Magnetic Susceptibility and Electrical Resistivity of Uranium Phosphides and UP-ThP Solid Solutions

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The magnetic susceptibility and electrical resistivity of uranium phosphides and UP-ThP solid solutions were measured. All the uranium phosphides exhibited paramagnetism at room temperature, and followed the Curie-Weiss law. The Néel point T_N for UP_2 and UP, and the Weiss constant θ were estimated. Ferromagnetic components made their appearance in UP_2 and UP, in the temperature range below T_N. With UP-ThP solid solutions, the changes according to composition observed in the values of T_N and θ indicated that UP is magnetically diluted by ThP, which latter compound is characterized by Pauli paramagnetism, and whose presence contributes to diminish the exchange interactions.

The electrical resistivity of UP increased rather rapidly with temperature up to a point corresponding to T_N beyond which the tendency changed sharply to a slightly negative coefficient. ThP showed a consistently low value of resistivity, were slowly rising with temperature, and that of UP–ThP solid solutions revealed a behavoir intermediate between those of UP and ThP.

I. INTRODUCTION

In recent years, the NaCl type of actinide compounds with high melting point have come to attract attention as potential nuclear fuel. Uranium monophosphide —which is one such compound— is reported by stable up to its melting point of 2,850°C[1] and said to have the greatest chemical stability among these compounds[2]. Thorium monophosphide also has good thermal and chemical stability, and it is felt that a UP-ThP solid solution should possess favorable properties as breeder type fuel. Yet little work has so far been done to obtain information on the properties of actinide compounds, and the present study has been aimed at elucidating the magnetic and electrical properties of uranium phosphides and UP-ThP solid solutions, through which an insight into the electronic structure and the nature of the chemical binding of NaCl type actinide compounds might be expected.

II. EXPERIMENTAL

1. Materials

Two methods of synthesizing uranium and thorium phosphides have appeared in literature: one involving the reaction of uranium (or thorium) powder with red phosphorus[3][4], and the other with phosphine gas[5]. In the present work the former process was adopted, for its advantage of obviating the troublesome preparation and purification of phosphine from pure red phosphorus (99.999%).

(1) Preparation of UP_2

The apparatus for synthesizing UP_2 is shown in **Fig. 1**. The reaction tube containing red phosphorus and finely milled uranium powder by hydride route was evacuated
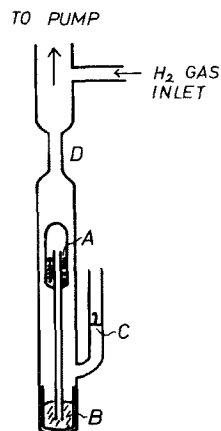
A: Red phosphorous, B: U metal,
C: Breakable seal

Fig. 1 Apparatus for preparation of UP_2

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($\sim 10^{-6}$mmHg) and sealed at the neck D. The reaction tube this sealed was placed into an electric furnace and heated to the predetermined temperature, *i.e.* 500°C.

The resulting products were analyzed by X-ray powder diffraction. In the products from reactions of duration shorter than 30 min, the principal phase revealed by the diffraction patterns was U_3P_4 with UP_2 as secondary phase. Reactions exceeding 1 hr produced UP_2 as the main phase, and above 2 hr, the patterns no longer showed any traces of U_3P_4 in the products. These findings may be taken to indicate that the UP_2 was formed by the reaction of phosphorus vapor with U_3P_4 which had been produced by the phosphorus-uranium reaction. For the succeeding measurements the samples were prepared by reaction maintained during more than 10 hr.

（2）Degradation of UP_2

In order to obtain information on the conditions requisite for stable existence of UP_2, the thermal degradation of UP_2 was examined by thermogravimetric analysis. A typical TGA curve obtained by heating UP_2, at a rate of 200°C/hr in vacuum is shown in **Fig. 2**. Degradation first began at about 600°C, and the weight loss was found to
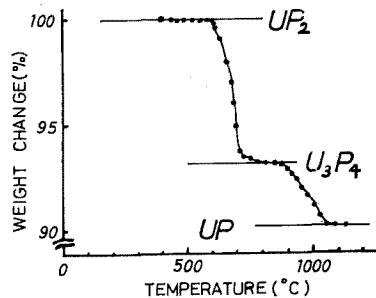

Fig. 2 TGA curve for degradation of uranium phosphides

correspond to the decomposition of UP_2 into U_3P_4.

A second phase of degradation took place at about 900°C, which corresponded to the decomposition to UP. Granted that the final product UP is stoichiometric (the point having been conclusively established quite recently[1]), the other level portions of the TGA curve correspond to stoichiometric U_3P_4 and UP_2 respectively. This TGA study furnished useful information in preparing single phase samples of the uranium phosphides.

