Magnetic structure of $NpPd_2Al_3$: Relevance to the coexistence of superconductivity and magnetism in UPd_2Al_3

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We report neutron-diffraction experiments to determine the low-temperature magnetic structure of $NpPd_2Al_3$, the isostructural Np analog of the heavy-fermion superconductor UPd_2Al_3. The systems orders initially at about 40 K with an incommensurate magnetic propagation vector $\mathbf{q}=(\frac{1}{3},\frac{1}{3},0.36)$. Below 25 K the intensity of this phase is reduced and a new commensurate magnetic phase with $\mathbf{q}=(\frac{1}{3},\frac{1}{3},\frac{1}{2})$ is observed as the dominant phase. The fact that we observe two magnetic phases in this system may have relevance to understanding the ground state in UPd_2Al_3. [S0163-1829(97)03402-4]

The heavy-fermion superconductor UPd_2Al_3 (Ref. 1) is markedly different from the other uranium-based analogous systems because of the large value of the antiferromagnetically ordered moment ($0.85\mu_B$ per mole) found at low temperature.[2] This is at least one order of magnitude greater than the moment found, for example, in URu_2Si_2, UPt_3,[3] or in the isostructural compound UNi_2Al_3.[4] Such a large value of the moment, although still smaller than that found in many other uranium compounds, would appear to require a major ''localized'' contribution, thus making the coexistence of superconductivity and magnetism below $T_c \approx 2$ K even more puzzling than for the other U-based systems. To resolve this apparent dichotomy Caspary *et al.*,[5] Feyerherm *et al.*,[6] and Steglich *et al.*[7] have suggested that the hybridization of the $5f$ with the conduction electrons in this material leads to part of the resulting $5f$ spectral density acting as localized and the remaining part acting as itinerant. This idea is supported by recent calculations of the UPd_2Al_3 Fermi surface[8] which are consistent with the observed de Haas–van Alphen spectra.[9,10] To explore the consequences of these ideas we have investigated the magnetism of the isostructural Np compound, which contains one more $5f$ electron than UPd_2Al_3.

$NpPd_2Al_3$ exhibits the same hexagonal $PrNi_2Al_3$-type structure as its U and Ce analogs. The lattice parameters are $a=5.391(1)$ Å and $c=4.196(1)$ Å at room temperature.[11] Mössbauer experiments[12] showed that the compound orders magnetically at $T \approx 38$ K with a complex magnetic structure and that the Np ions are trivalent ($5f^4$ configuration) as inferred from the isomer shift value ($+10$ mm/s relative to $NpAl_2$). From the fact that the electric-field gradient is the same above and below the ordering temperature it was suggested that the Np moments point along the hexagonal c axis. At low temperature the hyperfine field corresponds to a maximum moment of $1.67\mu_B$ per Np atom, and because less discrete hyperfine fields were needed to fit the spectra, the structure was assumed to simplify at the lowest temperatures. A possible crystal-field ground state for the Np^{3+} ions consistent with the hyperfine interactions has been proposed.[13] Subsequent resistivity measurements[11] (see inset of Fig. 1) showed that (1) a small ''s''-like anomaly occurs around the ordering temperature, and (2) a sharp drop in the resistivity occurs at $T_1=23$ K, suggesting a further important transition.

The samples for the neutron and magnetization experiments were prepared by arc melting in Karlsruhe as previously described[14] and treated similarly to those on which the Mössbauer[12] and resistivity[11] were measured. The samples were single phase as judged by x-ray diffraction. Small single crystals of 1– 2 mg were selected from the melt and one of them was encapsulated for neutron experiments. The magnetization measurements were performed in the temperature range 6–300 K on a polycrystalline sample of $m=73$ mg using a superconducting quantum interference device magnetometer at the CEA-Grenoble with applied fields up to $B=5$ T. Due to ferromagnetic impurities, which were not visible by x rays or metallography (perhaps small amounts of NpC), we observed an anomaly at $T \approx 135$ K, and this prevented using the low-field data in any analysis. Nevertheless, considering the higher-field data only, and assuming that the impurity is saturated, we observe (Fig. 1) (1) that the high-temperature effective moment is $\mu_{\rm eff} \approx 2.65\mu_B$ consistent with a Np^{3+}: $5f^4$ free-ion configuration ($\mu_{\rm eff} \approx 2.75\mu_B$), and (2) that an anomaly appears in low field at the Néel temperature (see inset).

