solutions with temperature around $T_d$ can be qualitatively followed by the concentration weighted sum of the magnetic susceptibilities of $UO_2$ and $Pr_2O_3$.

The $T_d$ temperature is considered to reflect the magnitude of magnetic interactions between uranium ions in the solid solution as the Néel temperature of $UO_2$ is related to the magnitude of magnetic interactions between uranium ions. From the experimental result that the $T_d$ temperature scarcely changes with Pr concentration, it is found that the magnetic exchange interactions between uranium ions are unchanged irrespective of the Pr concentration. In (U, Th)$O_2$ or (U, Y)$O_2$ solid solutions, the magnetic exchange interactions weaken with decreasing uranium concentration and the

Néel temperature decreases with decreasing uranium concentration (6, 7, 28). The Pr$^{3+}$ ion is not a diamagnetic ion such as Th$^{4+}$ or Y$^{3+}$, but a paramagnetic ion with the same electronic configuration ($f^2$) as that of the U$^{4+}$ ion and the experimental results show that the effect of the Pr$^{3+}$ ion on the Néel temperature is almost equal to that of the U$^{4+}$ ion in the range of the present Pr concentration.

Below the antiferromagnetic–paramagnetic transition temperature ($T_N$), UO$_2$ has a constant magnetic susceptibility. On the other hand, the paramagnetic ground state of Pr$_2$O$_3$ is singlet and the magnetic susceptibility has a constant value (i.e., the Van Vleck's temperature-independent paramagnetic susceptibility) below ca. 40 K (9). However, the magnetic susceptibilities for the present solid solutions increase again with decreasing temperature at very low temperatures ($<T_d$) and the degree of the increase becomes more prominent with increasing Pr concentration. These phenomena are not considered to be due to the effect of U$^{4+}$ or Pr$^{3+}$, but to the formation of U$^{5+}$. The U$^{5+}$ ion is a Kramers' ion with one unpaired electron and the ratio increases with increasing Pr concentration.

In the magnetic susceptibility vs temperature curve of Pr$_y$U$_{1-y}$P solid solutions, similar behavior has been observed (11–13). As mentioned in the introductory part of this paper, UP is a type I antiferromagnet with the Néel temperature $T_N = 121$ K at which the magnetization becomes zero. The NMR and neutron diffraction measurements show a sudden drop in the ordered moment to about 0.2 BM upon heating to 22.5 K (i.e., moment-jump transition temperature) (29). On the other hand, PrP is a paramagnet with a single level as a ground crystal field state. For the solid solutions with low Pr concentrations ($y < 0.2$), the Néel temperature does not appreciably change from that of UP (12, 13). This behavior is the same as that found in the Pr$_y$U$_{1-y}$O$_2$ solid solutions. In the curve of low-temperature susceptibility of the solid solutions with $y < 0.1$, a gradual vanishing of the susceptibility drop (moment-jump transition) is observed independent of Pr concentration at ca. 22 K (13), which is a similar behavior to that found around $T_d$ temperature in the curve of magnetic susceptibility of Pr$_y$U$_{1-y}$O$_2$ solid solutions. In the phosphide solid solutions, other broader susceptibility maxima are also found at lower temperatures (13).

## 5. Magnetic Moment

The effective magnetic moment per mole of Pr$_y$U$_{1-y}$O$_2$ solid solutions decreases with increasing Pr concentration as shown in Fig. 3. First, we will discuss this decrease of magnetic moment. The magnetic moment of Pr$^{3+}$ ion is 3.58 BM even when it is in a cation site of the fluoride structure (9). The effective magnetic moments of U$^{4+}$ and U$^{5+}$ are obtained above from the susceptibility data of two solid solutions with $y = 0.1$; $\mu_{eff}$(U$^{4+}$) = 2.84 BM and $\mu_{eff}$(U$^{5+}$) = 1.98 BM. In UO$_2$ lattice, the magnetic moment of the U$^{4+}$ ion is 3.12 BM. Since the magnetic moment of the U$^{4+}$ ion is known to decrease with decreasing uranium concentration in (U, Th)O$_2$ (7) or (U, Zr)O$_2$ (8) solid solutions, we assume that the magnetic moment of the U$^{4+}$ ion in the present solid solutions also decreases with decreasing uranium concentration, i.e., it is expressed by $\mu_{eff}$(U$^{4+}$) = 3.12–2.8$y$ ($0 \leq y \leq 0.1$). When the magnetic moments of Pr$^{3+}$, U$^{4+}$, and U$^{5+}$ are substituted in Eq. (9) (at $x = 0$), the magnetic moment of the solid solution is given by the following equation:

$$\mu_{eff} = \sqrt{y \cdot 3.58^2 + (1 - 2y) \cdot (3.12 - 2.8y)^2 + y \cdot 1.98^2}$$
$$\simeq \sqrt{9.73 - 20.20y + 42.78y^2}. \tag{10}$$

In the range $0 \leq y \leq 0.1$, $\mu_{eff}$ is found to decrease with increasing $y$, which corresponds to the experimental result as shown in Fig. 3. However, the magnetic moment obtained from the experiment is smaller than that calculated from Eq. (12). The reason for this fact would be that at low Pr concentration (high uranium concentration) the magnetic moment of $U^{4+}$ decreases more steeply than linearly with decreasing uranium concentration, which is expected from the experimental results found in (U, Th)$O_2$, (U, Zr)$O_2$, and (U, Th, Zr)$O_2$ solid solutions (30).

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