ANTIFERROMAGNETISM OF URANIUM AND THORIUM PHOSPHIDES

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Submitted February 22, 1968

Zh. Eksp. Teor. Fiz. 55, 151–156 (July, 1968)

The magnetic properties of solid solutions of the systems UP-ThP and UP_2-ThP_2 were investigated. Antiferromagnetism exists in alloys of uranium phosphide containing up to 50 at.%ThP. The Neel temperature decreases with increasing ThP content, from 129°K for pure UP to 115°K for a sample with 50 at.%ThP. The Curie-Weiss law is satisfied in the paramagnetic region. The paramagnetic Curie temperature is $\Theta_p > 0$ and decreases with increasing dilution of the uranium phosphide by the thorium, tending to zero. The effective magnetic moment μ_{eff} in the case of infinite dilution is 2.7 μ_B. The uranium diphosphide alloys are antiferromagnetic below 200°K. According to an x-ray structure analysis, all the alloys form solid solutions. In the alloys of the UP-ThP system, which have the structure of NaCl, the lattice parameter increases with increasing thorium content. UP_2-ThP_2 alloys have a structure of the Cu_2Sb type.

To study the magnetic properties of uranium phosphides, we employed the method of magnetic dilution, which makes it possible, while still retaining a definite magnetic ordering as the magnetic ions are replaced by nonmagnetic ones, to obtain valuable information concerning the character of the exchange interaction and concerning the influence of the intracrystalline field.

The objects investigated were alloys of uranium monophosphide UP and diphosphide UP_2, which according to [1,2] are antiferromagnetic with Neel temperatures 130 and 230°K respectively. Thorium was used for the dilution. The samples were synthesized by a method described earlier [3].

Samples containing 0, 20, 35, 50, 70, 90, 98, and 100 at.%ThP and the remainder UP were synthesized. In addition, the compounds UP_2, $U_{0.93}Th_{0.07}P_2$, $U_{0.8}Th_{0.02}P_2$, and UBi_2 were synthesized. To improve their inhomogeneity, the samples were subjected to additional heat treatment. Thus, for example, samples of the UP-ThP system were annealed in vacuum of 10^{-5}–10^{-6} mm Hg at 1500°C. The obtained samples were subjected to an x-ray structure analysis (copper K_α radiation with Ni filter), which has shown that all the synthesized samples are solid solutions with a crystal structure of the NaCl type for the UP-ThP system and of the Cu_2Sb type for the UP-ThP_2 system. The lattice parameters of the alloys of the UP-ThP system were determined (see Fig. 3 and Table I below). In the region of small ThP concentrations, the introduction of the thorium ions into the UP lattice is not accompanied by an appreciable decrease of the interatomic distance. A noticeable change of the lattice parameter is observed only starting with 40% ThP; above 50%, ThP satisfies the Vegard rule (dashed line in Fig. 3).

The magnetic properties of the obtained samples were investigated in the temperature interval 80–700° K and in magnetic fields 2–10 kOe. Measurements above room temperature were made in vacuum of 10^{-4} mm Hg. The absence of ferromagnetic impurities in the samples was demonstrated by measurements of the magnetic susceptibility in different magnetic fields.

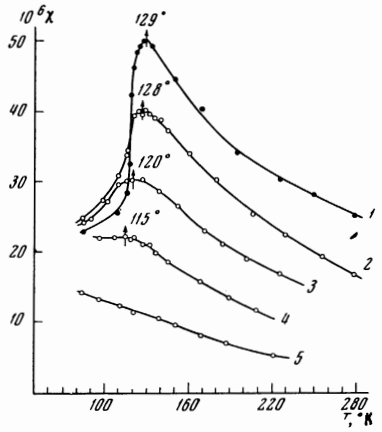

FIG. 1. Dependence of the specific susceptibility χ on T for the following samples: 1–UP, 2– 80% UP–20% ThP, 3–65% UP–35% ThP, 4–50% UP–50% ThP, 5–30% UP–70% ThP. The arrows indicate the Neel temperature.

THE UP-ThP SYSTEM

The results of the investigation have shown that alloys of the Up-ThP system containing up to 50 at.% ThP are antiferromagnetic with Neel temperatures in the range 115–130°K (Fig. 1). It is typical that the temperature of the antiferromagnetic transition shifts slightly towards low temperatures with increasing dilution; this is accompanied by broadening of the transition region, and the maximum of the susceptibility of a sample containing 50 at.% ThP is very weakly pronounced.

