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MAGNETIC PROPERTIES OF ACTINIDE LAVES PHASES

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MAGNETIC PROPERTIES OF ACTINIDE LAVES PHASES*

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SUMMARY

In this paper we review recent high-field (up to 80 kOe) magnetization, nuclear-gamma-ray resonance, and neutron diffraction measurements on a number of actinide ferromagnets with the C-15 Laves phase crystal structure. $NpAl_2$ and $NpOs_2$ are an interesting contrast; $NpAl_2$ behaves as a localized $5f$ system whereas $NpOs_2$ exhibits properties usually associated with itinerant ferromagnets. In the second part of the paper we report similar measurements on the series $AnFe_2$, where An = U, Np, Pu, and Am. The properties of these compounds suggest an increasing localization of $5f$ electrons as one proceeds from uranium to americium. The Pu ion in $PuFe_2$ is definitely trivalent $5f^5$, but the observation of a small negative moment on the Am site in $AmFe_2$ implies a partial occupancy of the Am^{2+} $5f^7$ state in this compound. This is the first indication of a mixed valence configuration in an actinide system.

INTRODUCTION

The magnetic properties of a large number of actinide Laves phases (C-15 crystal structure) have been studied at Argonne National Laboratory over the last few years. This structure is not only extremely common in intermetallic compounds but the close packing, and especially the nearest-neighbor actinide separation, indicates that direct overlap of the $5f$ wave functions may occur. Some years ago, Hill [1] suggested that the occurrence of magnetic ordering in actinide intermetallics could be correlated with a critical actinide-actinide separation. Although a number of important exceptions exist, the neptunium Laves phases provide strong support for this concept. Initial experiments on these compounds [2] suggested that as the actinide-actinide separation d_{An} is decreased, the magnetism changes from local-moment ($NpAl_2$) to itinerant behavior ($NpOs_2$ and $NpIr_2$) and finally to paramagnetism with no long-range order ($NpRu_2$). In the first part of this review, we discuss high-field studies [3] with magnetization, nuclear-gamma-ray resonance, and neutron-diffraction techniques on the compounds $NpAl_2$ and $NpOs_2$. In the second part of the paper we discuss experiments on the $AnFe_2$ compounds where An = U, Np, Pu, and Am. Although

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actinide compounds with the transition elements exhibit complex behavior [4], we observe the increasing dominance of the 5*f* electron shell, on going from uranium to americium, in determining the magnetic properties.

EXPERIMENTAL PROCEDURES

A. Magnetization

The bulk magnetizations were measured at 4.2 K by the Faraday technique [5] utilizing an electronic balance to determine the force on the sample (mass ∿0.1 g). The magnetization technique is extremely precise in determining the total moment of the material; of particular interest in the present studies is the high-field susceptibility since, in itinerant magnets, we expect this term to be reasonably large. Unfortunately, because of the generally high magnetocrystalline anisotropy in actinide intermetallics, complete saturation of these polycrystalline samples is not always achieved even at $H_{max} = 80$ kOe. This problem leads to uncertainties in interpretation. We have attempted to extrapolate the data to infinite field to obtain the saturation moments but the procedures are not necessarily reliable [4], particularly in the case of $NpFe_2$ and $PuFe_2$, which appear to have anisotropy fields in the mega-oersted range.

B. Nuclear Gamma-ray Resonance

Nuclear gamma-ray resonance (NGR) measurements were performed [6] using the 59.5 keV resonance in ^{237}Np and the 84.3 keV resonance in ^{243}Am. For the present discussion, the pertinent results are the magnetic hyperfine fields (H_{hf}) (primarily in the Np system), which give information on the local magnetic behavior of the Np ion. For well localized 5*f* electrons, the hyperfine field is proportional to $\mu\langle r^{-3}\rangle$ where μ is the magnetic moment on the Np ion and $\langle r^{-3}\rangle$ is averaged over all impaired electrons. Given this correlation, which has been demonstrated for a large number of materials [7], measurements of H_{hf} are frequently used to obtain a value of the magnetic moment, denoted μ^{hf} in the the following. If μ and H_{hf} are both known, then deviations from that relation may indicate delocalization effects. Because the hyperfine field is characteristic of the local environment, it is not sensitive to problems of domain alignment, and hence does not require bulk magnetic saturation as in the magnetization measurements. In general, measurements were performed on polycrystalline samples containing ∿200 mg/cm^2 Np, i.e., a total sample mass of ∿0.5 gm.

