Magnetic and electronic properties of antiferromagnetic $PuPd_5Al_2$

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A compound $PuPd_5Al_2$ was prepared and studied by x-ray diffraction, magnetic susceptibility, heat capacity, electrical resistivity, and thermoelectric power measurements. The crystal structure [$ZrNi_2Al_5$ type (e.g., $I4/mmm$), $a=4.1302$ Å, and $c=14.8428$ Å] was determined from single-crystal x-ray data. The compound orders antiferromagnetically at 5.6 K and exhibits a modified Curie–Weiss behavior with $\mu_{eff}=1.05\mu_B$ close to the intermediate coupling value ($1.01\mu_B$) for Pu^{3+} ions. Below T_N, the specific heat and the electrical resistivity are governed by electron-magnon scattering with a spin-wave spectrum typical of anisotropic antiferromagnetic systems. The Seebeck coefficient is negative in a whole temperature range and is close to -7 μV K^{-1} at 300 K.

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I. INTRODUCTION

Transuranium intermetallics show a large variety of exotic behaviors coming from $5f$-ligand hybridization. Physical phenomena such as long-range magnetic ordering, heavy-fermion ground state, and/or "non-Fermi liquid" behavior raised a great interest to the study of physical properties of these systems. Recently, this interest was even increased with the discovery of unconventional superconductivity in $PuCoGa_5$ and $PuRhGa_5$.[1,2] While these compounds are heavy-fermion superconductors with relatively high critical temperatures, 18.6 and 9 K, respectively, their neptunium counterparts $NpCoGa_5$ and $NpRhGa_5$ show antiferromagnetic ordering at low temperatures.[3,4] Surprisingly, the first neptunium-based superconductor was only recently discovered in $NpPd_5Al_2$.[5] It has been found that this material presents d-wave superconductivity ($T_c=4.9$ K) and heavy-fermion features ($\gamma=200$ mJ/mol K^2).[5] This leads to the interest in the study of the physical properties of the RPd_5Al_2 (R=rare earth, actinide) family of compounds. Very recently, $CePd_5Al_2$ was reported as an antiferromagnetic Kondo lattice with two magnetic transitions at 2.9 and 3.9 K (Ref. 6), while UPd_5Al_2 remains paramagnetic down to 2 K.[7]

Motivated by all these findings and searching for Pu-based superconductors, we have synthesized and examined the physical properties of the other member of $AnPd_5Al_2$ family, namely, $PuPd_5Al_2$. The compound we are interested in was studied by means of x-ray diffraction, magnetization, electrical resistivity, and thermoelectric power measurements performed in a wide temperature and magnetic field range (2–300 K, 0–14 T).

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $PuPd_5Al_2$ were prepared by arc melting the stoichiometric amounts of the elemental components in a Zr-gettered argon atmosphere. The sample was examined by x-ray single crystal and powder diffraction methods. Phase composition was determined by energy-dispersive x-ray analysis on a Philips XL40 scanning electron microscope. From the inner part of the specimen, small single crystals ($\sim 0.03\times 0.2\times 0.05$ mm^3) were selected and examined on Enraf–Nonius CAD-4 diffractometer with graphite monochromatized Mo $K\alpha$ radiation. The powder x-ray diffraction was done using a Bruker D8 diffractometer with Cu $K\alpha_1$ radiation. The crystal structure was refined from the single-crystal x-ray data and shown to be, like $NpPd_5Al_2$,[5] tetragonal with the $ZrNi_2Al_5$ type (e.g., $I4/mmm$) with lattice parameters $a=4.1302$ Å and $c=14.8428$ Å. The atomic coordinates obtained were as follows: Pu [$2a(0,0,0)$], Pd_1 [$8g(\frac{1}{2},0,0.1456)$], Pd_2 [$2b(\frac{1}{2},\frac{1}{2},0)$], and Al [$4e(0,0,0.2521)$]. A sketch of the crystal structure of $PuPd_5Al_2$ is shown in Fig. 1.

The magnetic properties were studied using a MPMS-7 device in the temperature range of 2–300 K and in magnetic fields up to 7 T. The electrical resistivity was measured from

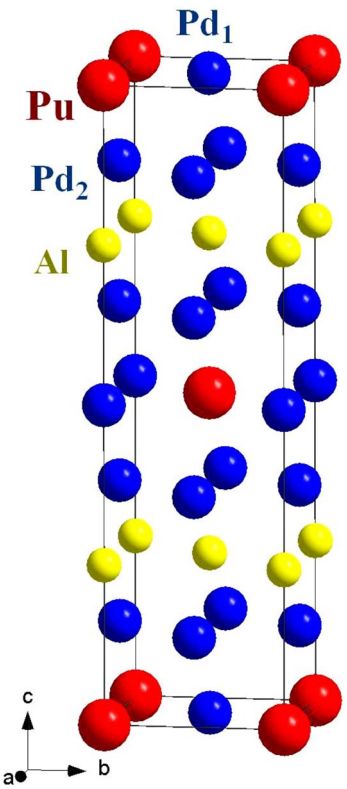

FIG. 1. (Color online) Crystal structure of $PuPd_5Al_2$.

