Transport and magnetic properties of the superconductor $NpPd_5Al_2$

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Crystals of the transuranium superconductor $NpPd_5Al_2$ have been prepared by arc melting stoichiometric amounts of constituent pure metals (Np 99.9%, Pd 99.99%, Al 99.999%). The single crystals (extracted from the batch) were examined by x-ray diffraction, magnetization, resistivity, magnetoresistivity, Hall effect, thermoelectric power, and heat capacity measurements under magnetic fields and at low temperature along the main crystallographic directions. The superconductivity is observed at $T_c \sim 5$ K. It is intrinsically related to the $ZrNi_2Al_5$ structure type (space group $I4/mmm$) and independent of the synthesis process. The specific heat measured down to 0.6 K shows that $NpPd_2Al_5$ is a nonmagnetic strong coupled type II superconductor presenting heavy fermion features ($\gamma_e \sim 190$ mJ mol^{-1} K^{-2}). The determination of the critical field by electrical resistivity indicates high anisotropic B_{c_2} values: ~4 T along [100] and ~15 T along [001]. Magnetoresistivity, Hall effect, and thermopower measurements point to strong electronic correlations that could be at the origin of superconductivity in this transuranium intermetallic compound.

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I. INTRODUCTION

Despite fascinating intrinsic properties, it has always been difficult to proceed to deep analysis of transuranium compounds due to their radioactivity and radiotoxicity. In the case of their 4f intermetallic counterparts, non-Fermi-liquid, heavy-fermion behavior and/or unconventional superconductivity have been observed with textbook examples such as $CeCu_6$,[1] $CeAl_3$,[2] and $CeCu_2Si_2$.[3] Nevertheless, the interest of the scientific community has been recently refocused on the actinoid-based compounds when superconductivity in plutonium-based ternaries, namely, $PuCoGa_5$ (Ref. 4) and $PuRhGa_5$ (Ref. 5) was reported at 18.6 and 9 K, respectively. These systems present relatively high superconducting transition temperature ($T_c > 2$ K) and large critical field B_{c2} values in comparison to heavy fermion superconductors (HFS) based on rare earths [$CeTIn_5$, T=Co, Ir (Refs. 6 and 7), or $CeCu_2Si_2$ (Ref. 3)] or uranium [UPt_3,[8] UPd_2Al_3,[9] UNi_2Al_3,[10] UBe_{13},[11] URu_2Si_2 (Ref. 12)]. In the neptunium-based compounds superconductivity had already been reported for $NpMo_6Se_8$ (Ref. 13) but superconducting features have not been unambiguously identified. Recently, Aoki *et al.* have observed superconductivity in $NpPd_5Al_2$ with $T_c \approx 5$ K.[14] Only few data were reported on this material and it was crucial to determine if the synthesis method used (Pb-flux)[14] could have induced an artifact on its superconducting properties. Also, it was important to produce this material by a different technique starting from another source of neptunium metal. This problem was at the origin of the simultaneous work on $PuCoGa_5$ at two separated places (LANL and ITU) when superconductivity in this plutonium intermetallic was discovered.[4] Therefore, to shed more light on the physical properties of $NpPd_5Al_2$, we decided to produce this compound starting from the three elements only (Np, Pd, Al) to get rid of the possible influence of lead flux contributions on superconductivity in this material. Then we perform a complete study of the magnetic, transport, and thermoelectric properties as well as specific heat measurements to determine the origin of superconductivity.

II. EXPERIMENTAL DETAILS

Samples were synthesized by arc melting stoichiometric amounts of constituent metals (Np 99.9%, Pd 99.99%, Al 99.999%) in a high purity argon atmosphere on a water-cooled copper plate, using a Zr metal button as an oxygen getter. Single crystals extracted from the batch were then examined by x-ray single crystal and powder diffraction methods. The phase composition was determined by energy dispersive x-ray (EDX) analysis on a Philips XL40 scanning electron microscope (SEM). Single crystals were examined on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo_{K_α} radiation. The powder x-ray diffraction pattern was recorded using a Bruker D8 diffractometer with Cu_{K_α} radiation. The crystal structure was refined from the single crystal x-ray data and shown to be tetragonal with the $ZrNi_2Al_5$ structure type (space group $I4/mmm$) and a=4.1410 Å and c=14.6851 Å being similar to the previous data.[14] The atomic coordinates obtained were as follows: Np [(0,0,0)], Pd1 [(1/2,0,0.1436)], Pd2 [(1/2,1/2,0)] and Al [(0,0,0.2563)].