C. Neutron Diffraction

Initially we obtained conventional neutron powder patterns (with unpolarized neutrons) and determined that the compounds were stoichiometric and single phase. Unpolarized neutron experiments are, however, unable to give quantitative information about the magnetic moments if they are small, and we have used a polarized neutron diffractometer to measure the nuclear-magnetic interference term in the magnetic cross section. This technique is especially useful for systems with small magnetic moments, but has the disadvantage that depolarization effects are present unless single crystals are used. To minimize this effect, we placed the sample in a 60 kOe magnetic field and made corrections by measuring the polarization of the transmitted neutron beam [8]. The depolarization decreases exponentially with increasing magnetic field, as anticipated from simple domain wall energetics, and the absolute value of the depolarization is related to the magnetocrystalline anisotropy of the sample. At low fields, large depolarization effects of 25.4% and 6.0% were observed in $NpFe_2$ and $PuFe_2$, respectively, whereas in the other materials considered in this review the neutron depolarization was negligible (<0.3%). Although this information cannot be directly related to the anisotropy field, the lack of saturation in the magnetization data for $NpFe_2$ and $PuFe_2$ is entirely consistent with the large neutron depolarization observed in these two materials.

From an analysis of the neutron-diffraction results we obtain (1) the magnitude of the localized moments on the separate atomic sites, and (2) the spatial extent of the magnetization density of each site. The former information is essential when more than one magnetic species is present, and the latter information is particularly important in understanding the electronic structure of $NpOs_2$ and $PuFe_2$. For actinide studies, the disadvantage of neutron experiments is that they require large samples; our experiments have been performed on samples with masses between 1 and 2 g.

RESULTS AND DISCUSSION

The magnetic properties of several actinide Laves Phases are given in Table I.

Table I. Summary of magnetic properties of some actinide Laves-phase compounds. d_{An} is the actinide-actinide interatomic distance; T_c is the ferromagnetic ordering temperature (except for $NpIr_2$ which is antiferromagnetic); $\bar{\mu}_o$ is the total moment deduced from magnetization experiments; the individual and total (per formula unit) atomic moments determined by neutron diffraction are μ_N and $\bar{\mu}_N$, respectively; μ_{Np}^{hf} is the actinide moment obtained from the neptunium hyperfine field; χ_M is the high-field molar susceptibility given by the magnetization data; the numbers in parentheses represent probable errors.

Compound	d_{An} (Å)	T_c (°K)	$\bar{\mu}_o$ (μ_B)	μ_{An}^{N} (μ_B)	μ_{Fe}^{N} (μ_B)	$\bar{\mu}^{N}$ (μ_B)	μ_{Np}^{f} (μ_B)	χ_M (10^{-3} emu/mole)
$NpAl_2$	3.37	5.6(1)	1.21(1)	1.50(5)	-	1.50(5)	1.52(4)	2.6(5)
$NpOs_2$	3.26	7.5(5)	0.44(3)	0.25(5)	-	0.25(5)	0.40(4)	10(10)
$NpIr_2$	3.25	7.3(5)	-	-	-	-	0.6(1)	-
$NpRy_2$	3.23	-	-	-	-	-	-	-
UFe_2	3.06	∿160	1.11(3)	0.06(1)	0.59(2)	1.24(5)	-	5(1)
$NpFe_2$	3.09	∿500	2.69(9)	1.09(3)	1.35(5)	3.8(2)	0.87(1)	0(2)
$PuFe_2$	3.11	∿600	2.28(8)	0.45(5)	1.47(5)	3.4(2)	-	3(2)
$AmFe_2$	3.16	∿600	3.13(9)	-0.4(1)	1.7(2)	3.0(2)	-	5(2)

A. $\underline{NpAl_2}$

NGR and neutron experiments give an atomic moment of 1.5 μ_B/Np, whereas the magnetization experiments give 1.2 μ_B per formula unit. The discrepancy of ∿0.3μ_B is characteristic of actinide ferromagnets and may be understood in terms of a negative conduction-electron polarization [9]. In a simple Russell-Saunders Hund's rule coupling scheme, the overall moment $\vec{J}$ of these systems is composed of an orbital moment $\vec{L}$ and a spin component $\vec{S}$ that are arranged antiparallel, i.e., $\vec{J} = \vec{L} - \vec{S}$. The effective conduction-electron polarization $\vec{s}$, which is primarily 6*d*-like, will be polarized parallel to the localized spin $\vec{S}$, hence $\vec{s}$ and $\vec{J}$ are antiparallel. The total moment is then represented by $gJ - 2s = \bar{\mu}_o$, the magnetization value. However, the conduction electron contribution has a diffuse distribution in real space so that its magnetic form factor *f* will drop rapidly to zero.