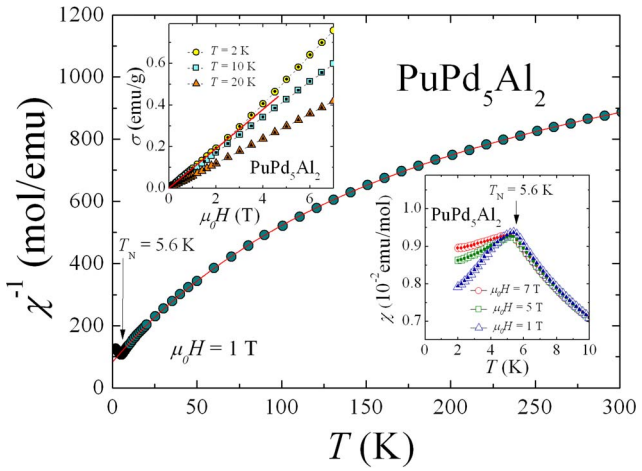

FIG. 2. (Color online) Temperature dependence of the inverse magnetic susceptibility of $PuPd_5Al_2$. The solid line is a modified Curie-Weiss fit. Lower inset: low-temperature susceptibility measured in several magnetic fields in zero field cooled (open symbols) and field cooled (full symbols) conditions. Upper inset: magnetization versus magnetic field taken at several temperatures and measured with increasing (open symbols) and decreasing (full symbols) magnetic fields. The solid line shows a straight line behavior.

2 to 300 K by a PPMS-9 setup. Heat capacity experiments were performed in the temperature range of 2.5–300 K and in magnetic fields up to 14 T using the PPMS-14 device. The thermoelectric power was measured from 6 to 300 K in a homemade setup using pure copper as the reference material. The measurements of all the physical properties of $PuPd_5Al_2$ (even using a very small mass amount of the material) were prevented below 2 K due to the self-heating effect arising from the radioactive decay of the ^{239}Pu isotope (W =1.9 mW/mg). Moreover, to avoid any contamination risk due to radiotoxicity of plutonium, all experimental studies were carried out using special encapsulation techniques.

III. RESULTS AND DISCUSSION

A. Magnetic properties

Figure 2 shows the temperature dependence of the inverse magnetic susceptibility of $PuPd_5Al_2$. Above 10 K, the $\chi^{-1}(T)$ curve is clearly curvilinear and may be well described by a modified Curie–Weiss law with an effective magnetic moment of $\mu_{eff}=1.05\mu_B$, a paramagnetic Curie temperature of $\Theta_p=-12.5$ K, and a temperature independent term $\chi_0=6.9\times10^{-4}$ emu/mol. The origin of the latter contribution is related to the core-electron diamagnetism, the Pauli paramagnetism, and the Van Vleck term. The experimental value of μ_{eff} is larger than the free Pu^{3+} ion value expected for LS coupling ($0.84\mu_B$), but it is close to $1.01\mu_B$, as anticipated for intermediate coupling. Indeed, it has been shown recently that the intermediate coupling is appropriate for the $5f$ states of the Pu metal and Pu-based intermetallics.[8,9] The negative sign of Θ_p refers to antiferromagnetic exchange interactions and is consistent with the antiferromagnetic ordering in the compound studied (see below).

As shown in the lower inset of Fig. 2, a distinct peak in $\chi(T)$ manifests an antiferromagnetic ordering below T_N =5.6 K. With increasing magnetic field, the maximum in the magnetic susceptibility gradually weakens and shifts to lower temperatures. The latter phenomenon indicates the presence of a complex magnetic structure in the compound. The upper inset in Fig. 2 displays the isothermal magnetization taken at several temperatures. The measurements were done with increasing and decreasing magnetic fields, and no hysteresis effect was observed. The antiferromagnetic character of the magnetic ordering in $PuPd_5Al_2$ is corroborated by a weak metamagneticlike transition at a critical field of about 2.5 T. This can be observed in the $\sigma(\mu_0H)$ graph determined at $T=2$ K (see the solid line in the upper inset in Fig. 2). However, the magnetic saturation is not reached even at the strongest applied field. For $T=2$ K and $\mu_0H=7$ T, the magnetic moment extracted is $0.1\mu_B$/Pu atom. This value is much smaller than the theoretical values calculated for the free Pu^{3+} ion, $\mu_{s,LS}=0.71\mu_B$ and $\mu_{s,int}=0.86\mu_B$, taking into account Russell–Saunders or intermediate coupling, respectively. This large reduction of the magnetic moment is most probably due to crystal field interactions. This clearly indicates the splitting of the $^6H_{5/2}$ ground multiplet in a tetragonal crystal field potential.

