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ABSTRACT

Both UC and UN are semi-metallic materials with the NaCl crystal structure and lattice parameters 4.96 and 4.89 Å, respectively. UC is nonmagnetic with a susceptibility that is temperature independent, whereas UN becomes antiferromagnetic at 53°K with ordering of the first kind. Solid solutions of the form $UC_{1-x}N_x$ exist for $0 \leq x \leq 1$. Neutron-diffraction experiments have been performed on five samples with $0.85 \leq x \leq 0.95$. Over this region of x both T_N and the ordered magnetic moment per U atom decrease linearly from $T_N = 53^\circ\text{K}$ and $0.75 \mu_B$ for UN ($x=1$) to $T_N = 30^\circ\text{K}$ and $0.35 \mu_B$ for $x = 0.88$. The composition $x = 0.86$ shows no ordering in the neutron experiments. The absence of magnetic order for $x < 0.88$ has been confirmed by magnetization measurements. In the range of x examined the effective paramagnetic moment is $3.25 \pm 0.10 \mu_B/\text{U atom}$, close to the value of $\sim 3.1 \mu_B$ for UN.

INTRODUCTION

A number of solid solutions of uranium compounds with the NaCl crystal structure have been examined during the last few years, for example, UAs-US.¹ In these systems, both end members are magnetic, the pnictides (N,P,As) being antiferromagnetic and the chalcogenides (S,Se) being ferromagnetic. Neutron-diffraction studies of intermediate compositions in these systems have shown that long-range magnetic structures exist. Such magnetic structures suggest that the exchange interactions are long range, but the precise nature of the exchange interaction remains obscure. In principle, studies of systems in which the magnetic interactions are diluted (rather than changed from antiferro- to ferromagnetic) should be easier to interpret. Magnetization studies on UP-ThP² and US-ThS³ compositions have shown that the critical concentration of thorium (i.e. that composition at which no magnetic ordering is observed is $\sim 40\%$).

A potentially similar system is that of UC-UN. Uranium carbide is nonmagnetic with a temperature-independent susceptibility. This temperature-independent susceptibility has been explained in terms of both a band model,⁴ and a localized $5f^2$ configuration in which the crystal-field ground state is the Γ_1 singlet.⁵ Uranium nitride is antiferromagnetic at 53°K with ordering of the first kind in which ferromagnetic (001) sheets of uranium moments are stacked in a + - sequence along the [001] axis. The magnetic moments within any sheet

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are parallel to the [001] axis.⁶ The effective paramagnetic moment, derived from the slope of the $1/\chi$ versus T curve at high temperature is $\sim 3.2 \mu_B/\text{U atom}$. This is close to both the free ion $5f^2$ and $5f^3$ values of $3.58 \mu_B$ and $3.62 \mu_B$, respectively. Surprisingly, therefore, the ordered moment at 5°K is only $0.75 \mu_B/\text{U atom}$. This low value of the ordered moment in UN poses the major problem in trying to understand the electronic structure of this material. The magnetic behavior of UN has been discussed (a) in terms of a $5f^3$ configuration⁵ with J-mixing that results in a lowering of the magnetic moment from the free-ion value, (b) in terms of a $5f^2$ configuration with a singlet-ground state (i.e., as in UC) but with a large exchange field that induces a magnetic moment at low temperature,⁷ and (c) in terms of an itinerant-band model⁸ which assumes a hybridization of the d and f electrons.

EXPERIMENTAL

The uranium carbide was obtained from high-purity fused rods. The uranium nitride was made by a gas reaction of uranium powder and NH_3 . An initial batch of stoichiometric $\text{UC}_{0.5}\text{N}_{0.5}$ was prepared by mixing the correct amounts of the constituent compounds, pressing a pellet and firing at 1600°C for 4 hours. It was necessary to crush the pellet and repeat, firing three times in all, to obtain a single phase material. Other compositions were produced from the $\text{UC}_{0.5}\text{N}_{0.5}$ by adding the necessary amount of UN, pressing a pellet, and repeating the firing procedure. The lattice parameters as determined by X-ray diffraction are given in Table I and are in good agreement with Anselin et al.⁹ No evidence for additional phases was observed in either the X-ray or neutron experiments.