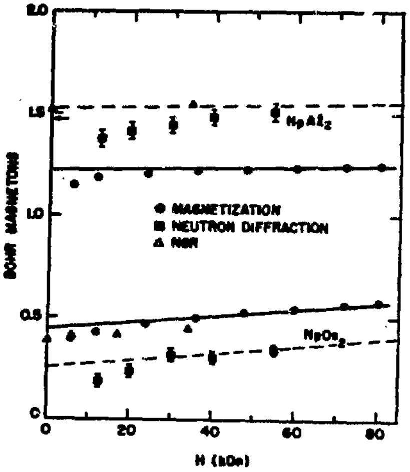

Fig. 1. Field dependence of the magnetic moment per neptunium atom for $NpAl_2$ *and* $NpOs_2$ *as determined by different techniques. The solid lines through the bulk magnetization data represent the limiting high-field susceptibility given in Table I. The dashed lines are drawn slightly above the neutron results to indicate the lack of complete saturation. The arrow on the ordinate axis is the unpolarized-neutron* ($H = 0$) *result for* $NpAl_2$*.*

The hyperfine field, being sensitive to $\langle r^{-3} \rangle$ for unpaired electrons, will also not measure the diffuse conduction electrons. The neutron and NGR results therefore represent the localized 5*f* moment, $\mu_o^N = \mu_o^{hf} = gJ$.

B. $\underline{NpOs_2}$

Whereas $NpAl_2$ behaves in a manner characteristic of other actinide (local moment) ferromagnets, the magnetic properties of $NpOs_2$ are quite different, and the results in Fig. 1 for $NpOs_2$ present an unusual dilemma. First, the moments derived from NGR and neutron experiments are in disagreement — the first observation of such disagreement in the 12 or so neptunium intermetallics examined to date with both techniques [7]. Second, both moments lie below the value of $\bar{\mu}_o$ as determined by magnetization experiments. These discrepancies suggest a spatial delocalization of the 5*f* electrons in $NpOs_2$.

We have shown [3] that a small modification of the wave function at large r leads to an appreciable change in the magnetic form factor, but a much smaller change in the term sensed by the hyperfine-field interaction $<r^{-3}>$. The neutron results give the product μf, where f, the magnetic form factor, is the Fourier transform of the magnetization density. If spatial delocalization occurs in $NpOs_2$, then the value of μ_{An}^{N} derived with a form factor appropriate to a localized system will be too low.

C. <u>UFe_2</u>

Neutron diffraction studies of single-crystal UFe_2 by Yessik [10] gave moments of 0.38 and 0.3 μ_B at the Fe and U sites, respectively. The fact that these values are somewhat lower than those in Table I may be attributed to variations in stoichiometry in Yessik's crystals. We have found, for example, that the Curie temperatures of different single crystals cut from Yessik's original samples vary between 147 to 162 K, with related variations in mean moment [11]. We conclude, from the small uranium moment and the absence of any appreciable anisotropy, that the $5f$ electrons are band-like in UFe_2.

D. <u>$NpFe_2$</u>

Previous experiments have shown that $NpFe_2$ is extremely anisotropic with a <111> easy axis of magnetization [4]. The discrepancy between the value of the moment determined by neutron and NGR techniques is probably due to a small transferred hyperfine field from the iron site. The more substantial difference between the total moments sensed by the magnetization and neutron measurements is presumably related to the lack of saturation discussed above.

E. <u>$PuFe_2$</u>

On the basis of the form factor results (Fig. 2), we conclude that the Pu ions in $PuFe_2$ are trivalent ($5f^5$). In the R-S coupling scheme, the ground state is $^6H_{5/2}$ with $\vec{L}$ (=5) and $\vec{S}$ (=5/2) opposing each other. The neutron cross section then has a maximum at a nonzero scattering angle, because the $\vec{L}$-$\vec{S}$ subtraction leads to regions of <u>negative</u> density with respect to the total magnetization. The neutron results from $PuFe_2$ are shown in Fig. 2. The values for $(\mu f)_{Fe}$ fall on a monotonically decreasing curve (broken line) corresponding to the iron form factor [12], whereas the results for $(\mu f)_{Pu}$ are essentially independent of scattering angle. The theoretical form factor is calculated for trivalent plutonium.

