PHYSICAL REVIEW B VOLUME 19, NUMBER 1 1 JANUARY 1979

Magnetic properties of neptunium and plutonium hydrides

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(Received 7 August 1978)

The magnetic susceptibility and magnetization of NpH_x and PuH_x ($2.0 \leq x \leq 3.0$) compounds have been measured between 4 and 700 K. The susceptibility of the NpH_x compounds is weakly temperature dependent and a crystal-field calculation based on the $5f^4(Np^{3+})$ ground-state configuration was in reasonable agreement with the experimental results for the dihydride (cubic CaF_2-type structure). The cubic plutonium dihydride has a susceptibility maximum, indicative of antiferromagnetic ordering, at 30 K. Cubic plutonium compounds with higher hydrogen concentrations order ferromagnetically with transition temperatures that increase with an increase in x and reach a maximum of 66 K at $x = 2.7$. The hexagonal plutonium trihydride becomes ferromagnetic at 101 K. Although the details of the ordering scheme and a complete crystal-field calculation await a neutron-scattering study, it appears that the most likely ground-state configuration is $5f^5(Pu^{3+})$.

I. INTRODUCTION

A considerable body of literature exists on the magnetic[1] and electronic[2] properties of rare-earth hydrides. The dihydrides, which are cubic with the CaF_2-type structure, are metallic and order magnetically below 40 K. The CaF_2-type structure can take up additional hydrogen, which has the effect of decreasing both the transition temperature and the "metallic" behavior of the compound. The hexagonal rare-earth trihydrides are semiconducting and do not order magnetically above 4 K. This relationship between the magnetic and electrical properties suggests[1] that the main magnetic coupling interaction involves indirect exchange via the conduction electrons, i.e., the Ruderman-Kittel-Kasuya-Yosida mechanism.

Both neptunium and plutonium form analogous cubic dihydrides and hexagonal trihydrides.[3] In view of the more extended nature of the $5f$-electron wave functions of the actinide ions, as compared with the $4f$-electron wave functions of the rare-earth ions, it is of interest to compare the magnetic properties of the actinide and rare-earth hydrides. Very few magnetic studies of either neptunium or plutonium hydrides have been made. The Mössbauer spectra (^{237}Np) of cubic neptunium hydrides[4] with H to Np ratio > 2 show that the neptunium atoms are sensitive to their local environment, i.e., the number of near-neighbor hydrogen atoms in the octahedral sites of the CaF_2-type structure. There is no evidence of long-range magnetic ordering. A brief report[5] showed that $PuH_{2.74}$ was ferromagnetic, with a Curie temperature (T_C) of 107 K. At 76 K, the magnetic moment was $0.24\mu_B$/mole at ~1 kOe. In a proton NMR study of the cubic plutonium hydride system,[6] it was concluded that the Pu ions possess localized $5f$ electrons for all hydrogen concentrations, and that the Ruderman-Kittel-Kasuya-Yosida coupling mechanism is dominant. From a comparison between the Knight-shift and spin-lattice relaxation-time results, antiferromagnetic ordering was predicted for the stoichiometric dihydride. A more detailed analysis was precluded by the lack of magnetic-susceptibility data. In light of the above, magnetization measurements have been performed on neptunium and plutonium hydrides in both the cubic and hexagonal phases over the temperature range 4–700 K.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The phase diagrams of the neptunium-hydrogen[7] and plutonium-hydrogen[8] systems show that in both cases the cubic dihydride exists over a range of stoichiometries, i.e., $1.9 \leqslant x \leqslant 2.7$, where x is the ratio of H to Np or H to Pu. Samples of neptunium hydride ($x = 2.04$ and 2.67) and plutonium hydride ($x = 1.99$, 2.33, 2.66, and 2.75) were prepared by reacting neptunium or plutonium metal with a known amount of hydrogen at ~200 °C. The resultant powders were encapsulated in aluminum tubes without exposure to the glove-box atmosphere, and reannealed to improve homogenization. The estimated uncertainty in the compositions is ~1%. Because of the difficulty in attaining thermodynamic equilibrium in the formation of neptunium and plutonium trihydrides,[7,8] these samples were prepared by saturating the metal with hydrogen, so that $x \simeq 3$. An x-ray determination of the phase structure is difficult because the hydride powders react very rapidly with oxygen to form NpO_2 or PuO_2, which also have the CaF_2-type structure; additionally, PuO_2 has a lattice parameter almost identical to that of PuH_2.

