Neutron diffraction study of PuP: The electronic ground state*

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The neutron elastic magnetic cross section has been measured from ferromagnetic ^{242}PuP at 4.2 K. As a result of the partial cancellation of $\vec{S}$ and $\vec{L}$ in the f^5 state, the cross section is independent of angle for $\sin\theta/\lambda < 0.35$ Å^{-1}. A detailed analysis, including the effects of intermediate coupling and J mixing, allows an identification of the electronic ground state. The conduction-electron polarization ($\sim 0.35\mu_B$) is antiparallel to, and almost half the magnitude of, the localized $5f$ moment ($0.77\mu_B$).

The lack of a unique microscopic model that describes the electronic properties of metallic actinide materials has led to a variety of phenomenological arguments, usually focusing on one special property of these complex materials. The most obvious analogy is with the lanthanide $4f$ series. However, because both the spin-orbit and crystal-field parameters are large in the actinide series,[1] the mathematical complexities reduce the usefulness of drawing simple parallels. Trivalent free-ion behavior is found in many $4f$ metallic systems; but, as yet, the electronic structure of a metallic actinide compound has not been unambiguously established. In the present paper, we present measurements of the neutron elastic magnetic cross section for PuP. The theoretical cross section is calculated with the tensor-operator formalism,[2] which incorporates the complications of spin-orbit, crystal-field, and exchange interactions in the $5f$-electron system. The agreement between theory and experiment allows us to draw definite conclusions about the ground-state configuration of the Pu ion.

The aim of the present experiment was to measure the elastic magnetic cross section $(d\sigma/d\Omega)_M$ of the plutonium ion. Since $(d\sigma/d\Omega)_M \propto [\mu f(\vec{\kappa})]^2$, where μ is the ordered magnetic moment and $f(\vec{\kappa})$ is the magnetic form factor, these measurements allow us to probe the radial and angular parts of the unpaired $5f$ electron distribution, and hence examine the electronic structure. The magnetic form factor $f(\vec{\kappa})$, where $\kappa = 4\pi \sin\theta/\lambda$ (θ is the Bragg scattering angle and λ is the incident neutron wavelength), is related to the Fourier transform of the magnetization density. For this experiment we have chosen the simple ferromagnet[3] PuP(T_C = 125 K) which has the NaCl crystal structure (a_0 = 5.651 Å). Since ^{239}Pu has a high fission cross section, the ^{242}Pu isotope was used. The experiments were performed with a polarized-neutron diffractometer at the CP-5 Research Reactor. The stoichiometry of the sample was confirmed by measuring the integrated intensities from an unpolarized-neutron powder scan. The polycrystalline sample (1.53 g) was in a 60-kOe magnetic field at 4.2 K. The easy axis of magnetization in PuP is [001] and the application of a high field causes preferred orientation and the rotation of some particles in the sample.[4] Reflections of the form $(hk0)$ were greatly enhanced in the diffraction pattern, whereas other reflections decreased in intensity. To determine the magnetic cross section, the intensity of neutrons diffracted from a Bragg plane was measured for the two neutron spin states. The cross section was independent of the applied field. By knowing the nuclear cross section ($b_{^{242}\mathrm{Pu}} = 0.81\times10^{-12}$ cm, $b_{\mathrm{P}} = 0.51\times10^{-12}$ cm) these measurements can determine the magnetic cross section directly. The experimental results for $\mu f(\vec{\kappa})$ are shown in Fig. 1. Small corrections, which amount to less than 2%, were made for imperfect polarization, incomplete spin reversal, and depolarization of the neutron beam through the polycrystalline sample.

The Fourier transform of the magnetic form factor gives the spatial distribution of the unpaired $5f$ electrons. For f^5 configurations, the Russell-Saunders Hund's rule state is $^6H_{5/2}$ ($L = 5$, $S = \frac{5}{2}$, and $J = L - S = \frac{5}{2}$). Therefore, the spin density is antiparallel to the orbital current density. Because the latter is more contracted in real space than the spin density, the subtraction leads to regions of *negative* density with respect to the total magnetization. The resultant Fourier transform has a maximum at $\kappa > 0$, so that the magnetic cross section should first increase as κ increases, then decrease for larger κ. Such an effect has been observed in samarium metal,[5] although the complicated magnetic structure of this element makes comparison with theory difficult.[6]

A number of important statements concerning the electronic structure of PuP can be drawn from Fig. 1 without additional analysis. First, the magnetization value[7] of $0.42\mu_B$ is much lower than the localized $5f$ moment [$(0.7-0.8)\,\mu_B$] seen by neutron diffraction. Such a discrepancy between the mag-