The neutron-diffraction experiments on a polycrystalline sample of $m=4.8$ g were performed at the DN5 instrument ($\lambda=2.49$ Å) at the Siloé reactor (CEA-Grenoble) and at the

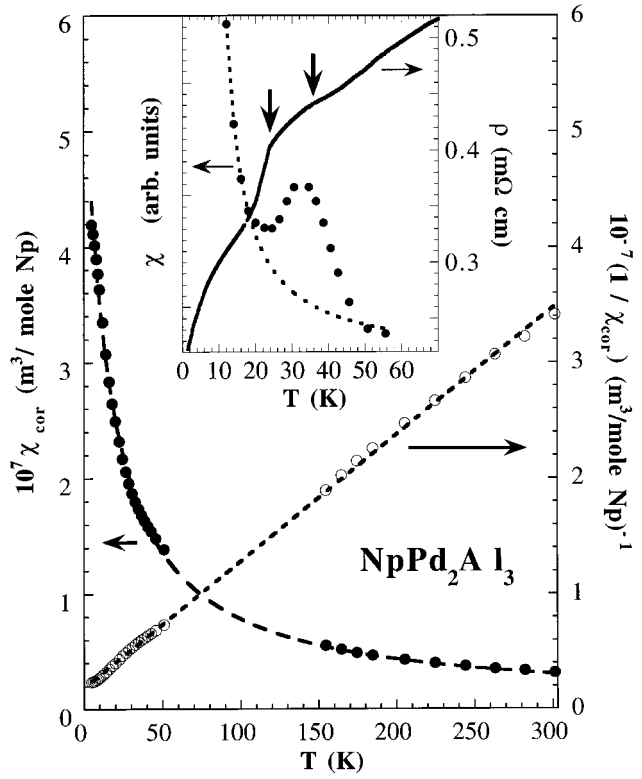

FIG. 1. Susceptibility χ and $(1/\chi)$ of a polycrystalline $NpPd_2Al_3$ sample as a function of temperature. Data between $T \approx 55$ and 140 K are excluded due to some ferromagnetic impurity. The dashed line through the $(1/\chi)$ points signifies $\mu_{\text{eff}} = 2.65\mu_B$. The inset shows the resisitivity [taken from Seret *et al.* (Ref. 11)] together with the low-temperature part of the susceptibility measured in $B = 0.02$ T. The observed anomalies around the ordering temperature and at $T = 23$ K are marked. Here the dotted line is a guide to the eye only.

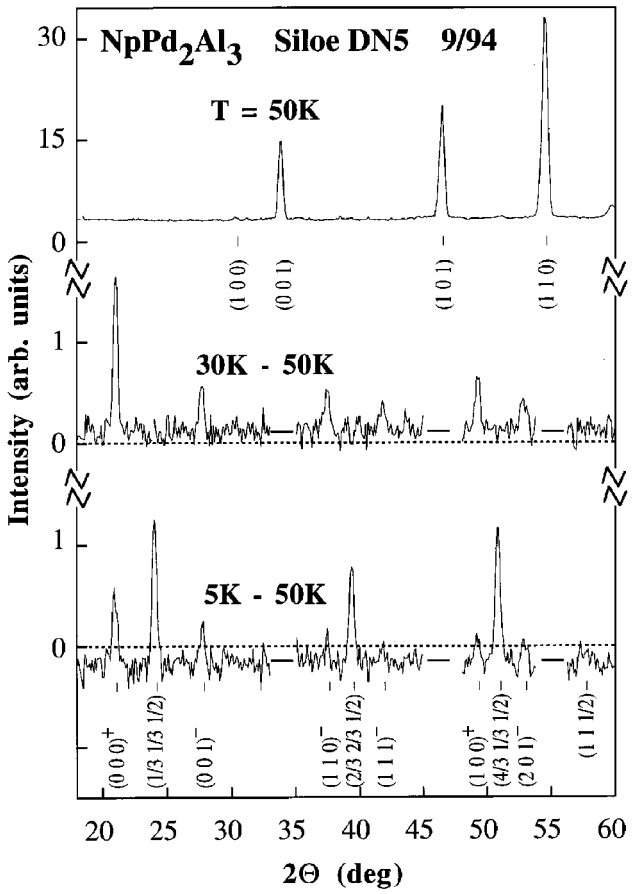

FIG. 2. Low-angle part of the neutron-diffraction pattern as obtained from the polycrystalline sample on DN5 of the Siloé reactor. The upper scan shows the data measured at 50 K, i.e., above T_N. Below are difference patterns as indicated, scaled by 15 with respect to the nuclear scan. The nuclear and commensurate magnetic reflections are indexed as (h, k, l). The reflections belonging to the incommensurate magnetic phase are indexed as $(h, k, l)^{\pm k}$ with the propagation vector $k = (\frac{1}{3}, \frac{1}{3}, 0.36)$.