The magnetization of each sample was measured in applied fields up to $H_a = 14.5$ kOe over the range 4–700 K by the Faraday method. The upper temperature limit was determined by the phase diagram.[7,8] The experimental procedure has been described previously[9]; the data above room temperature were obtained in an equivalent apparatus in which a furnace replaced the cryostat.

The field dependence of the magnetization for the neptunium hydride samples was of the form

$$\sigma = \sigma_0 + \chi H . \qquad (1)$$

H is the internal field, i.e., the applied field corrected for the demagnetizing field of the sample. A small remanent magnetization σ_0 was present in all samples even up to 700 K. The origin of this term, which is common in neptunium compounds,[9] is unclear. The molar susceptibility of the neptunium hydrides is plotted as a function of temperature in Fig. 1. In each case there is a weak temperature dependence. The susceptibility of the nominal dihydride has been calculated by a crystal-field model (discussed in Sec. III) and is shown as the solid line. The data for the $NpH_{2.67}$ sample shows that additional hydrogen in the CaF_2-type structure increases the molar susceptibility, while leaving the temperature dependence essentially unaffected. Because the site symmetry around each Np atom in the hyperstoichiometric dihydride is unknown, an analogous crystal-field calculation cannot be made.

The reciprocal molar susceptibilities of the plutonium hydrides are shown as a function of temperature in Fig. 2. The susceptibility maximum at 30 K in the stoichiometric dihydride ($x = 1.99$) is indicative of antiferromagnetic ordering, as suggested by the NMR results.[6] The samples with higher hydrogen concentrations, including the nominal trihydride, all order ferromagnetically as indicated by Fig. 2. The Curie temperatures were determined by plotting the data in the form σ^2 vs H/σ as illustrated in Fig. 3, which yields $T_C = 101$ K for PuH_3. In the ferromagnetic regime, the magnetization of the compounds cooled in zero field showed a large field dependence, indicative of a large magnetocrystalline anisotropy. Field cooling of these powdered samples through the Curie temperature, as shown in Fig. 4, substantially increased the magnetization and decreased the field dependence. The remaining field dependence was fitted, by least-squares analysis, to

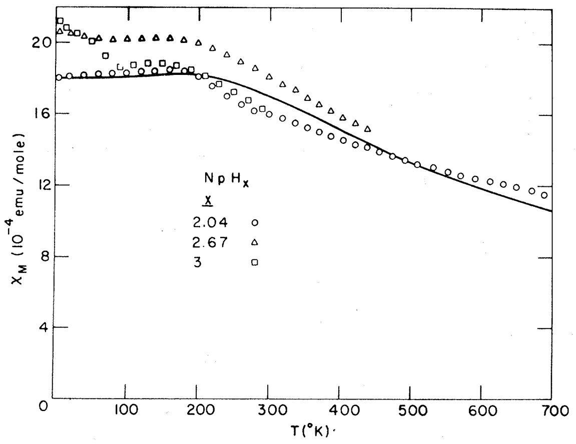

FIG. 1. Molar susceptibility vs temperature for neptunium hydrides. The solid line represents the results of a crystal-field calculation (see text).

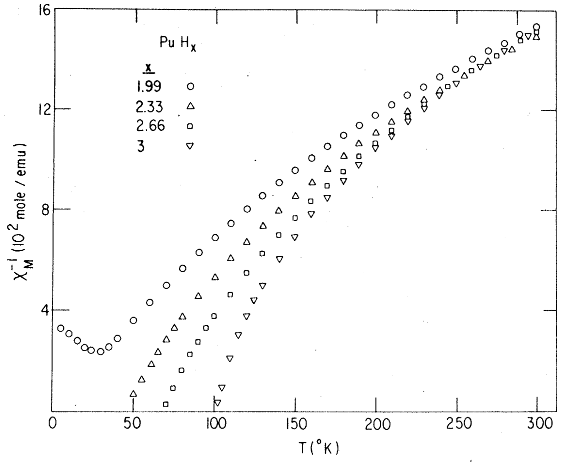

FIG. 2. Reciprocal molar susceptibility vs temperature for plutonium hydrides.