The magnetic properties were determined using a Quantum Design MPMS-7 device in the temperature range 2–300 K and in magnetic fields up to 7 T. Hall effect was measured from 6 to 300 K with a QD PPMS-9 device up to 9 T. The Hall resistance (R_H) has been determined by a four dc probe technique voltage measurement V_H under fields alternatively at +9 and −9 T. Field response $V_H(B)$ at fixed temperatures has been measured to confirm results obtained when ramping in temperature. Electrical resistivity experiment was performed in the temperature range 2–300 K and heat capacity from 0.6 to 300 K in magnetic fields up to 14 T using a QD PPMS-14 setup. The thermoelectric power was measured from 3 to 300 K in a homemade setup using pure copper as reference material. Due to the contamination risk generated by the radiotoxicity of neptunium, all operations of preparation and encapsulation have been performed in glove boxes under inert atmosphere (N_2). Interestingly, the measurements of the physical properties of $NpPd_5Al_2$ were observable be-

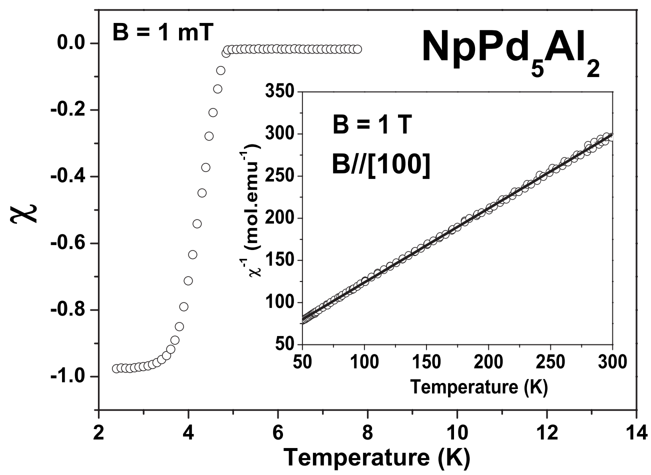

FIG. 1. Flux expulsion at the superconducting transition (T_c=5 K) observed by magnetic susceptibility for B=1 mT in the zero field cooling regime. The inset shows inverse magnetic susceptibility $\chi(T)^{-1}$ of a $NpPd_5Al_2$ single crystal ($B \parallel [100]$) with the Curie-Weiss law fit from 50 to 300 K.

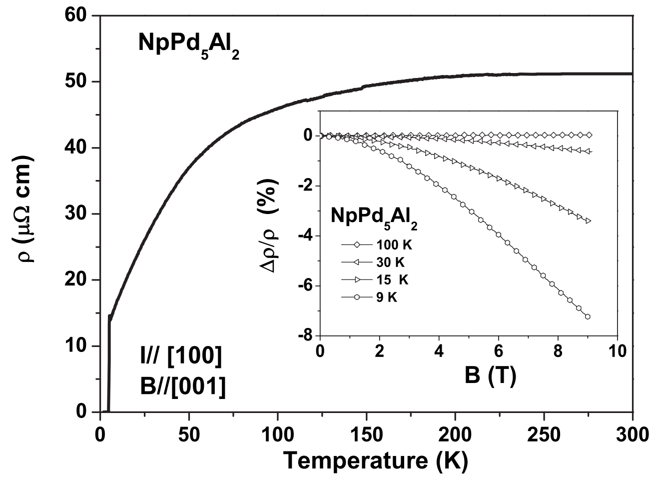

FIG. 2. Electrical resistivity measurements of a single crystal of $NpPd_5Al_2$ with applied current I parallel to the [100] direction. The inset shows magnetoresistance induced by field variation up to 9 T, with a field along the [001] direction for T=9, 15, 30, and 100 K.

low 1 K due to the relatively low self-heating effect of ^{237}Np ($t_{1/2}$=2.14×10^6 yrs; 2.03 μW/g). This is important especially for specific heat measurements in the superconducting state.