D2B instrument ($\lambda = 2.40$ Å) at the Institute Laue Langevin, Grenoble. Patterns taken at room temperature confirmed the hexagonal structure of this material. In Fig. 2 we show some of the data and results of the subtraction of data sets at different temperatures. Immediately below the Néel temperature a least-squares fit to the positions of the additional reflections arising from antiferromagnetism gives a propagation vector $\mathbf{q} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2} - \tau)$ with $\tau = 0.14(1)$. This corresponds to an incommensurate modulation of the magnetic moments along the hexagonal axis. These additional reflections are present for all $T < T_N$ and τ is independent of T. The presence of the incommensurate modulation at all temperatures below the Neél temperature and the observed distribution of hyperfine fields implies that there is a variation in the amplitude of the magnetic moment along the c axis. At low temperature the stabilization of unequal moments on atoms at equivalent sites in the lattice requires a strong Kondo interaction. However, at $T_1 \approx 25$ K a further transition occurs in which the intensities from the incommensurate modulation suddenly decrease in strength, while at the same time reflections corresponding to a commensurate magnetic structure with a propagation vector $\mathbf{q} = (\frac{1}{3}, \frac{1}{3}, \frac{1}{2})$, i.e., $\tau = 0$, appear. For both phases a fit to the intensities showed that the moments are parallel to the c axis. Such a conclusion is in agreement with the Mössbauer results. The simpler Mössbauer pattern found at the lowest temperatures may be understood by noting the dominance of the commensurate modulation for $T < T_1$.

To be sure of the complex wave vector in the incommensurate phase we performed experiments with the DN3 (two-axis with lifting detector) instrument at Siloé on a small single crystal of $m = 2$ mg ($V = 0.5$ mm^3). To improve the signal-to-noise ratio in this experiment small apertures had to be used in front of the detector, making it difficult to obtain reliable integrated intensities for different reflections. However, these experiments unambiguously confirmed the wave vector, and are also able to measure accurately the temperature dependence of a given reflection.

The temperature dependence of the magnetic intensities from both modulations is shown in Fig. 3. We note first that from all neutron experiments significant magnetic scattering at $T = 40$ K is observed, suggesting that the ordering temperature of our sample is about $T_N \approx 42$ K, and hence slightly higher than the transition temperature $T \approx 38$ K determined from the Mössbauer measurements.[12] Nevertheless, the temperature dependence and the absolute value of the magnetic moment (obtained by comparing the intensities of magnetic

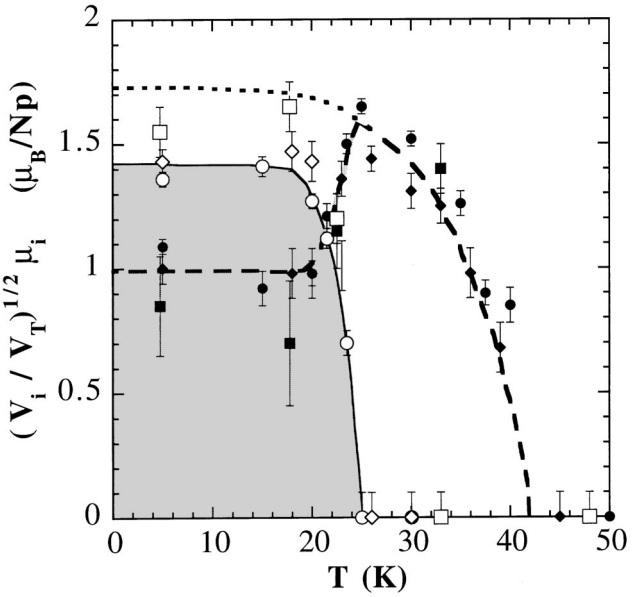

FIG. 3. Magnetic structure factors $F \propto (V_i/V_T)^{1/2}\mu_i$ (given in μ_B) as a function of temperature. The open (closed) points are from the commensurate (incommensurate) modulations. The single-crystal data are shown as squares, the results of the two experiments on a polycrystalline sample are shown as circles (Siloé, DN5) and diamonds (ILL, D2B). The lines and shadings are guides to the eye; the shading traces the growth of the commensurate fraction.