（3）Preparation of U_3P_4, UP and UP-ThP Solid Solution

The method of synthesizing U_3P_4, UP and UP-ThP solid solution has already been

Table 1 Magnetic properties of uranium phosphides and UP-ThP solid solutions

| Compound	Lattice parameter (Å)	Weiss constant θ	Néel point $T_N(°K)$	Magnetic moment $\mu_{eff}(\mu_B)$	Ref.
UP_2	$a=3.805, \ c=7.764$	77	203	2.24	P
	$a=3.810, \ c=7.764$	86	203	2.30	T
	$a=3.808, \ c=7.780$	80.5	206	2.29	A
U_3P_4	$a=8.214$	134		2.76	P
	$a=8.214$	138		2.77	T
	$a=8.207$	151		2.61	A
UP	$a=5.589$	-15	116	3.48	P
	$a=5.587$	3	123	3.56	T
	$a=5.589$	36	130	3.31	A
UP-8.4%ThP	$a=5.610$	-8	110	3.38	P
UP-15.4%ThP	$a=5.627$	-6	108	3.51	P
UP-32.4%ThP	$a=5.676$	-1	84	3.30	P

P : Present work
T : TRZEBIATOWSKI, W., TROC, R.: *Bull. Acad. Polon. Sci.*, Ser. chim., **11**, 661 (1963).
A : ALLBUTT, M., JUNKISON, A.R., DELL, R.M.: Int. Symp. on Compounds of Interest in Nuclear Reactor Technology, *Nucl. Metall.*, **10**, 65 (1964).

described in detail elsewhere[6]. The phosphides were prepared in an open system, as distinct from the closed system method for preparing UP_2. The lattice parameters of the samples used for measuring magnetic susceptibility and electrical resistivity are listed in **Table 1.** The compositions of the UP-ThP solid solutions were derived from the relation between lattice parameter and composition, which had been obtained earlier[6].

2. Magnetic Susceptibility

The magnetic susceptibility of UP_2, U_3P_4, UP and UP-ThP solid solutions was measured over the temperature range from 77° to 300°K by the Faraday method using a torsion balance. These compounds all exhibited paramagnetism at room temperature. **Figure 3** shows the temperature dependence of the magnetization of UP_2. The peak appearing at about 200°K indicates a transition to antiferromagnetic orientation and below 110°K the magnetization curve indicates the existence of ferromagnetism. The latter fact is substantiated by the hystereses exemplified by the two curves (● and ×) for $H=2$ KOe. The magnetization curve of U_3P_4 (not reproduced here) reveals transition to ferromagnetism with the Curie point at 134°K. This behavior showed itself to be independent of magnetic field strength between 2 and 8 KOe.
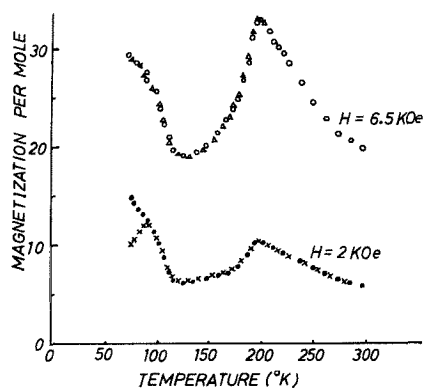
● : Cooled in $H=2$ KOe,
× : H increased from $H=-2$ KOe at liquid nitrogen temperature
○ : Cooled in $H=6.5$ KOe
△ : H increased from $H=-6.5$ KOe at liquid nitrogen temperature
Fig. 3 Magnetization of UP_2

With UP, antiferromagnetism made its appearance below 116°K, but the magnetization —as in the case of UP_2— appears to increase again near liquid nitrogen temperature and to exhibit signs of hysteresis in this region (**Fig. 4**).
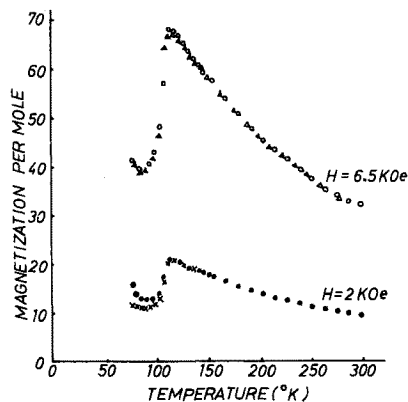
● : Cooled in $H=2$ KOe,
× : H increased from $H=-2$ KOe at liquid nitrogen temperature,
○ : Cooled in $H=6.5$ KOe,
△ : H increased from $H=-6.5$ KOe at liquid nitrogen temperature
Fig. 4 Magnetization of UP

In the paramagnetic region, these compounds obey the Curie-Weiss law. From the relation between reciprocal susceptibility and temperature, the effective magnetic moment μ_{eff}, Néel point T_N and Weiss constant θ were determined, and the results are given in Table 1 together with the values reported in literature. In the UP-ThP solution, UP can be judged to be magnetically diluted by its isomorphous ThP, since ThP shows Pauli paramagnetism[7]. In the present case, when the concentration of UP was higher than 67 $mol\%$, the solid solution obeyed the Curie-Weiss law, and increasing ThP concentration shifted T_N towards lower values and θ towards zero (Table 1). This can be attributed to diminution of exchange interaction. With lower concentrations of UP, the Curie-Weiss law was no longer obeyed as a result of the strong contribution of Pauli paramagnetism to the overall susceptibility.