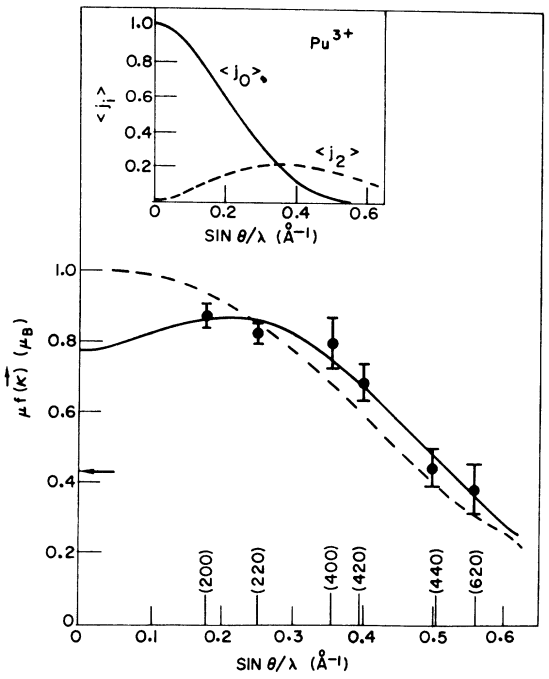

FIG. 1. Experimental points for the magnetic cross section from ferromagnetic ^{242}PuP at 4.2 K. The solid and dashed curves are the best fits to the data with $5f^5$ and $5f^4$ configurations, respectively. The arrow on the ordinate axis gives the total magnetic moment as determined by magnetization experiments. The insert shows the relativistic Dirac-Fock values for $\langle j_0 \rangle$ and $\langle j_2 \rangle$, see Ref. 11.

netization and neutron moments has been observed in a number of actinide ferromagnets.[4] The difference $\Delta\mu = \mu_{\text{total}} - \mu_{5f}$ varies between $-0.15\mu_B$ in US and $-0.3\mu_B$ in $NpAl_2$.[8,9] We believe the quantity $\Delta\mu$ is a measure of the conduction-electron polarization in these compounds. According to theoretical models,[10] this quantity should be parallel to $\vec{S}$ and proportional to $|\vec{S}|$. Both expectations are approximately fulfilled in the U, Np, and Pu series. Second, the shape of the form factor allows us to uniquely assign a $5f^5$ configuration and, hence, a Pu^{3+} ionization state. The dashed curve in Fig. 1 is the best fit with a $5f^4$ form factor and does not reproduce the experimental data, irrespective of the magnetic moment chosen.

The magnetic scattering length of the $(hk0)$ reflections, all of which have an angle of $\frac{1}{2}\pi$ between $\vec{\kappa}$ and $\vec{\mu}$, reduces to a scalar quantity that may be expressed[2] as

$$\mu f(\vec{\kappa}) = \mu(\langle j_0 \rangle + c_2\langle j_2 \rangle + c_4\langle j_4 \rangle + c_6\langle j_6 \rangle). \quad (1)$$

The magnetic moment μ and the coefficients c_i in Eq. (1) are defined by the ground-state wave function of the Pu^{3+} ion. The radial integrals $\langle j_i \rangle$, which are related to the spatial extent of the $5f$ electrons and are functions of κ only, can be determined from fully relativistic Dirac-Fock calculations.[11] The functions $\langle j_0 \rangle$ and $\langle j_2 \rangle$ are shown in the insert of Fig. 1. Since $\langle j_4 \rangle$ and $\langle j_6 \rangle$ are smaller than $\langle j_2 \rangle$ over the angular region of interest and their coefficients c_4 and c_6 are also small, the right-hand side of Eq. (1) essentially reduces to the first two terms. One can see from the insert of Fig. 1 that, if $f(\vec{\kappa})$ is to be greater than unity at finite values of κ, the contribution of $\langle j_2 \rangle$, i.e., the coefficient c_2, must be large. This is indeed the case; for the $^6H_{5/2}$ state the dipole approximation gives $c_2 = 6.0$. Other f configurations have c_2 values[11] ranging between 1.5 and 2.3. The results of the neutron experiment on PuP may be conveniently represented by plotting μ vs c_2, as in Fig. 2. The experiment defines an ellipse because of the correlation between the parameters.

