# Magnetization Density of 5*f* Electrons in Ferromagnetic PuSb

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The magnetization density of 5*f* electrons in PuSb has been measured by use of a single crystal and polarized neutrons. The spatial extent of the spin and orbital densities is such that the form factor has a maximum at $\sin\theta/\lambda \simeq 0.2$ Å$^{-1}$. The ground-state wave function is deduced. Evidence for anisotropic interactions is presented.

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Experiments measuring the solid-state properties of actinide compounds continually provide examples of unusual behavior. Examples of such behavior are the anisotropy observed in the magnetic correlations near the ordering temperature,[1] the strong damping of the spin excitations in the ordered state,[2] and, more recently, the discovery of superconductivity in systems exhibiting strong magnetic correlations.[3] A central question is whether this behavior is shown only by uranium compounds, since U is the first element of the actinide series, or whether the extended 5*f* electron wave functions make compounds of all the light actinides unusual. In the 4*f* series, for example, the properties of Ce are atypical whereas compounds of the following elements (Pr, Nd, etc.) exhibit properties that are well explained by localized 4*f* electrons and crystal-field theory. Detailed experiments on transuranium systems are, of course, complicated by the problems of radioactivity, toxicity, and material availability, so that the bulk of actinide research is performed on uranium compounds. To provide such information we have initiated a program[4] to grow large single crystals of transuranium compounds and perform the needed experiments. We report here on polarized-neutron experiments which determine the spatial extent of the 5*f* electrons in PuSb. The results show the necessity to consider the orbital moment and the highly anisotropic nature of the ground-state wave function.

Plutonium antimonide (face-centered-cubic NaCl structure with $a_0 = 6.225$ Å) orders antiferromagnetically at 85 K with an incommensurate structure[5] and then becomes ferromagnetic at 67 K with the magnetic moments always parallel to a cube axis. The bulk magnetization studies give $\bar{\mu} = (0.67 \pm 0.01)\mu_B$ and show a very large anisotropy.[6] Our measurements have been performed in an applied field of 46 kOe in which the material is ferromagnetic at all temperatures below 85 K. The single crystal ($\sim 2\times 2\times 1$ mm$^3$, weight 55 mg) was grown, oriented, and encapsulated at the Transuranium Institute, Karlsruhe, and placed in the cryomagnet on the D3 polarized-beam diffractometer at the Institut

Laue-Langevin, Grenoble. The experiment consists of measuring the ratio of intensities diffracted from the various Bragg planes as a function of neutrons polarized parallel and antiparallel to the magnetic moment, which we take as [001]. The measurements have been taken at four different neutron wavelengths to check for experimental difficulties connected with extinction (found to be negligible) and multiple scattering. We have used the $^{239}$Pu isotope with its large fission resonance at 0.29 eV, so that the scattering length *changes* as a function of neutron wavelength.[7] With respect to the scattering length of Sb ($b_{Sb}=0.564\times10^{-12}$ cm), we find $b(^{239}\text{Pu})=0.850(4)\times10^{-12}$ cm at 0.924 Å and $0.863(4)\times10^{-12}$ cm at 1.102 Å. The change as a function of neutron energy is in good accord with resonance theory, although no precise measurements of the absolute value exist for comparison. The absorption of $\sim 500$ b necessitates the use of a small crystal and, at the same time, reduces extinction. The crystal itself acts as a filter to reduce $\lambda/2$ contamination, since the resonance is at 0.53 Å.