Table I Properties of UC-UN Solid Solutions

Composition	a_0 (Å)	T_N (°K)	$\mu_B/\text{U atom}$
UN	4.892	53 ± 2	0.75 ± 0.05
UC _{.05} N _{.95}	4.896	40	0.65
UC _{.075} N _{.925}	4.898	36	0.54
UC _{.10} N _{.90}	4.900	32	0.45
UC _{.12} N _{.88}	4.901	30	0.35
UC _{.14} N _{.86}	4.904		
UC _{.50} N _{.50}	4.932		
UC	4.960		

Neutron-diffraction experiments on the samples listed in Table I were performed at the CP-5 Research Reactor. The variation of the ordered magnetic moment with composition is shown in Fig. 1. The magnetic structure in all ordered samples is the type-I arrangement (i.e., as in UN). The Néel temperatures determined by neutron diffraction are given in Table I. The neutron experiments are insensitive to ordered moments less than $0.25 \mu_B$ (indicated by the dashed line in Fig. 1). We have therefore, performed magnetization

Fig. 1. Variation of the ordered magnetic moment of 5°K as a function of composition

experiments on the samples $x = 0.88$ and $x = 0.86$ to test whether the critical composition x_c is less than the simple extrapolation of the straight line, which gives $x_c \sim 0.80$, in Fig. 1. The variation of $1/\chi$ versus T for the two samples is given in Fig. 2. From the high-temperature portion of the curve we obtain an effective paramagnetic moment of $3.2 \pm 0.1 \mu_B/U$ atom for both samples. The value for UN is $3.2 \mu_B/U$ atom. The paramagnetic Curie temperature (i.e., the intercept when $1/\chi = 0$) is $\theta = -420^\circ\text{K}$ for both samples. This is different from the value of $\theta = -320^\circ\text{K}$ quoted for UN. However, the determination of this constant is very sensitive to the extrapolation; to obtain an accurate value, the susceptibility at temperatures greater than 300°K must be measured. The low-temperature behavior of the susceptibility is quite different for the two samples and is illustrated in the insert. The neutron experiments indicate that the Néel temperature of the $x = 0.88$ sample is $30 \pm 2^\circ\text{K}$. At this temperature, we observe a minimum in $1/\chi$ indicating a paramagnetic to antiferromagnetic transition. For $x = 0.86$, on the other hand, no minimum is observed in $1/\chi$ and we conclude that this composition does not order magnetically. No evidence for short or long-range magnetic order was observed in the neutron experiments with the $x = 0.86$ sample.

DISCUSSION

de Novion and Costa¹⁰ have measured the magnetic susceptibility, specific heat, and electrical resistivity of eleven samples in the UC-UN system and obtained a critical concentration $x_c \sim 0.90$. Similarly, Ohmichi and coworkers have reported magnetic susceptibility¹¹ electrical resistivity, and thermoelectric power¹² of six samples and obtained a critical concentration $x_c = 0.40$. Although agreement between the authors exists on measurements of other properties, the

Fig. 2. Inverse molar susceptibility as a function of temperature for the two samples near the critical concentration.

unaltered. For low values of x in the $\text{Th}_{1-x}\text{U}_x\text{P}$ and $\text{Th}_{1-x}\text{U}_x\text{S}$ systems the uranium atoms behave as magnetic impurities in a nonmagnetic matrix and exhibit an effective paramagnetic moment per uranium atom in dilute alloys, e.g., 2% UP in ThP. Magnetic ordering occurs when the concentration of uranium is sufficient to sustain the exchange interactions. However, the situation in $\text{UC}_{1-x}\text{N}_x$ is quite different, and cannot be treated as a magnetic impurity problem. Not only does the ordered moment vanish with a small carbon concentration ($x_c = 0.86$) but no effective paramagnetic moment is observed for x less than 0.40.¹⁰ On the other hand, if the $5f^2$ configuration is correct for both UN and UC then the effective moment (as measured in the range 100-300°K) should disappear for values of x just less than x_c (i.e., greater than $x \sim 0.40$). This is because the exchange in the molecular-field theory is very small for $x < x_c$ (since no ordering is observed) and a temperature-independent susceptibility similar to that in UC should be observed at low temperature. Alternatively, if the ground state of UN is $5f^3$ and UC is $5f^2$, the magnetic properties of the system depend strongly on the nearest-neighbor environment around the uranium atom; this might explain the rapid quenching of the ordering as the carbon concentration is increased.

A more quantitative interpretation of the results on the UC-UN system must, in our opinion, await a more detailed understanding of the electronic properties of both UC and UN.

major difference in x_c , which is the most important magnetic property of the system, remains unexplained. This difference has in fact been the subject of a series of controversial exchanges in the literature.¹³

Our measurements give a value of $x_c = 0.86 \pm 0.02$ and are therefore in agreement with de Novion and Costa.¹⁰ The rapid quenching of the magnetic moment in UN with carbon substitution is particularly surprising considering that x_c for the UP-ThP and US-ThS systems is ~ 0.40 . In these latter systems the uranium atoms are replaced by nonmagnetic thorium atoms, whereas in the UC-UN system the uranium atoms are left

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