B. Heat capacity

Figure 3(a) shows the low-temperature dependence of the specific heat of $PuPd_5Al_2$. A distinct λ-shaped anomaly at $T_N=5.6$ K confirms the magnetic ordering in this compound. When applying magnetic field, the peak gradually weakens and shifts to lower temperatures [see the inset in Fig. 3(a)]. Above the magnetic ordering, the C_p/T ratio extrapolated to $T=0$ K is estimated as 67 mJ/mol K^2. It is similar to the Sommerfeld coefficient obtained for $CePd_5Al_2$ (60 mJ/mol K^2).[6] In order to estimate the magnetic contribution to the specific heat of $PuPd_5Al_2$, we have measured the specific heat of $ThPd_5Al_2$, which is its isostructural counterpart with no $5f$ electrons. With this assumption, the magnetic contribution to specific heat $\Delta C(T)$ may be expressed by the relation $\Delta C(T)^{PuPd_5Al_2}=C_p(T)^{PuPd_5Al_2}-C(T)_{ph}^{ThPd_5Al_2}$, as shown in Fig. 3(b). In this analysis, our unpublished $C(T)_{ph}^{ThPd_4Al_2}$ data were used. The Sommerfeld coefficient of $ThPd_5Al_2$ is 5 mJ/mol K^2.[10] Below the Néel temperature, the $\Delta C(T)$ curve may be well described by the model proposed by de Medeiros *et al.* (Ref. 11), which takes into account excitations of antiferromagnetic spin waves over a gap in the magnon spectrum. Assuming that the dispersion of antiferromagnetic magnons can be approximated by the relation $\omega=\sqrt{\Delta^2+Dk^2}$, in which Δ is the spin-wave gap while D stands for the spin-wave stiffness. The specific heat may be expressed as[11]

$$\Delta C(T)=\gamma^*T+c\Delta^{7/2}\sqrt{T}e^{-\Delta/T}\left[1+\frac{39T}{20\Delta}+\frac{51}{32}\left(\frac{T}{\Delta}\right)^2\right], \quad (1)$$

where the coefficient b is defined as $b\propto D^{-3/2}$.[11] The first term describes the electronic contribution to the specific heat.