In a sample with 70 at.%ThP, this maximum is not observed at all, but a deviation from the Curie-Weiss law is observed at temperatures 85–140°K. For alloys with a larger content of ThP, this law is satisfied. For alloys with a larger content of ThP, this law is satisfied in the entire investigated temperature interval, and Θ_p tends to zero (Fig. 2). From the data obtained

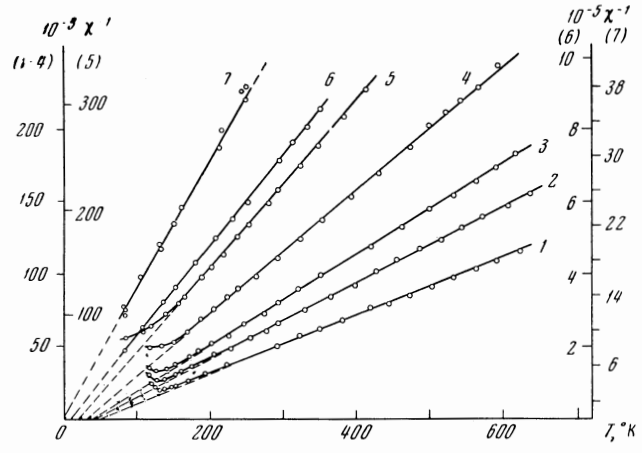

FIG. 2. Dependence of $1/\chi$ on T for the following samples: 1–UP, 2–80% UP– 20% ThP, 3–65% UP–35% ThP, 4–50% UP–50% ThP, 5–30% UP–70% ThP, 6–10% UP–90% ThP, 7–2% UP–98% ThP. The scales of $1/\chi$ for the samples are indicated by the numbers in the parenthesis.

in the paramagnetic region, we determined the values of Θ_p and of the magnetic moment μ_{eff} per atom of uranium. These values are shown in Fig. 3 and in Table I. It can be seen that Θ_p and μ_{eff} decrease with increasing thorium content. At maximum dilution, Θ_p is close to zero, and $\mu_{eff} = 2.7\ \mu_B$. All these regularities can be readily explained if account is taken of the results of neutron-diffraction investigations of UP [4]. It follows from these results that in uranium monophosphide there is a layered magnetic structure, such that there is a positive interaction in the basal planes between the magnetic moments of the uranium atoms, and a negative interaction between the neighboring layers. In the alloys investigated by us, the positive interaction is apparently much stronger than the negative one, and this has led to a positive value of Θ_p. The possible existence of such a case in layered antiferromagnets was indicated already by Landau [5]. Therefore when uranium monophosphide is diluted by thorium atoms the weaker interaction between the layers is the first to vanish, followed by the interaction within the layer. We recall that in each layer the magnetic moments are already perpendicular to the basal plane.

We can conclude from all the foregoing that the constant Θ_p in the UP-ThP system is determined essentially by the exchange interaction between the uranium atoms.

Unlike the UF-ThS [6], system in the UP-ThP system the effective magnetic moment μ_{eff} per atom of

Compound	$\chi\cdot10^6$, $T=290°$ K	Θ_p, °K	μ_{eff}, μ_B	Θ_N, °K	$T=\frac{\chi\cdot10^6}{\Theta_N}$	a_0, Å
UP [2]	20,2	+49±1	3,24	129	51,0	5.58
UP [1]	20,4	+3±1	3,56	123	—	5,587
UP	—	+36	3,31	130	—	—
80% UP — 20% ThP	15,2	+44±1	3,22	128	41,0	5,59
65% UP — 35% ThP	12,4	+40±1	3,21	120	30,8	5,62
50% UP — 50% ThP	8,8	+32±1	3,1	115	22	5,70
30% UP — 70% ThP	4,55	+21±2	2,9	—	—	5,74
10% UP — 90% ThP	1.42	+8±6	2,8	—	—	5,81
2% UP — 98% ThP	0,36 •	0±8	2,7	—	—	5.82

• $T = 200°$ K.

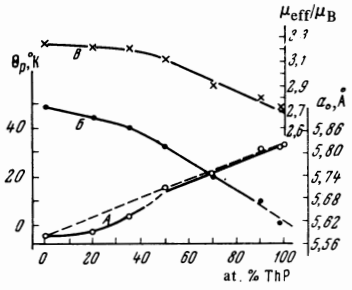

FIG. 3. Dependence of the lattice parameter a_0 (curve A), of the paramagnetic Curie temperature Θ_p (curve B), and of the effective magnetic moment μ_{eff} (curve C) on the ThP content in the alloy.

uranium decreases with increasing dilution, and tends to 2.7 μ_B at maximum dilution. This differs from the value of μ_{eff} calculated for the ground state of $^3H_4$ in the presence of LS coupling or of a "quenched" orbital angular momentum (μ_{eff} is respectively equal to 3.56 and 2.83 μ_B).

Nor does the obtained magnetic moment agree with the electron configuration of uranium $5f^2$ for jj coupling (3.84 μ_B). We see that all these values exceed the value of μ_{eff} obtained by us from the paramagnetic region. To explain the obtained results it is apparently necessary to take into account the influence of the intracrystalline field, which leads to a splitting of the ground state. We note that in the investigated temperature interval there is no observed influence of the multiplet levels on the temperature variation of the paramagnetic susceptibility. These results agree with the conclusions of Hutchinson and Candela [7], who have shown that in certain uranium compounds the influence of the intracrystalline field leads to a splitting of the ground level and to a decrease of the magnetic moment determined from the paramagnetic region.