The quantity $\mu f(\vec{Q})$ shown in Fig. 1 represents the Fourier component of the total (i.e., spin and orbital) magnetization density as a function of the scattering vector $\vec{Q}$ ($|\vec{Q}|=4\pi\sin\theta/\lambda$), where $\mu$ is the magnetic moment due to $5f$ electrons and $f(\vec{Q})$ is the form factor such that $f(0)=1$. The results may be analyzed by the relationship

$$\mu f(\vec{Q})=\mu[\langle j_0\rangle+(C_2+\Delta C_2\sin^2\Theta)\langle j_2\rangle + C_4\langle j_4\rangle], \quad (1)$$

where

$$\langle j_l\rangle=\int_0^\infty U_{5f}^2(r)\,j_l(Qr)\,dr.$$

The $\langle j_l\rangle$ functions are transforms of the single-ion radial probability functions $U_{5f}^2(r)$ with Bessel functions of order $l$, and depend on $|\vec{Q}|$ only. We have taken these from relativistic Dirac-Fock wave functions[8] and plot both $\mu\langle j_0\rangle$ and $\mu C_2\langle j_2\rangle$ in Fig. 1. Terms in $C_4\langle j_4\rangle$ are small and we have neglected the even smaller terms in $C_6\langle j_6\rangle$. The term $\Delta C_2\sin^2\Theta$ represents the fact that the magnetization density may have a quadrupole moment, i.e., an anisotropy depending on the angle between the direction of interest and the moment direction $\vec{\mu}\parallel[001]$. Thus for all reflections within the scattering plane perpendicular to the moment of the form $(hk0)$, $\Theta=0$, whereas for (202), for example, $\Theta=45°$. This azimuthal angle $\Theta$ should not be confused with the Bragg angle $\theta$. A least-squares fit with Eq. (1) gives

$$\mu=(0.745\pm0.020)\mu_B,\quad C_2=3.80\pm0.07,$$
$$\Delta C_2=1.30\pm0.15,\quad C_4=-0.21\pm0.07,$$

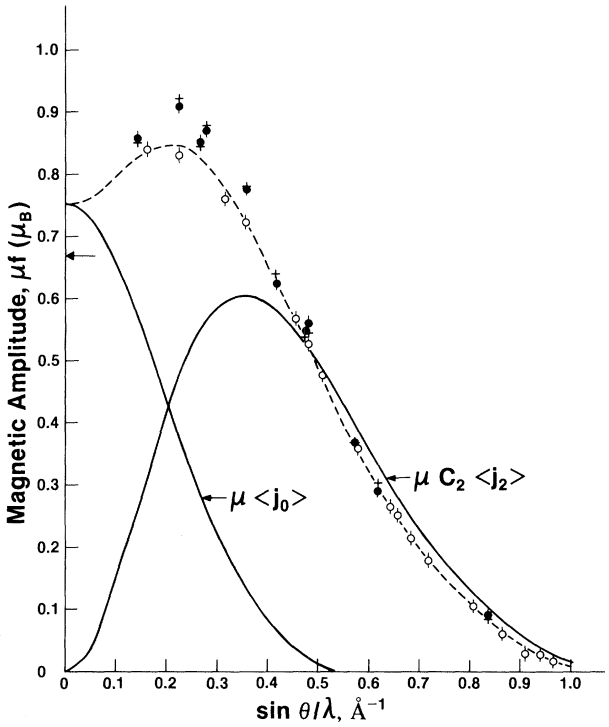


FIG. 1. The magnetic amplitude as a function of $\sin\theta/\lambda$ ($=Q/4\pi$) for ferromagnetic PuSb at 10 K. The moment direction is [001]. Open points correspond to reflections $(hk0)$, i.e., in the scattering plane, and the broken curve represents the best fit for these reflections. Solid lines show the two major components of Eq. (1). Reflections out of the scattering plane are represented by solid points, and the calculated values for them by crosses. The bulk magnetization value (Ref. 6) is indicated by an arrow on the ordinate axis.

with $\chi^2=1.03$ and the agreement shown in Fig. 1.

