MAGNETIC PROPERTIES OF URANIUM AND PLUTONIUM LAVES PHASES
WITH 3d TRANSITION ELEMENTS

by

D. J. Lam and A. T. Aldred

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Presented At:

20th Annual Conference on Magnetism and Magnetic Materials,
San Francisco, California, December 3-6, 1974

U of C AUA USAEC

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

MAGNETIC PROPERTIES OF URANIUM AND PLUTONIUM LAVES PHASES
WITH 3d TRANSITION ELEMENTS*

D. J. Lam and A. T. Aldred
Argonne National Laboratory, Argonne, Illinois 60439

ABSTRACT

We have measured the magnetization of UMn_2 , UFe_2 , UCo_2 , UNi_2 , PuMn_2 , PuFe_2 , PuCo_2 , and PuNi_2 from 4-300 K in fields up to 14 kOe. The susceptibility of UMn_2 shows a small maximum near 240 K (which may indicate an antiferromagnetic transition) in agreement with previous results. Our data for UFe_2 , UCo_2 and UNi_2 are not in good agreement with earlier work; the ferromagnetic ordering temperature (158 K) of a single crystal sample of UFe_2 is lower than any reported value, UNi_2 orders ferromagnetically at 30 K, and UCo_2 may order below 5 K. In contrast, PuMn_2 , PuCo_2 and PuNi_2 have small weakly-temperature-dependent susceptibilities. PuFe_2 is ferromagnetic at room temperature, in agreement with previous Mössbauer results, and has a saturation moment of $\sim 2.6 \mu_B/\text{mole}$.

INTRODUCTION

In the past year an extensive study of the magnetic properties of neptunium-based C-15 Laves phases has been undertaken at Argonne National Laboratory.^{1,3} The magnetic characteristics of the compounds where the second component is not a 3d transition element show a regular dependence on neptunium-neptunium distance.^{1,2} However, the Laves phases of neptunium with the 3d transition metals (Mn, Fe, Co, Ni) show no such simple correlations, although they all order magnetically at low temperatures.³

To further study the magnetism of actinide Laves phases, we have made magnetization measurements from 4 to 300 K in applied fields up to 14 kOe on the uranium and plutonium Laves phases with Mn, Fe, Co, and Ni. All the compounds have the C-15 structure except for UNi_2 which has the hexagonal C-14 Laves phase structure.

The samples were prepared by arc melting (weight losses were negligible except for the Mn compounds) and were polycrystalline in nature. In the case of UFe_2 , the single-crystal used in the neutron-diffraction experiments of Yessik⁴ was available.

*Work supported by the U. S. Atomic Energy Commission.

RESULTS

The procedures for data analysis and determination of magnetic susceptibilities are given in Ref. 1. In particular, the magnetization of the Np compounds in the paramagnetic regime showed a small ferromagnetic component (determined in the data analysis) which had a substantial temperature dependence and could not be attributed to an impurity. Similar effects, of greater or lesser magnitude, were observed in the present investigation. Metallographic examination of the UMn_2 , UCo_2 , and UNi_2 samples showed no evidence (<1%) of any second phase. It is, again, difficult to rationalize this behavior in terms of the phase equilibria or possible impurities.

UMn₂

The temperature dependence of the reciprocal molar susceptibility χ_M^{-1} (Fig. 1) is in good agreement with the previous study of Lin and Kaufman.⁵ In particular, the small susceptibility maximum near 2 K is reproduced (however, around 240 K in the present work). Inasmuch as no neutron-diffraction experiments have been performed on this compounds, the possibility of an antiferromagnetic transition cannot be verified.

UFe₂

Previous magnetic measurements on polycrystalline material⁶ had shown a range of Curie temperatures from 172 to 195 K, and a saturation magnetization equivalent to $\sim 1 \mu_B/\text{mole}$; neutron-diffraction studies⁴ indicated that the moment is associated almost entirely with the Fe atoms. The present work on UFe_2 , which will be presented more fully in a separate publication, shows that $\langle 111 \rangle$ is the easy axis of magnetization. The magnetization of a sample with this $\langle 111 \rangle$ axis oriented parallel to the magnetic field has a small linear field dependence ($\chi = 7 \times 10^{-3} \text{ emu/mole}$) and the spontaneous moment at 4 K is $1.05 \mu_B/\text{mole}$. The Curie temperature of this sample, as determined from Arrott plots, is 158 K—substantially lower than previous results. The susceptibility above the Curie temperature is given in Fig. 1.

UCo₂

The susceptibility shows approximately Curie-Weiss behavior between 50 and 300 K (Fig. 1). The rapid increase in susceptibility below 50 K may pre-
sage the onset of magnetic ordering at very low temperatures (below 5 K). These results are not in agreement with the sketchy published data.⁶

UNi₂

Previous results⁶ are again incomplete. The present molar susceptibility is almost identical with

that of UCo_2 down to ~ 100 K (Fig. 1). Below 100 K there is again a rapid increase in susceptibility, similar to but more pronounced than that in UCo_2 , and the compound orders ferromagnetically (as indicated by Arrott plots) at 30 ± 1 K. Although the low-temperature magnetization is quite small (the moment at 5 K and ~ 13 kOe is $0.12 \mu_B/\text{mole}$, the relative increase with field ($\sim 11\%$ from 3 to 13 kOe) is similar to that in NpFe_2 .³ The approach to saturation was fit by the procedure given in Ref. 3 and yielded $\mu_{\text{sat}} = 0.13 \mu_B/\text{mole}$; the high-field susceptibility was zero (within the statistical uncertainty).