III. RESULTS

Magnetic measurements performed for single crystals (with typical size $2\times1\times0.3$ mm^3) extracted from the batch revealed the superconducting transition at $T_c\sim5$ K (see Fig. 1). This value agrees very well with T_c reported in Ref. 14. Measurements at low temperature (down to 2 K) indicates $B_{c_1}\sim10$ mT. Above 50 K the magnetic susceptibility, with field $B\parallel[100]$, is very well described by a Curie-Weiss law with effective magnetic moment μ_{eff}, $\sim3.02\mu_B$, and θ_p=−42 K. The effective moment μ_{eff} is larger than the free Np^{3+} ion ($5f^4$) expected for Russell-Saunders coupling ($2.68\mu_B$) and smaller than the Np^{4+} ($5f^3$) configuration ($3.62\mu_B$). The observed reduction in μ_{eff} with respect to the free ions value could be due to an interplay of crystal electric-field (CEF) and Kondo-type screening effects. θ_p in fact is negative and relatively enhanced in absolute value. This aspect is usually displayed by systems with strong Kondo-type interactions. Using the Hewson relation (Ref. 15), the Kondo temperature may be so estimated as $T_K=|\theta_p|/4\sim10$ K.

With decreasing temperature, a slight decrease of the electrical resistivity until 100 K is observed (Fig. 2). Then a negative curvature develops with a strong decrease down to 5 K where superconducting collapse appears. A T-linear resistivity dependence is present below 12 K that may indicate a possible non-Fermi-liquid behavior. The mean free path l of electronic carriers is calculated assuming then that $NpPd_5Al_2$ is in the Np^{4+} configuration and considering the relation between l and ρ.[16] Taking the residual resistivity ρ_0 close to 10 $\mu\Omega$ cm for the 0 K limit, we obtain a lower residual resistivity ratio (RRR) and $l\sim126$ Å: this is slightly bigger than the coherence length reported ($\xi_0\sim94$ Å).[14] Therefore this material presents clean type II superconductor features although the ratio between l and ξ_0 is relatively low. Figure 2 shows the magnetoresistivity $\frac{\Delta\rho}{\rho}$ taken at a selected temperature (inset, Fig. 2) on the same oriented single crystal with field B applied along the [001] direction. The overall shape and the magnitude of $\frac{\Delta\rho}{\rho}(B)$ are similar to the one observed in the systems with strong Kondo interactions. It may indicate that the decrease of the resistivity with magnetic field can be an indication of an increase of electronic correlations due to the progressive increase of the Kondo interactions.[17]

To determine the type of carriers present in $NpPd_5Al_2$ we performed Hall (Fig. 3) and Seebeck (inset, Fig. 3) effect

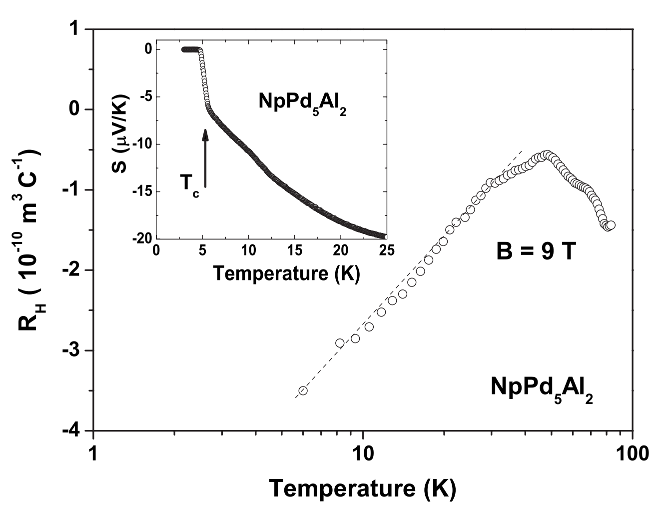

FIG. 3. Hall effect R_H of a $NpPd_5Al_2$ single crystal with I =5 mA along the [100] direction, B=9 T along the [001] direction, and Hall voltage V_H along the [010] direction. R_H is displayed on a logarithmic T scale and presents a maximum at 50 K. The inset shows the Seebeck coefficient $S(t)$, with heat current J along [100]: T_c is clearly visible around 5 K.