It is also seen from our results that when UP solid solutions are diluted with thorium, the Neel temperature drops insignificantly and the antiferromagnetism vanishes at a certain concentration (50 at.%ThP). A similar picture is observed in antiferromagnetic compounds of 3d-transition metals [8,9]. Thus, for example, vanishing of the antiferromagnetism at 30 at.%MgO and La_2O_3 was observed in the MnO-MgO and Cr_2O_3-La_2O_3 systems, upon dilution, simultaneously with a slight shift of the Neel temperature towards lower temperatures. On the other hand, in antiferromagnetic compounds of rare-earth metals at the same dilution, the antiferromagnetic ordering is still retained [10]. Simultaneously, there are observed anomalously large values of the susceptibility in the paramagnetic region. In [10] this circumstance is attributed to the occurrence of coupled pairs or so-called "clusters." The UP-ThP system investigated by us occupies an intermediate position between the antiferromagnetic compounds 3d and 4f of the transition metals, inasmuch as attributes of both groups appear here. This indicates once more that the actinides, particularly uranium, also occupy an intermediate position with respect to magnetic properties between 3d and 4f transition metals.

THE SYSTEM UP_2-ThP_2 AND THE COMPOUND UBi_2

Figure 4 and Table II show the results of an investigation of the magnetic properties of solid solutions of certain samples of the UP_2-ThP_2 system and the compound UBi_2. All these samples are antiferromag-

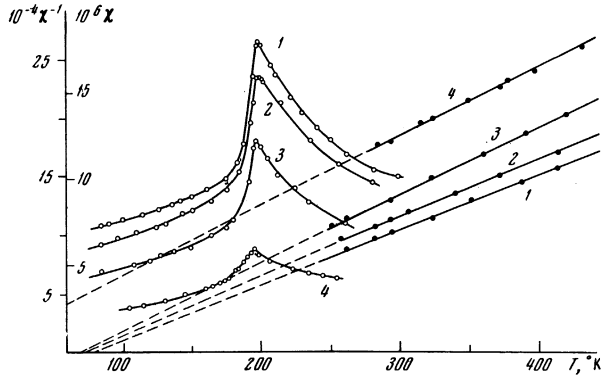

FIG. 4. Dependence of $1/\chi$ on T(●) and of χ on T(○) for the following samples: 1–UP_2, 2–93% UP_2–7% ThP_2, 3–80% UP_2–20% ThP_2, 4–UBi_2.

nets with a Neel temperature approximately 200°K. In the paramagnetic region, the magnetic susceptibility follows the Curie-Weiss law, and in the compound UBi_2 we have $\Theta_p < 0$, whereas in UP_2, just as in UP, $\Theta_p > 0$.

X-ray structure and neutron diffraction investigations have shown [12] that the compounds UP_2 and UBi_2, which have the same body-centered tetragonal structure of Cu_2Sb, have different types of antiferromagnetic ordering. It is significant, that both these compounds are uniaxial antiferromagnets, and the natural axis of antiferromagnetism is directed along the c axis. According to the conclusions of the spin-wave theory [11], in uniaxial antiferromagnets at temperatures $T < \Theta_N$, under definite conditions, it is possible to observe a quadratic dependence of the magnetic susceptibility on the temperature. It is seen from Fig. 5 that this dependence, in the case of our antiferromagnets, is satisfied in a wide temperature range, approximately from 0.35 Θ_N to 0.9 Θ_N, and this interval decreases somewhat as the nonmagnetic thorium ions are introduced. It is typical that the slope of the

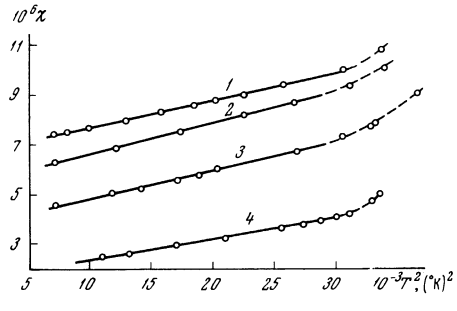

FIG. 5. Dependence of χ on T^2. The notation is the same as in Fig. 4.

Compound	$\chi\cdot10^6$, T=293°K	Θ_p, °K	μ_{eff}, μ_B	Θ_N, °K	$\chi\cdot10^6$, $T=\Theta_N$
UP_2 [2]	10.2	+80±1	2.30	199±1	18.4
UP_2 [1]	10.6	+86	2.30	203	—
UP_2	—	+80±1	2.29	206	—
93% UP_2 – 7% ThP_2	9.1	+74±1	2.28	198±1	16.7
80% UP_2 – 20% ThP_2	7.8	+68±1	2.27	196±1	12.8
	5.7	−38±1	3.22	195±1	6.0
UBi_2 [12]	—	−53	3.4	183	—

$\chi(T^2)$ lines does not depend on the composition. It is of great interest to carry out further investigations on single crystals at lower temperatures, where according to the theory a dependence of the susceptibility on the field should appear and the character of the dependence of the susceptibility of the temperature should change.

In conclusion, the authors are grateful to Professor E. I. Kondorskiĭ for valuable remarks.

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Translated by J. G. Adashko
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