Effects of Neutron Irradiation on Magnetic Properties of UP*

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A number of studies have been performed on the magnetic properties of antiferromagnetic uranium monophosphide (UP, $T_N = 123.2$ K) because of its interesting magnetic behavior, which helps in the fundamental understanding of the chemical bonding and electronic structure of the actinides. However, little study has been carried out on the electrical properties of UP [1, 2], which can also provide important information on the above subjects. The electrical resistivity is useful in evaluating the electronic configuration and the effect of additive elements and crystalline defects in metallic materials, and hence in the actinide compounds, with a variety of radiation-induced defects.

In fact, remarkable changes have been observed in physical properties, such as lattice parameters, electrical resistivity and magnetic character, of several uranium compounds (as nuclear fuels) after neutron irradiation [3]. The effects of neutron irradiation (fission damage) are especially pronounced in the magnetically ordered state of the above substances. For example, antiferromagnetic UN ($T_N = 52$ K) [4–6] and ferromagnetic US ($T_C = 180$ K) [6–8] are such cases.

In the present study, we have examined the effects of fission damage on the magnetic properties of UP by measuring the magnetic and electric properties. The change in magnetic parameters and shift of the 'characteristic' temperatures [2] are discussed, comparing the results of fission damage on UN and US with the same NaCl-type structure as UP.

Experimental

Preparation and the characteristics of the specimen (sintered UP) have been reported before [9]. The conventional four-probe d.c. method was employed for the electric measurements, while the magnetic measurements were carried out by the Faraday method at low temperature. Neutron irradiation was done at room temperature with the Kyoto University Reactor (KUR) in the thermal neutron fluence (or fission dose) between 2.3×10^{20} (2.0×10^{21}) and 3.0×10^{22} n/m^2 (2.6×10^{23} f/m^3).

Results and Discussion

The low-temperature electrical resistivity (ρ) and magnetic susceptibility (χ) of UP (without fission damage) are illustrated in Fig. 1, indicating the five 'characteristic' temperatures [2]. T_{MJ} (the moment jump at 23 K) and T_N (the Néel point at 123 K) were clearly visible in both measurements, and T_{MIN} (a minimum in χ at 90 K) and T_{MAX} (a maximum at 133 K) were easily found in the susceptibility. Whereas T_{CWL} was detected at 190 K, above that the inverse of χ obeyed the Curie–Weiss law. These temperatures were revealed at the same positions in the temperature dependence of the resistivity [2]. For instance, the temperature coefficient of the resistivity ($d\rho/dT$) altered at T_{CWL}. A linear temperature dependence ($\rho = -bT + c$, hence $d\rho/dT$ is constant with a negative value) just started at T_{CWL} and lasted up to 830 K [10]. It was of interest that UP showed a semiconductor-type resistivity above the Néel point.

Effect of Fission Damage on Magnetic Susceptibility

Typical examples of the temperature-dependent magnetic susceptibility (χ) and the inverse susceptibility ($1/\chi$) are shown in Fig. 2 for two irradiated UP samples (1.1×10^{22} and 2.6×10^{23} f/m^3), compared with that of non-irradiated UP. All measurements were made at 0.4 T (tesla) after zero-field cooling. Figure 2 indicates that fission damage introduces a variety of changes in the magnetic properties of UP. Remarkable features are as follows:

(1) The magnetic susceptibility increases with fission dose, especially in the antiferromagnetic state.

(2) Both the transition points (T_{MJ} and T_N) seem to shift to lower temperatures and be ambiguous with increasing fission damage.

(3) The specimens with higher fission damage (doses higher than 10^{23} f/m^3) show different magnetic behavior, particularly above the Néel point. No evidence of T_{MAX} was recognized in those specimens.

(4) In the paramagnetic state, on the other hand, the Curie constant increases, hence the derived effective Bohr magneton numbers (n_{eff}) become larger with fission damage, which is in contrast to the case of UN [4–6].