To examine the significance of the neutron results, we start by calculating the values of μ and c_2 based on the wave functions of the $^6H_{5/2}$ free-ion state and the corresponding crystal-field states Γ_8 (a quartet) and Γ_7 (a doublet). The free-ion $^6H_{5/2}$ result is given by the solid square, and the solid circles represent results for the $^6H_{5/2}$ crystal-field states. The numerical results are given in Table I. In all cases, the values of c_2 are larger than found experimentally. However, this model ignores the strong spin-orbit coupling. From spectroscopic studies,[12] the spin-orbit parameter $\xi = 2260$ cm^{-1}, and because of the admixture of higher S and L states, the values of c_2 are reduced (open circles in Fig. 2).

Next, we have considered the admixture of the $J = \frac{7}{2}$ state (and higher J multiplets) into the wave

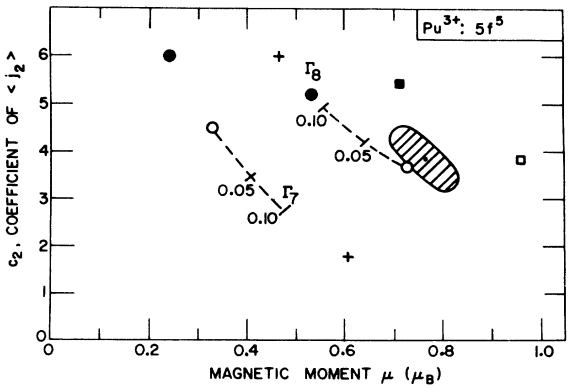

FIG. 2. Variation of the magnetic moment vs c_2 for theoretical models for Pu^{3+}. The shaded ellipse is the area defined by fitting the experimental points in Fig. 1 with Eq. (1). The symbols correspond to models discussed in the text.

TABLE I. Summary of calculations for PuP. The quantities μ and c_2 are defined in Eq. (1). $\langle L\rangle$ and $\langle S\rangle$ are the expectation values of the orbital and spin angular momenta, respectively. Apart from the first three entries, all calculations are done using intermediate coupling wave functions. The last three entries use a truncated basis set of ten free-ion J manifolds and include the effects of crystal-field and exchange interactions (ex).

Wave function		$\langle\mu\rangle$ μ_B	$\langle L\rangle$	$\langle S\rangle$	c_2
$^6H_{5/2}$	Free ion	0.714	4.28	−1.79	5.42
	Γ_8	0.525	3.15	−0.44	5.21
	Γ_7	0.239	1.42	−0.59	6.00
$J=\frac{5}{2}$	Free ion	0.962	4.04	−1.53	3.80
	Γ_8	0.724	2.94	−1.11	3.62
	Γ_7	0.329	1.34	−0.50	4.48
$J=\frac{7}{2}$	Γ_8	−0.429	−0.57	+0.07	1.21
	Γ_7	−1.288	−1.71	+0.21	1.26
$A_4\langle r^4\rangle=+200$ cm^{-1}+ex		1.037	3.95	−1.46	3.47
$A_4\langle r^4\rangle=-400$ cm^{-1}+ex		0.883	4.08	−1.60	4.17
$A_4\langle r^4\rangle=-480$ cm^{-1}+ex		0.733	2.20	−0.73	3.13
Experimental PuP		0.77±0.07	···	···	3.8±0.7

function. Such effects arise from the large crystal-field interaction found in ionic actinide systems[13] and are assumed to be present in metallic compounds.[1] Our calculations show that even a small admixture of the $J=\frac{7}{2}$ state drastically affects both μ and c_2. The positions marked 0.05 correspond to the results for the wave function

$$\psi(\Gamma_i)=0.9987\left|J=\tfrac{5}{2},\Gamma_i\right\rangle-0.0500\left|J=\tfrac{7}{2},\Gamma_i\right\rangle, \quad (2)$$

and the positions marked 0.10 correspond to the coefficient of the $J=\frac{7}{2}$ state. The comparison with experiment indicates that the ground state is almost completely (>99%)$J=\frac{5}{2}$. As a consequence, we find an upper limit of $|A_4\langle r^4\rangle|<500$ cm^{-1} is put on the crystal-field strength, otherwise the admixture of the $J=\frac{7}{2}$ state leads to significant discrepancies between the calculated and experimental values of c_2 and μ. The crosses in Fig. 2 correspond to results[13] for the Pu^{3+} wave function in CaF_2, in which $A_4\langle r^4\rangle=-1080$ cm^{-1}. An earlier model[14] for PuP derived from high-temperature susceptibility results also overestimates $A_4\langle r^4\rangle$.