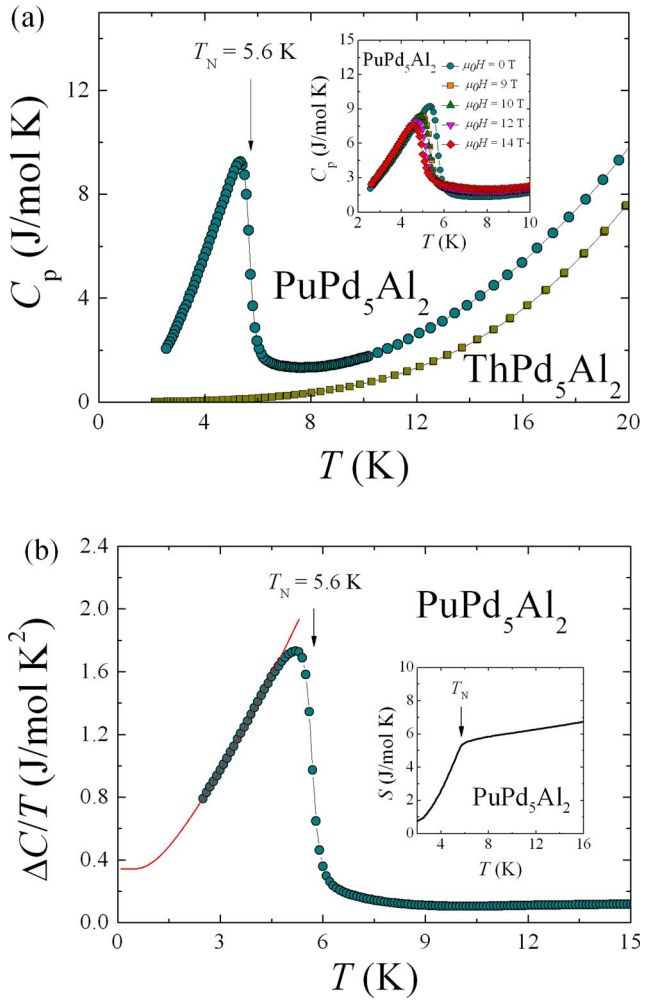

FIG. 3. (Color online) (a) Temperature dependence of the specific heat of $PuPd_5Al_2$ (circles) and $ThPd_5Al_2$ (squares). Inset: low-temperature specific heat measured in several magnetic fields. (b) the magnetic contribution to the specific heat. The solid line is a fit of Eq. (1) to the experimental data. Inset: low-temperature entropy of $PuPd_5Al_2$.

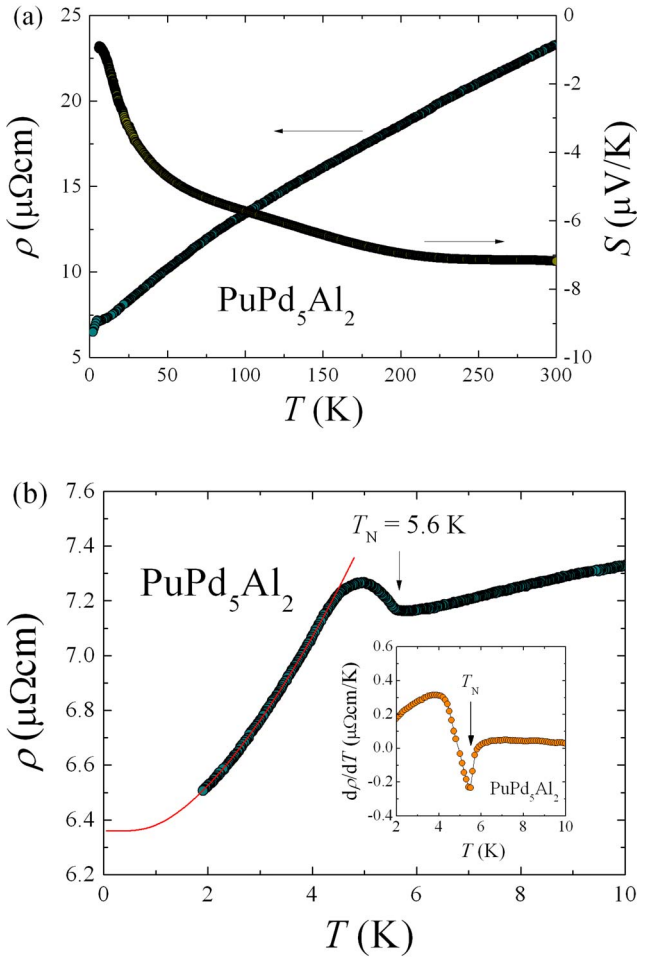

FIG. 4. (Color online) (a) Temperature dependence of the electrical resistivity (left axis) and thermoelectric power (right axis) of $PuPd_5Al_2$. (b) Low-temperature part of the resistivity of $PuPd_5Al_2$. The solid line is a fit of Eq. (2) to the experimental data. Inset: low-temperature variation of the derivative of the resistivity of $PuPd_5Al_2$.

Shown as a solid line in Fig. 3(b), below 4.5 K, this expression describes very well the experimental data of $PuPd_5Al_2$ with the following parameters: $c = 1.04 \times 10^{-2}$ J/mol K^4, $\Delta = 3.7$ K, and $\gamma^* = 341$ mJ/mol K^2. The so-obtained value of Δ is reasonable with respect to the Néel temperature and is similar to that derived from the electrical resistivity data (see below). The so-obtained magnetic contribution to the specific heat provides the magnetic entropy $S = \int \frac{\Delta C(T)}{T} dT$ shown in the inset of Fig. 3(b). At the magnetic transition, the entropy is 5.4 J/mol K which is much smaller than expected for a sixfold degeneracy of the $^6H_{5/2}$ multiplet. It clearly indicates a splitting of the ground multiplet in a tetragonal crystal field potential. Moreover, at T_N, the entropy is close to a value of $R \ln 2$, corresponding to a doubly degenerated ground state. The small deviation from the expected value of $R \ln 2$ at T_N may be due to the straightforwardness of the estimation used or due to the presence of short-range magnetic correlations.