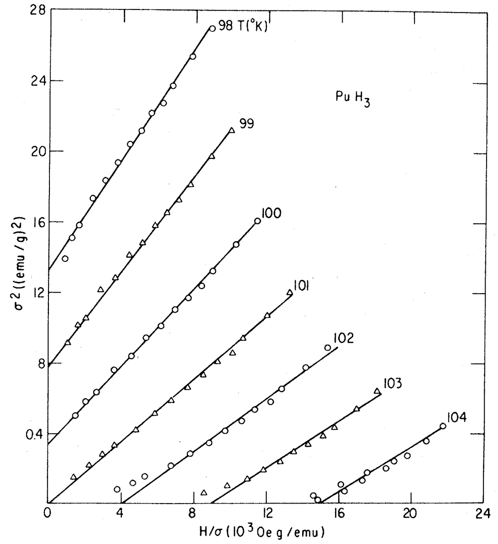

FIG. 3. σ^2 vs H/σ plots for PuH_3 at temperatures in the vicinity of the Curie temperature ($T_C \simeq 101$ K).

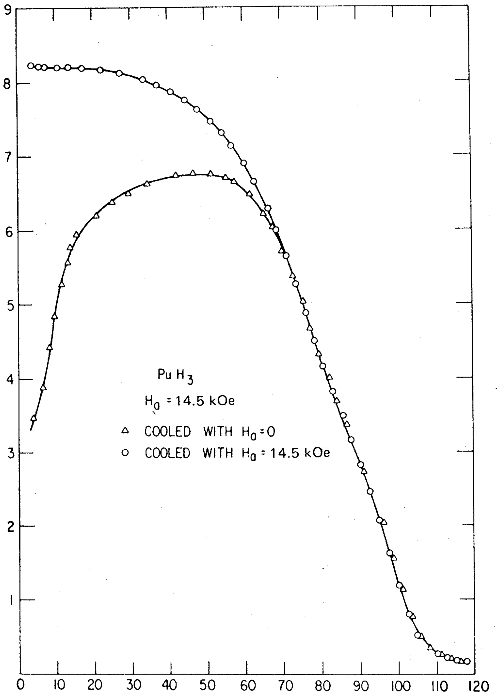

FIG. 4. Magnetization at the maximum applied field (14.5 kOe) vs temperature for PuH_3 cooled in both zero field and the maximum applied field.

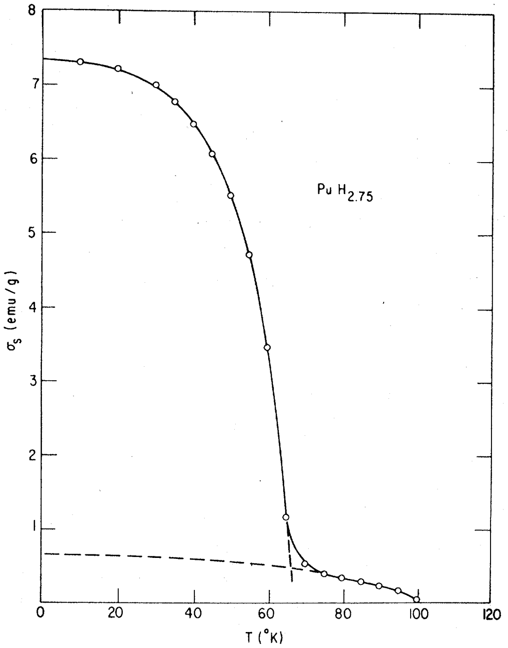

FIG. 5. Spontaneous magnetization σ_s, obtained by fitting to Eq. (2), vs temperature for $PuH_{2.75}$. Note the presence of two ferromagnetic transitions at ~ 65 and ~ 100 K.

$$\sigma = \sigma_s(1 - a/H) + \chi H \qquad (2)$$

over the field range 2.0–14.5 kOe for each isotherm. A plot of $\sigma_s(T)$ vs $T^{3/2}$ was used to yield an extrapolated value of $\sigma_s(0)$ from which the saturation moment $\bar{\mu}_0$ (μ_B/atom) was determined. A summary of these results is given in Table I.