In fitting the experiment and theory quantitatively, we use the experimental values of μ and c_2 and the truncated basis set scheme[1] to determine the sign and the approximate magnitude of the two cubic-field parameters relevant to the symmetry of the Pu ion in PuP. The values for the two crystal-field parameters are $A_4\langle r^4\rangle\approx-450$ cm^{-1} and $|A_6\langle r^6\rangle|\leq30$ cm^{-1}. With this crystal-field strength and in the absence of an exchange field, the Γ_7 and Γ_8 levels are quite closely spaced (~15 cm^{-1}) with Γ_7 lower in energy. The exchange field will mix these levels because of the large magnetic interaction, as indicated by the high ferromagnetic transition temperature ($T_C=125$ K). We use the Weiss molecular-field approximation to obtain the magnetization value and the magnetic ground-state eigenvectors, $|\psi_m\rangle$. The values for the magnetic moment μ and c_i are then calculated from the $|\psi_m\rangle$ at the measuring temperature of 4.2 K. The resultant μ and c_2 fall into the cross-hatched area in Fig. 2 (see Table I).

In conclusion, the present experiment and analysis have led to an identification of the ground-state configuration of PuP in terms of first-principle parameters, but a number of important questions remain unanswered. The neutron cross section indicates the need (as expected) to consider the strong spin-orbit coupling but (surprisingly) shows that the crystal-field strength is about half that found in ionic compounds.[13] In addition, the sign of the crystal-field interaction is *opposite* to that found in similar lanthanide systems, e.g., for SmP ($a_0=5.78$ Å) Birgeneau *et al.*[15] give $A_4\langle r^4\rangle=72$ cm^{-1}. Of equal interest is the large discrepancy between the total moment (as measured by magnetization experiments) and the localized $5f$ moment (as determined by neutron experiments). To further investigate this discrepancy, which is also found in U and Np compounds,[8,9] we intend to measure the diffuse cross section from PuP for $\sin\theta/\lambda<0.2$ Å^{-1}. Our measurements also suggest that neutron experiments on a number of samarium compounds would rigorously test

the crystal-field models proposed for these systems.[16]

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[1]*The Actinides: Electronic Structure and Related Properties*, edited by A. J. Freeman and J. B. Darby, Jr. (Academic, New York, 1974), see especially S. K. Chan and D. J. Lam, Vol. I., Chap. 1.

[2]W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Oxford U.P., London, 1971), Chap. 6, p. 127; G. H. Lander, J. Faber, Jr., A. J. Freeman, and J. P. Desclaux, Phys. Rev. B 13, 1177 (1976).

[3]D. J. Lam, F. Y. Fradin, and O. L. Kruger, Phys. Rev. 187, 606 (1969).

[4]A. T. Aldred, B. D. Dunlap, D. J. Lam, G. H. Lander, M. H. Mueller, and I. Nowik, Phys. Rev. B 11, 530 (1975).

[5]W. C. Koehler and R. M. Moon, Phys. Rev. Lett. 29, 1468 (1972).

[6]H. W. de Wijn, A. M. van Diepen and K. H. J. Buschow, Solid State Commun. 15, 583 (1974).

[7]We are grateful to A. T. Aldred for measuring the magnetization of our ^{242}PuP sample. The results are the same as given in Ref. 3.

[8]F. A. Wedgwood, J. Phys. C 5, 2427 (1972).

[9]A. T. Aldred, B. D. Dunlap, and G. H. Lander, Phys. Rev. B 14, 1276 (1976).

[10]A. J. Freeman, J. O. Dimmock, and R. E. Watson, in *Quantum Theory of Atoms, Molecules, and the Solid State*, edited by P. Lowdin (Academic, New York, 1966), p. 361; D. M. Eagles, Z. Phys. B 21, 69 (1975); 21, 79 (1975).

[11]A. J. Freeman, J. P. Desclaux, G. H. Lander, and J. Faber, Jr., Phys. Rev. B 13, 1168 (1976). We are grateful to A. J. Freeman for supplying us with the $\langle j_i \rangle$ integrals for Pu ions.

[12]J. G. Conway and K. Rajnak, J. Chem. Phys. 44, 348 (1966); N. Edelstein, H. F. Mollet, W. C. Easley, and R. J. Mehlhorn, J. Chem. Phys. 51, 3281 (1969).

[13]D. J. Lam and S. K. Chan, Phys. Rev. B 9, 808 (1974).

[14]D. J. Lam and F. Y. Fradin, Phys. Rev. B 9, 238 (1974).

[15]R. J. Birgeneau, E. Bucher, J. P. Maita, L. Passell, and K. C. Turberfield, Phys. Rev. B 8, 5345 (1973).

[16]H. W. de Wijn, A. M. van Diepen, and K. H. J. Buschow, Phys. Rev. B 7, 524 (1973); 8, 5134 (1973), and references therein.