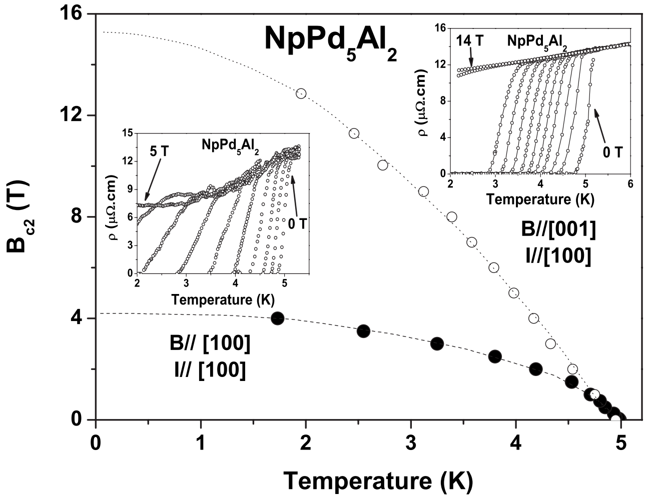

FIG. 4. Critical fields $B_{c_2}(T)$ of the $NpPd_5Al_2$ single crystal along the [100] and [001] directions determined by electrical resistivity. The insets show the superconducting transition shifted under field for both directions.

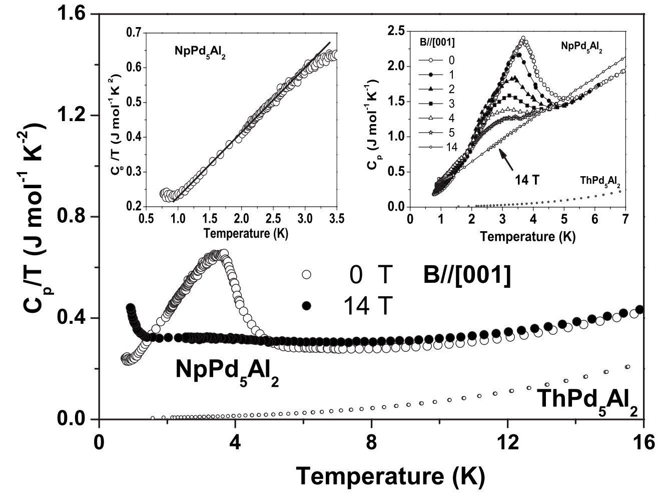

FIG. 5. C_p/T of $NpPd_5Al_2$ at 0 T and 14 T. C_p/T of $ThPd_5Al_2$ is presented in comparison for phonons contribution substraction. The progressive disappearance of a superconducting transition under a magnetic field (inset, right) and the nonexponential behavior of C_e/T (inset, left) in a superconducting state are presented.

measurements. The Hall coefficient is negative in whole temperature range that may indicate domination of the electrons in electrical transport. Moreover, $V_H(B)$ decreases linearly with a field for the temperature range examined confirming an electronlike behavior of the carriers. According to the Fert and Levy theory,[18] in the dense Kondo systems, the Hall effect is dominated by skew scattering processes, incoherent at high temperatures and intrinsic at low temperatures. At an intermediate temperature R_H presents a maximum around a characteristic temperature related to the coherence effect. The general shape of R_H in $NpPd_5Al_2$ with a maximum at 50 K is similar to $4f$ and $5f$ electron-based HFS.[19] The absolute values vary by almost one order of magnitude from -0.4 to -3.55×10^{-10} m^3 C^{-1} indicating a reduction of the effective number of carriers or a decrease of the global mobility. These values are one order of magnitude higher than simple metals but similar to those derived for HFS.

The inset of Fig. 3 presents a low-temperature dependence of the thermoelectric power of $NpPd_5Al_2$. At 25 K the Seebeck coefficient shows a large negative value of about -20 μV/K. With decreasing temperature the magnitude of the thermopower decreases down to T_c, where $S=0$, as expected for the superconducting state. The negative sign of thermopower in the normal state agrees very well with the negative sign of the Hall coefficient and both indicate electronlike character of electrical and heat transport. The strongly enhanced value of the Seebeck coefficient (one order of magnitude larger than in simple metals) is characteristic of systems with strong electronic correlations.