Most form factors fall monotonically with increasing $Q$, so that the shape of the form factor in Fig. 1 is of particular interest. Since the coefficient of $\langle j_2\rangle$ is so large, and the function itself is 0 at $Q=0$, it results in an $f(Q)$ with a *maximum* at $\sin\theta/\lambda\simeq0.2$ Å$^{-1}$. If the orbital moment were absent, $C_2\simeq0$, so that this maximum is an unambiguous signature of the *trivalent* ground state and of the very large orbital moment associated with that state.[9] Such form factors are also found for $Sm^{3+}$ ions.[10] In the latter case a localized picture is appropriate, but—at least for uranium compounds—such an interpretation cannot explain many of the unusual properties.[1-3] However, all theories, whatever their origin, must address the large orbital moment, and recent theoretical work by Brooks and Kelly[11] emphasizes this. Our experiment also finds a significant difference between the moment from the correlated $5f$ electrons

$[(0.745 \pm 0.020)\mu_B]$, which is the intercept of the broken curve at $Q = 0$, and that for the total magnetization,[6] $(0.67 \pm 0.01)\mu_B$, which is marked by the arrow in Fig. 1. This discrepancy, also found in uranium ferromagnets,[12] has been ascribed to the negative polarization of $6d$ electrons, which contribute to the bulk magnetization only.

In the absence of a complete theory for the light actinide compounds we address the experimental results in terms of a localized $5f^5$ state. Figure 2 shows $C_2$ plotted as a function of $\Theta$, or $q^2$ (the magnetic interaction vector). The Russell-Saunders ${}^6H_{5/2}$ crystal-field states $\Gamma_8$ (quartet) and $\Gamma_7$ (doublet) clearly have both $C_2$ and $\mu$ very different from the experimental result (see Fig. 2). Spectroscopic measurements on dilute actinide systems show the importance of the large spin-orbit interaction leading to intermediate coupling (IC) within the $J = \frac{5}{2}$ manifold, and, indeed we find that the $\Gamma_8$ IC wave

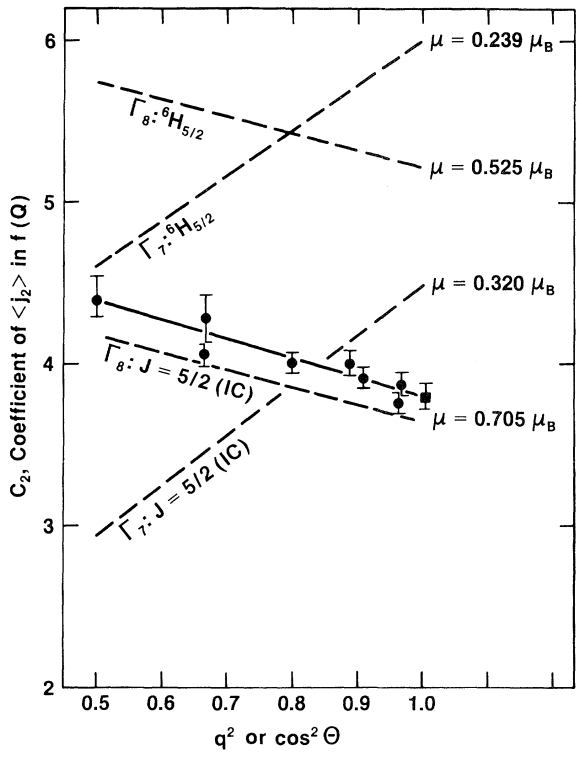


FIG. 2. Values of $C_2$, and $\Delta C_2$ (represented by the slope of $C_2$ vs $\cos^2\Theta$), as defined in Eq. (1) for experiment, solid points and solid line, and for various crystal-field ground states. The magnetic moments of these states are also given on the extreme right. $\Theta$ is the azimuthal angle between the moment and scattering plane and $q^2$ is the usual square of the magnetic interaction vector. IC denotes intermediate-coupling wave functions, whereas ${}^6H_{5/2}$ denotes the Russell-Saunders ground state.