3. Electrical Resistivity

The temperature dependence of the electri-

cal resistivity of UP and UP-ThP solid solutions were determined with use made of rod samples measuring $2 \times 2 \times 20$ mm prepared by sintering at $1,700° \sim 1,800°C$. The results are presented in **Fig. 5** where the plots are not corrected for the presence of pores created by sintering. The resistivity of UP is seen to have a positive temperature coefficient up to about $120°K$, above which point it abruptly changes to a weak negative value. The maximum resistivity agrees well with the Néel point ($116°K$). The resistivity of ThP is very small, comparable to that of transition metals, and the temperature coefficient is positive throughout the range of covered[7]. The UP-ThP solid solutions are seen to exhibit a temperature dependent resistivity behavior intermediate between UP and ThP, and the 82.3%UP-17.7%ThP specimen shows a resistivity neutral to change in temperature above the Néel point. **Figure 6** plots the dependence on composition ratio exhibited by the resistivity of UP-ThP solid solutions at room temperature. The resistivity is seen to be affected markedly by the inclusion of even small amounts of ThP at the UP-rich end, while the presence of UP at the ThP-rich end has only little effect.
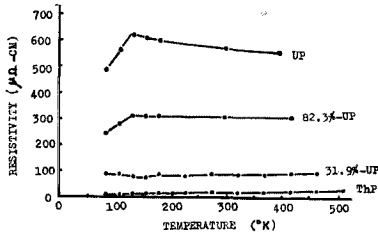

Fig. 5 Electrical resistivity *vs.* temperature for UP and UP-ThP solid solutions
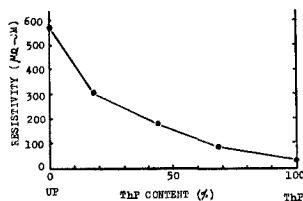

Fig. 6 Dependence of resistivity at room temperature on ThP content of UP-ThP solid solutions

III. DISCUSSION

It is most likely that the magnetic moment of uranium compounds is due mainly to localized $5f$ electrons. Allbutt *et al.*[8] have presumed from measurement of magnetic susceptibilities that UN and UP has the $5f^2$ configuration with some quenching of orbital momentum, and U_3P_4 and UP_2 the $5f^1$ configuration. Sidhu *et al.*[9] have studied antiferromagnetic UP by neutron diffraction technique, to find that the $5f^3$ configuration is consistent with the experimental value of the magnetic form factor. Recently, Grunzweig-Genossor *et al.*[10] have reported the results of a theoretical study of magnetism in UX type compounds, assuming $^3H_4$ ($5f^2$ configuration) as the ground state.

Since, in the uranium atom, the mean radius of the $5f$ wave function is much larger than that of the $4f$ wave function in rare earth atoms, a model valid for rare earth metal compounds based on the Russel-Saunders coupling approximation would appear unsuitable for application to uranium compounds. On the other hand, since the coefficient of electronic specific heat of NaCl type uranium compounds has very large values[11] —indicating very high density of states at the Fermi level— it should stand to reason to seek the explanation of various physical properties by considering a band model, with a narrow $5f$ band at the position of the Fermi level. On the basis of the band structure calculations previously carried out[12] and of considerations on certain electronic properties, the following description of the electronic structure of uranium compounds is proposed.

(1) The energy bands comprise broad $7s$ and $6d$ band, and a narrow $5f$ band, which is further split into a number of sub-bands by crystalline field and spin-orbit interaction. The Fermi level lies within the $5f$ band, so that UN and UP would both have about one $5f$ electron and US about two $5f$ electrons.

(2) The orbital momentum of the $5f$ electrons is strongly quenched by the crystalline field, which is an aspect quite different from that of the $4f$ electrons in

rare earth compounds.

(3) The energy differences between the ground state and the nearest excited states are relatively small, so that the latter states have a predominant influence on the effective moments.

(4) The intra-atomic exchange interaction between the localized $5f$ electrons and the conduction $6d$ and $7s$ electrons gives rise to the contribution from these last-mentioned electrons to the magnetic moment.

In contrast to the relatively simple behavior exhibited by the magnetism of U_3P_4, characterized by the sole appearance of ferromagnetism, at low temperature, UP and UP_2 have a complicated magnetism, with ferromagnetic components appearing at low temperature below their Néel points. A similar behavior has been reported in a number of other materials, including certain uranium compounds, such as U_3Te_4, UTe, U_3Se_4 and USe[13], as well as NpC[14]. Moreover, a peak in specific heat at $22°K$[15] and a change of magnetic moment at about $33°K$[16] have also been reported for UP. Our cursory observation of magnetic susceptibility below liquid nitrogen temperature in UP_2 has revealed a transition at about $50°K$. The authors are undertaking further susceptibility measurements below liquid nitrogen temperature, as also a theoretical study on the magnetic behavior of these compounds.

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