To determine the critical field B_{c2} of $NpPd_5Al_2$ (Fig. 4), we performed electrical resistivity measurements on a single crystal applying magnetic field B along [100] and [001] directions, respectively (insets, Fig. 4), down to 2 K. The estimated $B_{c_2}(0\ \mathrm{K})$ values are $\sim$4.3 T for the [100] direction and $\sim$15 T for the [001] direction. Looking closer to the slope at T_c we observe some differences with published values. For the [001] direction we extract $-(\frac{dB_{c_2}}{dT})_{T_c}=5.2$ T/K ($\ll$31 T/K) (Ref. 14) and for [100], $-(\frac{dB_{c_2}}{dT})_{T_c}=3.3$ T/K ($<$6.4 T/K).[14] It is interesting to calculate the Pauli-limited critical field[20] $H_{p0}=1.85T_c\sim9$ T. The estimations of orbital-limited critical fields $B^*_{c_2}(0\ \mathrm{K})=-0.692T_c(\frac{dB_{c_2}}{dT})_{T_c}$ (Ref. 21) are clearly too big with slope values at T_c previously reported. We got 22.2/107 T and 11.4/18.0 T along the [100]/[001] directions, respectively, for data taken from Ref. 14 and in our case. This material presents a lot of similarities with Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) materials as discussed in Ref. 22 for $PuTGa_5$ (T=Co,Rh) and identified in $CeCoIn_5$.[23] $NpPd_5Al_2$ is a clean type II superconductor strongly paramagnetic limited and anisotropic. The lower slope values at T_c point to the influence of defects or impurities which are less problematic at lower temperatures on the critical field shape.

Finally, we report on the measurement of heat capacity C_p under the magnetic field (right inset, Fig. 5) applied along the [001] direction. To estimate the electronic contribution to the total specific heat of $NpPd_5Al_2$ we assumed that $ThPd_5Al_2$, its isostructural analog that contains no $5f$ electrons, is a good approximation of the phonon part in $NpPd_5Al_2$. Taking into account the specific heat data of the Th-based phase,[24] we therefore estimate that the electronic specific heat in $NpPd_5Al_2$ is as large as $\gamma_e\sim190$ mJ mol^{-1} K^{-2}. At T_c, we observe a jump $\frac{\Delta C}{C}\sim2.0$ indicating that $5f$ carriers participate to the superconductivity. Considering $\frac{C_e}{T}$(T) in the superconducting domain, we got a linear behavior with temperature from 1 to 3.5 K (left inset, Fig. 5) characteristic of line nodes. We observe a clear increase of $\frac{C_p}{T}$ for 14 T when approaching the 0 K limit. In heavy fermion, strong correlations induce divergence behavior of $C_p\sim T^3\ln T$,[25] but we can also consider the possibility that, at very low temperatures, a Schottky-type anomaly coming from the Np nucleus is present, induced by magnetic fields and hyperfine interactions.

IV. SUMMARY AND CONCLUSION

Superconductivity is clearly observed in the transuranium compound $NpPd_5Al_2$ at $T_c \sim 5$ K. It is related to the $ZrNi_2Al_5$ structure type and is weakly sensitive to the synthesis method. This material presents clear nonmagnetic type II HFS features with strong anisotropic behavior in normal and superconducting states. Magnetization, magnetoresistance, thermopower, and specific heat point to strong electronic correlations developing at low temperatures. Low-temperature transport and specific heat properties such as the Pauli-limitation interplay of the superconducting critical field stress the comparison with cerium- and uranium-based HFS (UBe_{13}, $CeCoIn_5$, or $CeCu_2Si_2$): this qualifies this material as a candidate to observe the FFLO state at a low temperature and under a high magnetic field. The nonexponential shape of the specific heat in the superconducting state demonstrates the nonconventional aspect while the coupling mechanism remains unclear. Measurements are in progress to analyze intrinsic properties of $NpPd_5Al_2$ in the normal (Mössbauer spectroscopy) and superconducting state (thermal conductivity).

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