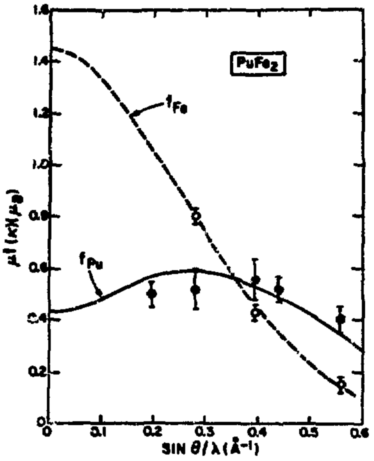

Fig. 2. Values for the product of the magnetic moment μ *and the magnetic form factor* $f(\kappa)$ *as a function of scattering angle for the Pu and Fe ions in* $PuFe_2$*. The solid and broken curves are theoretical form factors for Pu and Fe, respectively.* $(\kappa = 4\pi \sin\theta/\lambda)$

F. $AmFe_2$

The neutron experiments on $AmFe_2$ were performed on a very small sample (0.87 g) so that accurate results were not anticipated. Nevertheless, measurements on the (220) reflection, which has no contribution from the iron sublattice, show that a small moment of $\sim 0.4\mu_B$ exists at the Am site, and that it is antiparallel to the Fe moment of $1.7\mu_B$. NGR studies on ^{243}Am in $AmFe_2$ in the ordered state have detected only line broadening. This could arise from hyperfine splittings due to either the small moment at the Am site or transferred effects from the large iron magnetic moment.

If the Am ion is trivalent, the ground state (f^6:$^7F_0$) is nonmagnetic and the energy gap between the $^7F_0$ and excited $^7F_1$ state is $\sim$2700 cm^{-1}, so that the moment induced by the internal exchange field on the Am^{3+} ion should be essentially zero [13]. However, any ions with the Am^{2+} configuration have a ground state (f^7:$^8S_{7/2}$) that readily supports a magnetic moment. Further evidence to support this hypothesis of a mixed-valence situation comes from the sign of the Am moment. As discussed by Taylor [14], in the lanthanide-iron

Laves phases, the transition metal moment is coupled antiparallel to the lanthanide (or actinide) spin component $\vec{S}$. Thus, for $\vec{J} = \vec{L} - \vec{S}$ ions the Laves phase compounds are ferromagnetic (as is found for UFe_2, $NpFe_2$, and $PuFe_2$), whereas for $\vec{J} = \vec{L} + \vec{S}$ ions, the lanthanide and *3d* moments are aligned antiparallel (ferrimagnetic). Inasmuch as the f^7 state has $\vec{J}$ parallel to $\vec{S}$, the ferrimagnetic arrangement in $AmFe_2$ is compatible with a partial occupancy of the $Am^{2+}:f^7$ state. The anisotropy in $AmFe_2$ is smaller than in $NpFe_2$ or $PuFe_2$, and we observe better agreement between $\bar{\mu}_o$ and $\bar{\mu}_o^N$.

CONCLUSIONS

The present compounds aptly demonstrate the rich variety of behavior found in actinide magnetism. To understand these effects quantitatively, we require band theorists to calculate wave functions (eigenvectors) rather than energy states (eigenvalues), but this is a formidable challenge. The large conduction-electron polarization found in the localized system $NpAl_2$, is similar to that found [9] in US and PuP. A neutron scattering experiment that could establish the spatial extent of this diffuse magnetization density would be of considerable value. In $NpOs_2$ we find a large high-field susceptibility of $\sim 10^{-2}$ emu/mole and preliminary experiments suggest a delocalization of the unpaired electrons in a manner similar to that found in the itinerant ferromagnet $ZrZn_2$ [15]. More detailed experiments, preferably on single crystals, are required. The magnetic properties of UFe_2 (small anisotropy, small uranium moment) favor a model for the electronic structure in which the *5f* electrons are partially delocalized. The large magnetic anisotropy in $NpFe_2$ and $PuFe_2$, together with the large moments on the actinide ions and the magnetic form factors, suggest that a localized electron model is appropriate and the respective configurations are then $5f^4$ and $5f^5$. In $AmFe_2$, we propose the presence of a mixed valence system, the time- and space-averaged configuration being $0.95\ 5f^6 + 0.05\ 5f^7$.

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