As noted earlier, there was cause for concern about the composition and crystal structure of "PuH_3." To elucidate this point, one additional sample with H to Pu ratio of 2.75 was made up; according to the phase diagram,[8] this sample should contain both the cubic and hexagonal phases. An analysis of the magnetic isotherms obtained from this sample showed that it indeed had two magnetic transitions (Fig. 5), at ~100 K (hexagonal phase, "PuH_3") and ~65 K (cubic phase, H to Pu ratio ≃ 2.7). The saturation magnetizations of the two phases (Fig. 5) indicate a mass ratio of approximately 90% cubic phase to 10% hexagonal phase, which is again consistent with the phase diagram. This result strongly suggests that the PuH_3 sample is hexagonal, although the precise stoichiometry is not defined.

III. DISCUSSION

The actinide-actinide interatomic distances in these hydrides are ~5 Å in the cubic CaF_2-type structure and ~4 Å in the hexagonal structure, and the 5*f* electrons are probably well localized—a conclusion also drawn from previous NMR results.[6] It thus seems appropriate to use a crystal-field model to calculate the temperature depen-

TABLE I. Magnetic properties of PuH_x compounds.

x	T_c (K)	σ_s (0) (emu/g)	$\bar{\mu}_0$ (μ_B/atom)	a [a] (Oe)	χ [a] (10^{-5} emu/g)
2.33	46(1) [b]	10.24(3)	0.442(1)	119(25)	5.8(3)
2.66	66(1)	7.28(3)	0.315(1)	35(2)	3.6(3)
3	101(1)	8.14(1)	0.353(1)	30(2)	0.8(3)

[a] Average value for isotherms up to 0.5 T_c.

[b] Numbers in parentheses represent estimated uncertainties in last significant figure.

dence of the magnetic susceptibility. The application of crystal-field calculations to actinide ions has been considered in detail by Chan and Lam.[10] Because of the large magnitude of both the crystal field and the spin-orbit interaction, J is generally not a good quantum number for $5f$ ions. It is therefore necessary to use intermediate coupling rather than Russell-Saunders coupling in the calculation, and to take into account mixing of the various J manifolds. In applying such a calculation, the first problem is to assign an electron configuration to the actinide ion. In view of the weakly temperature-dependent susceptibility of the neptunium hydrides, the most likely nonmagnetic ground-state configuration is $5f^4(\mathrm{Np}^{3+})$. On this basis, a complete calculation can then be made, but only for the stoichiometric dihydride in which the local site symmetry around each actinide ion (i.e., eightfold cubic) is well defined. The solid line in Fig. 1 represents the results of such a calculation with the fourth- and sixth-order crystal-field parameters $V^4 = 550\ \mathrm{cm}^{-1}$ and $V^6 = -210\ \mathrm{cm}^{-1}$, respectively. The ground state is a Γ_3 doublet; the first and second excited states, Γ_4 and Γ_5 triplets, are located 512 and 549 cm^{-1} above it, respectively. The next state, a Γ_1 singlet, is 1851 cm^{-1} above Γ_5. Note that the characteristics of the experimental temperature dependence of the susceptibility (Fig. 1) provide a severe constraint on the size and magnitude of the crystal-field parameters. In the context of a point-charge model, the sign of the parameters should determine the sign of the surrounding ligand charges, and presumably, the charge of the hydrogen ion. However, the t_{2g} band of actinide $6d$ electrons is fairly narrow and probably near the Fermi energy. In the case of PuP,[11] the existence of this narrow actinide $6d$ band causes a large conduction-electron polarization and also accounts for the sign of the fourth-order crystal-field parameter, which is opposite to that derived from the point-charge model.