An example of the shift (T_{MJ}) of one of the 'characteristic' temperatures is illustrated in Fig. 3, in which the magnetic susceptibility is plotted for the same specimens as in Fig. 2. The shift of T_{MJ} to lower temperatures because of fission damage was

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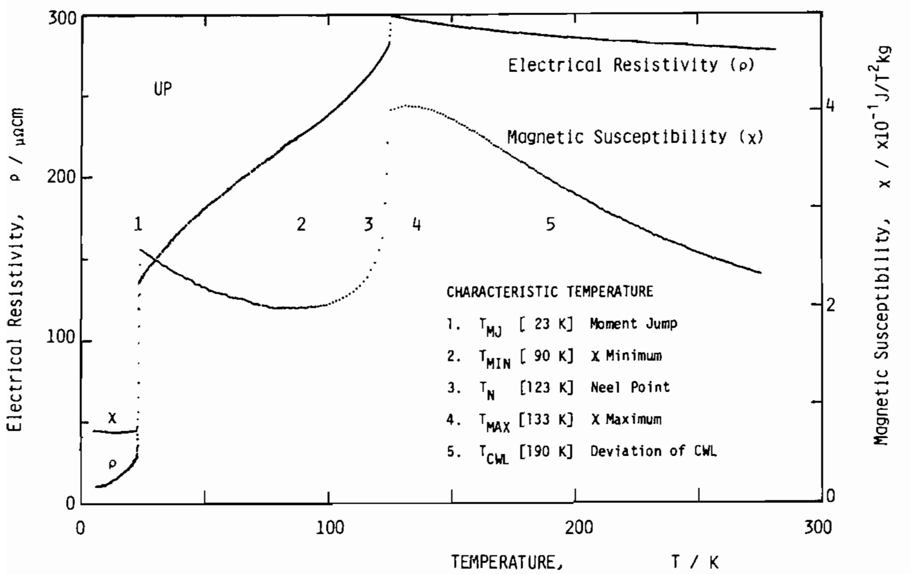

Fig. 1. Low-temperature electrical resistivity (ρ) and magnetic susceptibility (χ) of UP. Five 'characteristic' temperatures are indicated.

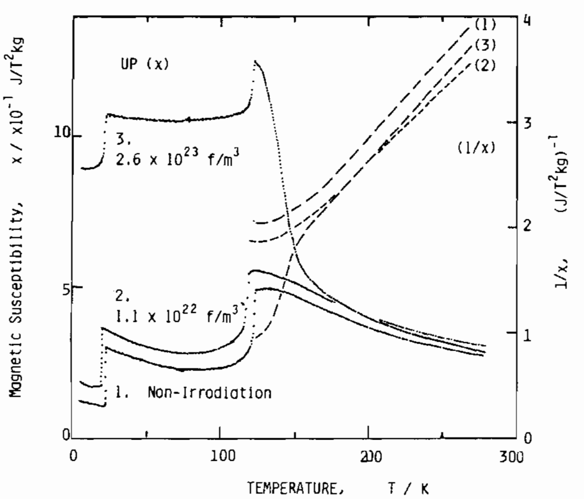

Fig. 2. Magnetic susceptibility (χ) and the inverse susceptibility ($1/\chi$) of UP irradiated to 1.1 and 26.0×10^{22} f/m^3, compared with non-irradiated UP.

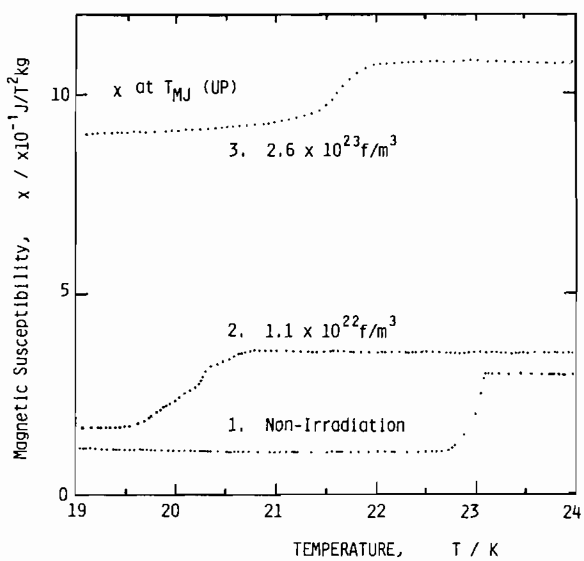

Fig. 3. Magnetic susceptibility of UP at the moment jump (T_{MJ}). The specimens are the same as in Fig. 1.

clearly discerned. In addition, it seemed that the jump took place within a wider temperature range in the irradiated UP than in non-irradiated UP. However, it was not understood why the temperature shift was wide in UP with a low fission dose (1.1×10^{22} f/m^3) compared to a high fission dose (2.6×10^{23} f/m^3), while a lattice expansion due to fission damage was large in the latter (see Table I).