C. Transport properties

The temperature dependence of the electrical resistivity of $PuPd_5Al_2$ is shown in Fig. 4(a). The overall shape and magnitude of the $\rho(T)$ are typical of metallic conductors and differs from the one observed in $NpPd_5Al_2$ (Ref. 5). With decreasing temperature, the electrical resistivity decreases down to a magnetic ordering temperature showing a broad hump around 120 K. The origin of this upward structure may be explained by strong crystal field interactions, and the position of the hump can give an estimation of the total crystal field splitting in this material. Just below T_N, the resistivity exhibits a distinct maximum at 5 K [see Fig. 4(b)]. As shown in the inset in Fig. 4(b), the temperature dependence of the derivative of the resistivity shows a negative divergence of the Suezaki–Mori type.[12] The Néel temperature defined as the minimum in the $\frac{d\rho}{dT}(T)$ curve is 5.6 K, which agrees very well with magnetic and specific heat studies. The increase of the electrical resistivity below the Néel temperature might be associated with an enhanced scattering of conduction electrons due to the formation of a "magnetic" Brillouin zone

boundary in the ordered state. Another explanation might be the presence of a gap on a part of the Fermi surface due to the formation of a spin-density-wave state.[13] To clarify the origin of this phenomenon, further neutron spectroscopy studies are required. Below the magnetic phase transition, the electrical resistivity may be described by a scattering process of conduction electrons on the antiferromagnetic spin waves. Taking into account a similar approach and the same dispersion relation of magnons, like in a specific heat analysis (see above), the electrical resistivity of $PuPd_5Al_2$ may be expressed by[11,14]

$$\rho(T) = \rho_0 + a\Delta^2 \sqrt{\frac{k_B T}{\Delta}} e^{-\Delta/k_B T} \left[1 + \frac{3\Delta}{2k_B T} + \frac{2}{15}\left(\frac{\Delta}{k_B T}\right)^2 \right], \tag{2}$$

where Δ is the spin-wave gap and the coefficient a is related to the spin-wave stiffness D by $a \propto D^{-3}$.[14] Below 4.5 K, the fitting procedure [the solid line, Fig. 4(b)] yielded the following parameters: $\rho_0 = 6.36\ \mu\Omega$ cm, $a = 0.07\ \mu\Omega$ cm/K^2, and $\Delta = 3.1$ K. It is worth noting that the value of the magnon gap so obtained is similar to that derived from the specific heat analysis (see above).

Figure 4(a) shows the temperature dependence of the thermoelectric power of $PuPd_5Al_2$. At room temperature, the Seebeck coefficient is close to $-7\ \mu$V/K. With decreasing temperature, the Seebeck coefficient decreases toward zero at $T = 0$ K. Moreover, the negative sign of the thermopower in the whole temperature range may suggest that in $PuPd_5Al_2$, electrons are main carriers in electrical and heat transport.

IV. SUMMARY AND CONCLUSIONS

A compound $PuPd_5Al_2$ was synthesized and studied in a wide temperature and magnetic field range. It crystallizes, like the superconducting $NpPd_5Al_2$, in the tetragonal unit cell of $ZrNi_2Al_5$ type. All results obtained indicate that while $NpPd_5Al_2$ is a heavy-fermion superconductor at 4.9 K, $PuPd_5Al_2$ orders antiferromagnetically below 5.6 K. The magnetic measurements revealed that the effective magnetic moment obtained ($1.05\mu_B$) is very close to that anticipated for an intermediate coupling between $5f$ electrons ($1.01\mu_B$). The presence of the crystal field splitting of the Pu^{3+} multiplet results in the doublet being a ground state. Below T_N, the temperature dependencies of the specific heat and the electrical resistivity are characteristic of anisotropic antiferromagnets with a gap in the magnon spectrum. The Seebeck coefficient has a value of about $-7\ \mu$V/K at $T = 300$ K. Its negative value in the whole temperature range suggests an electron domination in electrical and heat transport. It is worth noting that the enhanced value of the Sommerfeld coefficient obtained in $PuPd_5Al_2$ ($\gamma \sim 67$ mJ/mol K^2 above magnetic transition) might suggest the presence, in this material, of moderately enhanced Kondo interactions. However, this conclusion is not supported by a metallicke electrical resistivity observed in $PuPd_5Al_2$. It differs significantly from the textbook examples of the systems with Kondo interactions. Interestingly, a similar overall shape of the temperature dependency of the electrical resistivity was observed recently in $CePd_5Al_2$ reported as an antiferromagnetic Kondo lattice.[6] In this case, the Sommerfeld coefficient is estimated as 60 mJ/mol K^2.[6] Therefore, to shed more light on the character of the magnetic and electronic structures of $PuPd_5Al_2$, future experiments such as neutron spectroscopy, magnetoresistivity, and Hall effect measurements are required, some of which are presently underway.

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