Although a full crystal-field calculation has not been made for neptunium trihydride, the site symmetry of the Np ion here is hexagonal, and the $5f$ electrons will be affected by an additional axial field V^2. This field will perturb the cubic crystal-field levels and modify the energy-level diagram of the $5f^4$ configuration. The fact that both the magnitude and temperature dependence of the susceptibility are almost the same for both neptunium di- and trihydride (Fig. 1) indicates that either the level scheme for the trihydride gives coincidentally the same susceptibility as the dihydride, or, more likely, the axial field in the trihydride is weak and the energy-level diagram of the Np^{3+} ion is not substantially changed from the dihydride.

An initial analysis of the temperature dependence of the molar susceptibility χ_m of the plutonium hydrides (Fig. 2) was made in terms of a modified Curie-Weiss law:

$$\chi_m = \chi_0 + \chi_f = \chi_0 + C/(T - \Theta)\ , \tag{3}$$

where χ_f is the susceptibility of the local $5f$ electrons and χ_0 represents a temperature-independent (Pauli) susceptibility. The results of this analysis are given in Table II. Note that only in the case of the $x = 1.99$ sample does Eq. (3) provide a good representation of the data. The value of μ_{eff} (~1.0) for $\mathrm{PuH}_{1.99}$ is close to that found in many plutonium intermetallic compounds containing Pu^{3+} ions.[12] There is a monotonic decrease in μ_{eff} and an increase in χ_0 and Θ as the hydrogen concentration increases.

By analogy with NpH_x and other plutonium intermetallic compounds with $\mu_{\mathrm{eff}} \simeq 1\mu_B$, the expected electron configuration for the Pu ion in plutonium hydride is $5f^5(\mathrm{Pu}^{3+})$. If the sign and magnitude of the crystal-field parameters are assumed to be the same for NpH_2 and PuH_2, the crystal-field ground state is a doublet Γ_7, with a quartet Γ_8 excited state located 70 cm^{-1} above it. Because of the small energy separation, the Γ_7 ground state and the Γ_8 excited state will be mixed by the exchange field in the ferromagnetic regime. The magnetic ground-state wave function consists of a mixture of 97% of the $J = \frac{5}{2}$ manifold and approximately 2% and 1% of the $J = \frac{7}{2}$ and $J = \frac{9}{2}$ manifolds, respectively. A Brillouin plot of reduced magnetization versus reduced temperature for the ferromagnetic hydrides (Fig. 6) shows reasonable conformance to $J = \frac{5}{2}$ behavior. The ordered moment per Pu ion given by the magnetic ground state (1.0 μ_B) is substantially higher than the values derived from the experimental saturation magnetization and given in Table I. Such behavior is typical of ferromagnetic actinide intermetallics,[13] although a detailed analysis of this point in the plutonium hydrides awaits a neutron-diffraction study. The apparently low values for the ordered moment derived from the bulk magnetization values, usually taken as evidence of a negative conduction-electron polarization,[13] are also indicated by the $\bar{\mu}_0/\mu_{\mathrm{eff}}$ ratio for the ferromagnetic compounds (≤ 0.56), which is lower than expected for a purely local $5f$ moment.[10] The persistence of magnetic order as x increases from 2 to 3 suggests that the conduction-electron concentration is not substantially decreased. This behavior is in contrast to that of the rare-earth hydrides,[1] where the metallic behavior of the dihydrides gives way to semiconducting behavior in the trihydrides.

The Knight shift K of the ligand nucleus in intermetallic actinide compounds may be given [cf. Eq.

TABLE II. Results of modified Curie-Weiss fit [Eq. (3)] to the paramagnetic susceptibilities of plutonium hydrides PuH_x.

x	T_c (K)	T_c (K)	θ (K)	C (10^{-2} emu K/mole)	μ_{eff} [a] (μ_B /mole)	χ_0 (10^{-4} emu/mole)	Temperature range (K)
1.99	···	30(1) [b]	5(1)	11.3(1)	0.96(1)	2.7(1)	40–300
2.33	46(1)	···	45(1)	8.0(1)	0.80(1)	3.9(1)	50–315
2.66	66(1)	···	68(1)	7.3(1)	0.77(1)	3.7(2)	75–310
3	101(1)	···	98(1)	5.0(2)	0.63(2)	4.4(2)	110–315

[a] Calculated from C by the expression $\mu_{eff} = 2.84\, C^{0.5}$.