At the antiferromagnetic transition point (T_N), the same trend as in T_{MJ} was observed in the shift of T_N in the magnetic measurements. For instance, T_N shifted to lower temperatures with fission damage in earlier stage of irradiation, but the shift became narrow in the specimens with higher fission doses. As shown later, the temperature shift of T_N, and T_{MJ} as well, with fission damage obtained here were also revealed (with the same trend) in the resistivity measurements. The effect of fission damage on several important magnetic parameters of UP are summarized in Table I.

The irradiated UP with the highest fission dose (2.6×10^{23} f/m^3) showed different magnetic behavior, as shown in Fig. 2. A most remarkable feature was revealed in the paramagnetic region just above

TABLE I. Change of Magnetic Parameters of UP due to Fission Damage

Fission dose (f/m^3)	$\Delta a/a$ ($\times 10^{-4}$) (nm)	$T_{MJ}(\Delta T_{MJ})$ (K)	$T_N(\Delta T_N)$ (K)	$\theta_\alpha(\Delta\theta_\alpha)$ (K)	$n_{eff}(\Delta n_{eff})$ (μ_B)
1.1×10^{22}	3.3	20.1(−2.7) [20.2][a]	118.5(−4.7) [118.0]	5.6(−8.8)	4.02(+0.66)
2.6×10^{23}	4.1	21.5(−1.3) [21.7]	121.4(−1.8) [122.8]	28.8(+14.4)	3.32(−0.04)
Non-irrad.	0.55872	23.2 [23.2]	123.2 [123.3]	14.4	3.36

[a]Values in square brackets are derived from electrical resistivity.

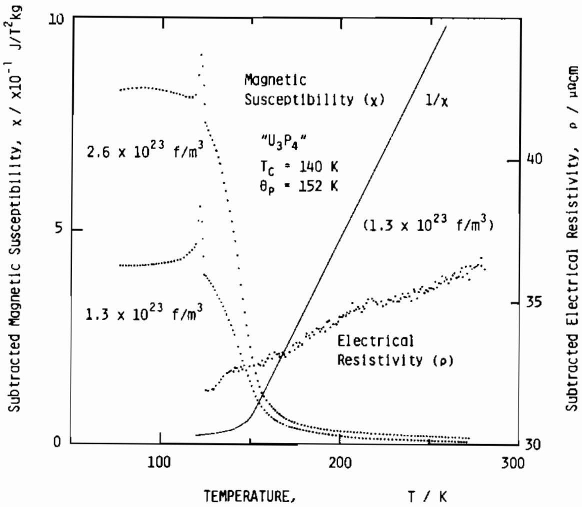

Fig. 4. Subtracted magnetic susceptibility (χ_{sub}) from irradiated to non-irradiated UP and $1/\chi_{sub}$. The ferromagnetic behavior, a steep drop in χ_{sub} (T_C = 140 K) and good agreement with the Curie–Weiss law (θ_P = 152 K) suggest formation of 'U_3P_4' during neutron irradiation at high fission doses.

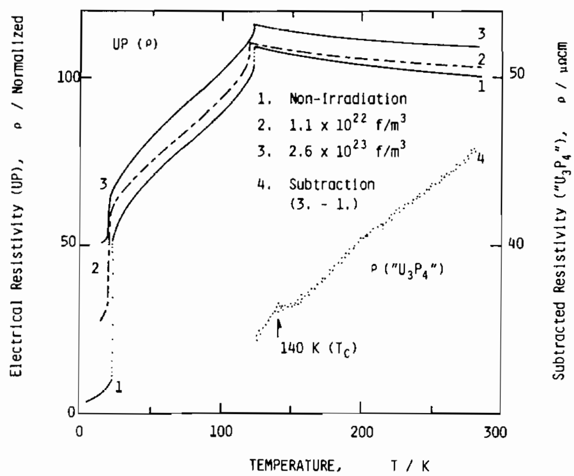

Fig. 5. Electrical resistivity of UP with and without fission damage. The specimens are the same as in Figs. 2 and 3. The increased resistivity (the subtraction from irradiated (2.6×10^{23} f/m^3) to non-irradiated UP) indicates a knee at 140 K, which is identical to the T_C of 'U_3P_4'.

the Néel point. A new straight line (the Curie–Weiss law) appeared between 145 and 160 K in the $1/\chi$ *versus* T plot, while above 190 K the inclination (the Curie constant) was almost identical to non-irradiated UP. The subtraction of the magnetic susceptibility from the irradiated (1.3 and 2.6×10^{23} f/m^3) to non-irradiated UP are shown in Fig. 4. Both showed a ferromagnetic-type temperature dependence, which indicated a sharp drop at about 140 K and an apparent paramagnetic Curie point (θ_P) at 150 K. On the other hand, in the X-ray examination, we observed new diffraction peaks other than UP which could be assigned to 'U_3P_4'. Therefore, it was suggested that in the highly irradiated UP a phase change took place during neutron irradiation: a transformation of UP to U_3P_4 (which is ferromagnetic below 140 K with θ_P = 152 K [11]).