PuMn_2

This compound shows an almost temperature independent susceptibility between 5 and 300 K (Fig. 2).

PuFe_2

Previous Mössbauer measurements⁷ had shown that PuFe_2 is ferromagnetic at 300 K with a hyperfine field at the Fe site. The present work confirms this result, and the $\sim 7\%$ change in magnetization between 5 and 300 K suggests a Curie temperature in the neighborhood of 600 K. The large field dependence of the magnetization ($\sim 17\%$ increase from 3 to 13 kOe independent of temperature) again suggests a large magnetocrystalline anisotropy. The maximum moment attained was $2.09 \mu_B/\text{mole}$ at 5 K and ~ 13 kOe. An approach to saturation analysis yielded $\mu_{\text{sat}} = 2.6 \mu_B/\text{mole}$ and again a zero high-field susceptibility term (in sharp contrast to NpFe_2).

PuCo_2

The susceptibility increases slowly from 2.3×10^{-3} emu/mole at 300 K to 2.9×10^{-3} emu/mole at 5 K (Fig. 2).

PuNi_2

The susceptibility increases slowly from 1.4×10^{-3} emu/mole at 300 K to 1.7×10^{-3} emu/mole at 50 K, with a more rapid increase below 50 K (Fig. 2).

DISCUSSION

The magnetic properties of the uranium and plutonium Laves phases studied here are summarized in Table I. For the compounds where there is a substantial linear χ^{-1} vs T region, Curie-Weiss constants have been determined and are reported in Table I. These results may be compared with the more detailed data available for the corresponding neptunium Laves phases.³ The most striking feature is the greater magnitude of the ordering temperatures of the Fe compounds relative to the other compounds -- presumably a reflection of the strong $d-d$ exchange. Similar behavior is observed in the corresponding lanthanide

compounds.⁸ The uranium atoms in UFe_2 carry almost no moment, whereas the Np atoms have a moment of 1μ in NpFe_2 , and the Pu atoms appear to have little or no moment in PuFe_2 . (The hyperfine field at the iron site in PuFe_2 is a factor of two larger than that in NpFe_2 , although the bulk moment in PuFe_2 is smaller than in NpFe_2 .)⁷ When the behavior of the Mn, Co, and Ni compounds are considered in this context, a trend becomes evident. It appears that the uranium atoms have little or no moment in any of the $3d$ compounds, the neptunium atoms in all the $3d$ compounds carry moments, and the plutonium atoms again are non-magnetic in all these compounds, except possibly PuFe_2 . This behavior is in contrast to the corresponding lanthanide compounds⁸ and presumably indicates strong $f-d$ hybridization. We may speculate that a substantial transfer of f electrons from the actinide atoms to the d bands leaves essentially no localized f electrons at the uranium atoms in these compounds. The corresponding data for the neptunium compounds³ are not inconsistent with one electron per neptunium site. If there were two localized f electrons per plutonium site, we would again expect a non-magnetic crystal-field ground state⁹ and this is consistent with the present data. However, a more complete understanding of these materials will await a more detailed atomistic study of their magnetic behavior.

REFERENCES

1. A. T. Aldred, B. D. Dunlap, D. J. Lam, and I. Nowik, Phys. Rev. B 10, 1011 (1974).
2. A. T. Aldred, D. J. Lam, A. R. Harvey, and B. D. Dunlap, Phys. Rev., to be published.
3. A. T. Aldred, B. D. Dunlap, D. J. Lam, G. H. Lander, M. H. Mueller, and I. Nowik, Phys. Rev. (B1, Jan 1975); see also paper of this conference.
4. M. Yessik, J. Appl. Phys. 40, 1133 (1969).
5. S. T. Lin and A. R. Kaufman, Phys. Rev. 108, 1171 (1957).
6. D. J. Lam and A. T. Aldred in *The Actinides: Electronic Structure and Related Properties*, (J. B. Darby, Jr., and A. J. Freeman, eds., Academic Press) Vol. I, Chap. 3.
7. J. Gal, Z. Hadari, E. R. Bauminger, I. Nowik, S. Ofer, and M. Perkal, Phys. Lett. 31A, 511 (1970).
8. K. N. R. Taylor, Advances in Physics, 20, 551 (1971).
9. B. Bleaney, Proc. Roy. Soc. A276, 28 (1963).

Fig. 1. Reciprocal molar susceptibility as a function of temperature for UMn_2 , UFe_2 , UCo_2 , and UNi_2 .

Fig. 2. Reciprocal molar susceptibility as a function of temperature for PuMn_2 , PuCo_2 , and PuNi_2 .

TABLE I.

Magnetic properties of uranium and plutonium Laves phases with Mn, Fe, Co, and Ni.

	UMn ₂	UFe ₂	UCo ₂	UNi ₂	PuMn ₂	PuFe ₂	PuCo ₂	PuNi ₂
Magnetism	AF(?)	F	P	F	P	F	P	P
Ordering Temp. (°K)	~240	158		30		~600		
$\bar{\mu}_{\text{site}}$ (μ_B /mole)		1.05		0.13		~2.6		
CW range (°K)			50-290	100-290				50-300
μ_{eff} (μ_B /mole)			2.61	2.50				4.1
θ (°K)			-505	-445				-1200
χ_M (300 K) (10^{-3} emu/mole)	2.4	8.2	1.0	1.0	3.0		2.3	1.4
χ_M (5 K) (10^{-3} emu/mole)	2.8	-	5.7	-	3.0		2.9	2.9