[b] Numbers in parentheses represent estimated uncertainties in last significant figure.

(3)] by

$$K = K_0 + K_f \qquad (4)$$

where K_0 represents a contribution from s electrons that is approximately temperature independent, and the temperature-dependent term K_f is thought to arise from the localized $5f$ electrons. In the indirect exchange-coupling model, K_f can be expressed by the relation[10]

$$\frac{dK_f}{d\chi_f} = H_{eff} \frac{d(\langle S_z \rangle / H)}{d\chi}, \qquad (5)$$

where H_{eff} [$= J_{sf}(0) N_s(E_F) H_{hfs}$] is an effective field per Bohr magneton at the ligand nucleus, and $\langle S_z \rangle$ is the spin projection of the magnetic moment. $J_{sf}(0)$ is the exchange-coupling parameter per spin, determined by the Fourier component of the effective s-f exchange integral for momentum transfer $\vec{Q} = \vec{K} - \vec{K}' = 0$, $N_s(E_F)$ is the s-electron density of states for one-spin direction at the Fermi level, and H_{hfs} is the contact hyperfine field.

Figure 7 shows K (for protons) for $PuH_{2.65}$ (calculated from the parameters in Table II of Ref. 6), plotted against χ for $PuH_{2.66}$ with temperature as an implicit parameter. The behavior is linear over the temperature range 160–300 K. The negative intercept for $\chi = 0$ indicates the presence of a high-frequency susceptibility term. The slope of the K vs χ curve in Fig. 7 is 1.1 mole/emu; dK/dx varies between 1.0 and 1.5 for other hydrogen concentrations. The calculated value of $d(\langle S_z \rangle / H)/d\chi = -1.28$, based on the crystal-field eigenvalues and eigenvectors of the Pu^{3+} ion, when taken with the experimental $dK/d\chi$ and substituted in Eq. (5) yields $H_{eff} = -4.8$ kOe. By comparison, if J is assumed to be a good quantum number and the operator equivalent $S_z = (g_J - 1) J_z$ is employed, then

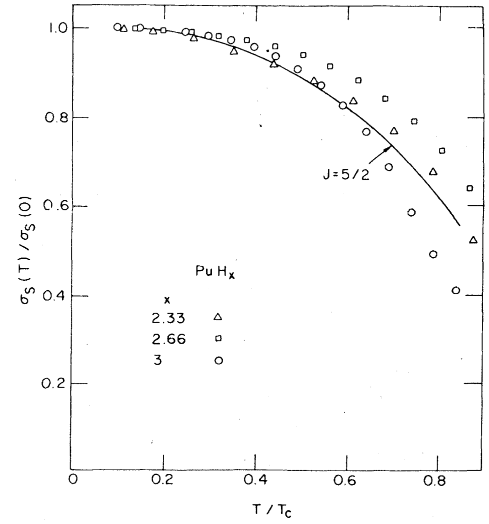

FIG. 6. Reduced magnetization vs reduced temperature for ferromagnetic plutonium hydrides. The solid line represents the $J = \frac{5}{2}$ Brillouin function.

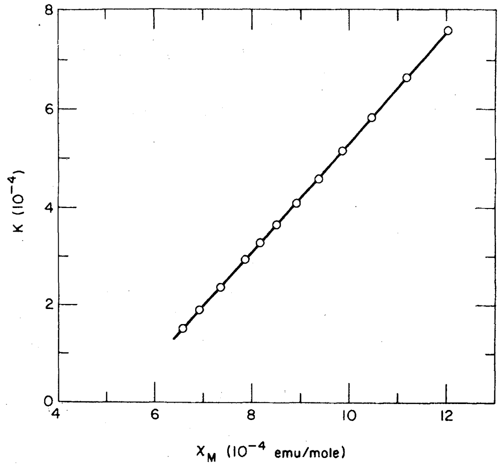

FIG. 7. Proton NMR Knight shift K for $PuH_{2.65}$ (Ref. 6) vs the molar susceptibility of $PuH_{2.66}$, with temperature (ranging from 160 to 300 K) as an implicit parameter.