function with $\mu = 0.705\mu_B$ and $C_2 = 3.62$ is a good representation of the data. The refinement is not very sensitive to $C_4$. For the $\Gamma_8$ ground-state wave function $C_4$ varies between $-0.42$ and $-0.18$ for $\Theta = 0°$ so that the value is consistent with this wave function. The magnetization density of such a state is highly flattened (oblate) in the plane perpendicular to the moment [i.e., a positive $\Delta C_2$ in Eq. (1)], and it is this feature that our data so clearly confirm. However, our expectation based on an analogy with the lanthanide NaCl compounds[13] is that the $\Gamma_7$ doublet would be the ground state. The $\Gamma_7$ state has a prolate density (i.e., a negative $\Delta C_2$) and is totally inconsistent with the data (see Figs. 2 and 3). The anisotropic nature of the ground state almost certainly plays a key role in defining the properties of this and similar systems, and our results provide both a motivation and a test for theories to explain such anisotropic behavior.[14]

We have also measured $C_2$ and $\Delta C_2$ as a function of temperature. $C_2$ is independent of temperature in agreement with our expectation (from optical studies of actinide systems) that the next $J$ multiplet ($J = \frac{7}{2}$) is separated by at least 2000 K from the $J = \frac{5}{2}$ ground state. The coefficient $\Delta C_2$ as shown in Fig. 3 is difficult to measure at high temperature because such measurement is done via the dipole moment $\mu$, which decreases as shown in the lower half of Fig. 3. Despite the large error bars, $\Delta C_2$ seems to increase slightly with increasing temperature before disappearing in the paramagnetic state. This behavior is quite different from that of the isotropic $J = \frac{5}{2}$ (free-ion) ground state and perhaps even inconsistent with that expected from the anisotropic $\Gamma_8$ state.

In summary, our measurements have for the first time characterized the ground-state wave function of the $5f$ electrons in a metallic transuranium system. Although the state may be described with a localized model assuming a $5f^5$ $Pu^{3+}$ ion, it bears no relation to that found for the well-localized $4f^5$ analog $Sm^{3+}$. The implication is that a further anisotropic interaction, possibly of the Coqblin-Schrieffer type,[6] overwhelms the natural crystal-field preference for a $\Gamma_7$ ground state, and produces a wave function with an oblate magnetization density remanent of the $\Gamma_8$ state. The appearance of this interaction leads to the suggestion that many Pu compounds will probably show unusual behavior similar to that found for uranium systems. This contradicts the generally held view that we should see gradual "localization" as one moves further across the actinide series. Of course, the microscopic properties of Am and Cm metallic systems

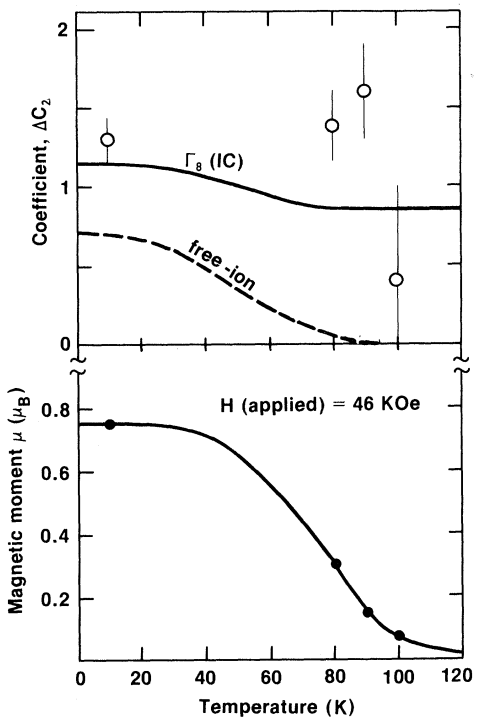


FIG. 3. Temperature dependence of $\Delta C_2$ (top section) and $\mu$ (lower section) as defined in Eq. (1). Also shown are the calculations of $\Delta C_2$ for a free-ion and the $\Gamma_8$ ground state. The solid curve in the lower section represents the temperature dependence of the dipole moment as measured in a magnetization experiment with a similar applied magnetic field.

remain uncharted territory, but our results emphasize that as a start a consistent theoretical approach needs to be found for all light (U,Np,Pu) actinide compounds.

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