with nuclear reflections) in the temperature range from 25 K to T_N are quite similar. To determine the actual Np moments when the temperature is below 25 K is complicated as two different modulations are observed. Apart from structure and geometric factors the magnetic intensities in diffraction experiments are sensitive to the product $(\mu_i^2 \times V_i/V_T)$ where μ_i is the magnetic moment and V_i/V_T is the fractional volume of the sample with that magnetic structure. Thus, it is not possible to say uniquely from our experiments whether the two magnetic structures at low temperature exist in different or the same volume of the sample.

An interpretation of the apparent coexistence of two phases in a large polycrystalline sample is that it arises from physically different phases as a result of slightly different stoichiometries or lattice distortions. The observed variation of the ordering temperature in different experiments supports this assumption. For simplicity let us first assume that the diffraction patterns arise from physically different parts of the sample, i.e., that $V_{\rm inc}+V_{\rm comm}=V_T$, where $V_{\rm inc}$ and $V_{\rm comm}$ are the volumes occupied by the incommensurate and commensurate structures, respectively. At 25 K, $V_{\rm inc}=V_T$, but at 5 K this is reduced to $V_{\rm inc}\approx 1/3 V_T$. The magnitude of the Fourier component associated with this modulation extrapolates from $1.5\mu_B$ at 30 K to about $1.7\mu_B$ at 5 K. (Strictly speaking the moment is twice the Fourier component for a centrosymmetric structure, but we shall quote only numbers related to moments.) The remaining 2/3 of the volume ($=V_{\rm comm}$) then corresponds to a Fourier component of also $1.7\mu_B$. These are clearly in excellent agreement with the Mössbauer results. We have also observed a small intensity of the third-order satellite from the commensurate modulation at the position $(1,1,\frac{1}{2})$, which suggests at least partial squaring of this modulation at low temperature.

An alternate, more intriguing, possibility is that both structures exist in the same volume at low temperature. This is suggested by the observation that the ratio of commensurate/incommensurate intensity is the same for a large polycrystalline sample and a small single crystal. If variations in stoichiometry were important this agreement would appear highly fortuitous; but this does not constitute a proof that both phases exist in all the sample volumes. Whichever of these interpretations is correct, we argue both magnetic phases are intrinsic to $NpPd_2Al_3$.

The magnetic structure of $NpPd_2Al_3$ is quite different from that found in the isostructural uranium compound, in which the propagation wave vector is $\mathbf{q}=(0,0,\frac{1}{2})$ and the moment direction is perpendicular to the hexagonal c axis. But, despite these differences, there is an interesting aspect of the magnetic phase diagram of the Np compound that may be relevant to the physics of the U compounds. Our experiments suggest the magnetic response is finely balanced between two energy minima. Just below the Néel temperature, and with an associated ''s''-like anomaly in the resistivity, as found in Cr,[15] an incommensurate spin-density modulation develops. Because of the strong Kondo interaction that we have argued is necessary to stabilize this modulation, it is tempting to associate this ordering with an itinerantlike part of the $5f$ spectral density. At $T_1=25$ K, and associated with a conspicuous anomaly in the resistivity, a commensurate Fourier component appears in addition to the incommensurate modulation. This phase transition is unusual. Rather than τ, the incommensurate wave vector, tending to zero as a function of temperature, as in a classic phase transition, both sets of reflections (τ finite and $\tau=0$) are observed together. We suggest the localized part of $5f$ spectral density dominates the low-temperature commensurate magnetic structure.

In conclusion, it is exactly this two-component behavior of the $5f$ spectral density that has been suggested as responsible for the coexistence of the large moment ($0.85\mu_B$) and superconductivity in UPd_2Al_3. Since Np compounds are usually more ''magnetic'' than their uranium counterparts, both parts of the spectral density in $NpPd_2Al_3$ order magnetically at low temperature. Whereas in both compounds the localized portion of the $5f$ spectral density might be responsible for a commensurate magnetic order, we suggest that the itinerantlike response in UPd_2Al_3 results in a Kondo state (characteristic temperature $T^* \approx T_N$) and subsequent superconductivity at low temperature ($T_c=2$ K).

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