$H_{eff} = -2.5$ kOe. Both of these H_{eff} values are smaller than the value of -6.5 kOe derived in Ref. 6, with no magnetic-susceptibility input. If we assume the same H_{hfs} for the hydrogen in PuH_x as in β-UH_3,[14] namely, $H_{hfs}^{M} = 19.7$ kOe, then $J_{sf}(0)N_s(E_F) = -0.243$. This can be compared to the value of $J_{sf}(0)N_s(E_F) = -0.297$ derived for β-UH_3. Again, a complete analysis, along the lines of Ref. 13, awaits a neutron-scattering study to determine the crystal-field parameters for the plutonium ions in PuH_x.

In summary, the weak temperature dependence of the measured magnetic susceptibility of the neptunium hydrides implies a $Np^{3+}(5f^4)$ ground-state configuration. A crystal-field calculation yields a good fit to the experimental data with closely defined fourth- and sixth-order parameters. Magnetic ordering occurs in the plutonium hydrides, varying from antiferromagnetic in the stoichiometric cubic dihydride ($T_N = 30$ K) to ferromagnetic in the cubic dihydrides with excess hydrogen and the hexagonal trihydride ($T_C = 101$ K). The temperature dependence of the paramagnetic susceptibility suggests that the ground-state configuration is $Pu^{3+}(5f^5)$. With the same crystal-field parameters as for neptunium dihydride, the magnetic ground-state wave function consists almost entirely of the $J = \frac{5}{2}$ manifold, and the experimental Brillouin plot shows reasonable conformance to $J = \frac{5}{2}$ behavior. However, the expected ordered moment per Pu ion ($1.0\mu_B$) is substantially higher than the experimental bulk moment value ($<0.5\mu_B$). The significance of this discrepancy may be ascertained by a neutron-diffraction study. Additionally, inelastic-neutron-scattering experiments are necessary to determine the crystal-field levels. Only when such results become available is a more-complete theoretical investigation justified.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy. Helpful discussions with G. H. Lander and F. Y. Fradin are acknowledged.

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[1] For example, W. E. Wallace, S. K. Malik, T. Takeshita, S. G. Sankar, and D. M. Gualtieri, J. Appl. Phys. 49, 1486 (1978).

[2] e.g., G. G. Libowitz, Ber. Bunsenges. Phys. Chem. 76, 838 (1972).

[3] G. G. Libowitz, in *Metal Hydrides*, edited by W. Mueller, J. P. Blackledge, and G. G. Libowitz (Academic, New York, 1968), Chap. 11.

[4] M. H. Mintz, J. Gal, Z. Hadari, and M. Bixon, J. Phys. Chem. Solids 37, 1 (1976).

[5] C. E. Olsen, T. A. Sandenaw, and B. T. Matthias, J. Appl. Phys. 34, 1358 (1963).

[6] G. Cinader, D. Zamir, and Z. Hadari, Phys. Rev. B 14, 912 (1976).

[7] R. N. R. Mulford and T. A. Wiewandt, J. Phys. Chem. 69, 1641 (1965).

[8] R. N. R. Mulford and G. E. Sturdy, J. Am. Chem. Soc. 77, 3449 (1955); 78, 3897 (1956).

[9] A. T. Aldred, B. D. Dunlap, D. J. Lam, and I. Nowik, Phys. Rev. B 10, 1011 (1974).

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

[11] P. Jena, R. Emmons, D. J. Lam, and D. K. Ray, Phys. Rev. B 18, 3562 (1978).

[12] D. J. Lam and A. T. Aldred, in Ref. 10, Chap. 3.

[13] G. H. Lander and D. J. Lam, Phys. Rev. B 14, 4064 (1976).

[14] G. Cinader, M. Peretz, D. Zamir, and Z. Hadari, Phys. Rev. B 8, 4063 (1973).