Effect of Fission Damage on Electrical Resistivity

The effect of fission damage on the electrical resistivity of UP is shown in Fig. 5, in which the temperature dependences are represented for the irradiated specimens, as in Figs. 2 and 3. The resistivity in Fig. 5 is normalized in such a way that the value of each original UP (before irradiation) at 285 K is 100, because of a slight difference in the electrical resistivity for each original specimen. An increase in the resistivity was clearly observed with increasing fission dose, both in the antiferro- and paramagnetic regions. In studies on UN [4–6] and US [6–8] with fission damage, the resistivity increase was much pronounced in the magnetically ordered state. Thus, the effect of fission damage on UP was somewhat different from other uranium compounds.

In the resistivity measurements two transition points, T_{MJ} and T_N, of the irradiated UP again shifted to lower temperatures with fission dose, as found in the magnetic measurements. Figure 6 shows

TABLE II. Shift of Characteristic Temperatures in UP due to Fission Damage

Fission dose (f/m^3)	T_{MJ} (K)	T_{MIN} (K)	T_N (K)	T_{MAX} (K)	T_{CWL} (K)
1.1×10^{22}	20.1 [20.2][a]	82 [80]	118.5 [118.0]	128 [129]	188 [190]
2.6×10^{23}	21.5 [21.7]	70 [65]	121.4 [122.8]	[125]	170 [175]
Non-irrad.	23.2 [23.2]	89 [91]	123.2 [123.3]	132 [133]	190 [190]

[a]Values in square brackets are derived from resistivity, while others are from magnetic susceptibility.

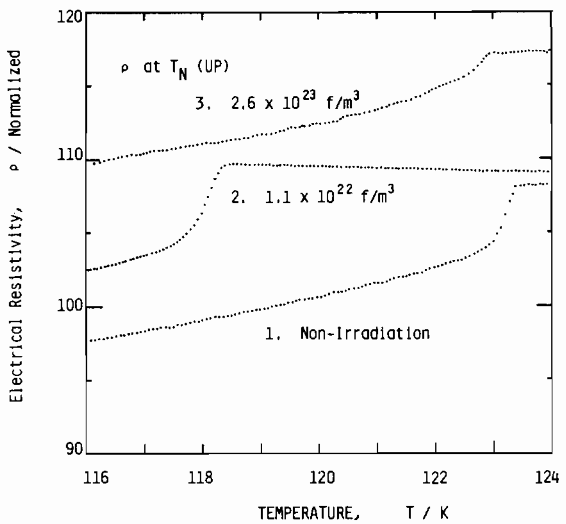

Fig. 6. Electrical resistivity of UP at the Néel point (T_N). The specimens are the same as in Fig. 5.

in more detail the temperature shift of T_N because of fission damage. In addition to the shift, the antiferromagnetic transition seemed to be ambiguous due to the introduction of fission-induced defects. The amount of the resistivity jump at T_N, and at T_{MJ} as well, was retarded in the irradiated UP (see Fig. 5). The other three 'characteristic' temperatures (T_{MIN}, T_{MAX} and T_{CWL}) also showed the shift with fission damage, as summarized in Table II. Good agreement was found between the measurements of two different physical properties: electrical resistivity and magnetic susceptibility.

Evidence of the new phase ('U_3P_4') was also found in the resistivity of UP with high fission doses (higher than 10^{23} f/m^3). Again we took the subtraction of the electrical resistivity from the irradiated (2.6×10^{23} f/m^3) to non-irradiated UP. The results are shown in Fig. 5 (curve 4) and also in Fig. 4 for UP irradiated to 1.3×10^{23} f/m^3. The temperature dependence of the subtracted resistivity above 130 K resembled that of U_3P_4 [12]. In fact, a knee was observed at 140 K, which was identical to the Curie point of U_3P_4 [11, 12]. On the other hand, in both measurements, no evidence of U_3P_4 and other phases was found in irradiated UP with lower fission doses. It should be noticed here that the resistivity difference in Figs. 4 and 5 was large below 130 K (in the antiferromagnetic region), indicating an extra increase in the electrical resistivity because of fission-induced magnetic disorder in neutron-irradiated UP.

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