Evidence for Moment Fluctuation Effects in the Metallic Nuclear Magnet $PrNi_5$

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For the first time the dc magnetization of a metallic nuclear magnet, $PrNi_5$, has been directly measured down to well below the nuclear magnetic ordering temperature in magnetic fields up to 37.6 mT. The ratio of the Curie constant to the saturation magnetization is found to be $(32 \pm 9)\%$ larger than the same ratio expected for the localized hyperfine enhances moments with the known enhancement factor $1 + K = 12.2 \pm 0.5$. Contributions of moment fluctuations are discussed.

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$PrNi_5$ is a metallic compound in which Ni is nonmagnetic and Pr^{3+} ions show temperature-independent Van Vleck paramagnetism below 2 K. On account of the hyperfine coupling between Pr^{3+} ion $4f$ electrons and ^{141}Pr nuclei, the system behaves as a hyperfine-enhanced nuclear magnet (HENM) and is described by an effective nuclear-spin Hamiltonian.[1,2] We have demonstrated[1] that the hyperfine-enhanced nuclear-spin system orders ferromagnetically at 420 ± 20 μK and determined the parameters of the Hamiltonian, for the first time for any magnetic system, purely from the thermodynamic analysis of the specific heat as a function of temperature and magnetic field. Specifically the hyperfine enhancement factor $1 + K$, the effective nuclear exchange parameters,[1] and also the sign and magnitude of the small total quadrupole-type interaction parameter[3] have been obtained. Furthermore, from the analysis, which is described in detail in Refs. 1 and 4, we obtained the enhanced nuclear saturation magnetization $M_s = (1.52 \pm 0.09) \times 10^{-1}$ J/T mole and the nuclear Curie constant $C_N = \chi_N (T - \Theta) = 1.41 \pm 0.07$ mJK/T^2 mole. These were in good agreement with the viewpoint of localized enhanced nuclear moments with the same enhancement factor $1 + K = 12.2 \pm 0.5$.

In this Letter we report on the first direct measurements of the magnetization of the metallic HENM $PrNi_5$ down to 50 μK, well below the nuclear magnetic ordering temperature, and its comparison with the specific-heat analysis results.[1,4] Although both measurements give the same ordering temperature $T_c = 420 \pm 20$ μK and Curie-Weiss behavior of the susceptibility above T_c, the ratio between the nuclear Curie constant C_N and the saturation magnetization M_s was found to differ for the two kinds of experiment.

The ratio C/M_s is one of the indications for spin (moment) fluctuations in a magnet[5]; in the case of magnetic insulators or rare-earth metals where the fluctuations are described by the well-defined local magnetic moments the ratio is given by

$$C/M_s = Ng^2\mu_B^2 J(J+1)/(3k_B N g \mu_B J)$$
$$= g\mu_B(J+1)/3k_B$$

where g is the g factor, μ_B is the Bohr magneton, J is the total angular momentum, and k_B is the Boltzmann factor. On the other hand, when the long-wavelength part of the fluctuations plays an important role the ratio becomes larger than the number given by the formula.

The long-wavelength fluctuating part of the moment would not cause a sizable contribution to the saturation magnetization compared to localized spin (moment) contributions. It may manifest itself, however, as an additive fluctuating moment which adds to the localized spin moments and enlarges the Curie constant. Such behavior of the long-wavelength spin fluctuations has been seen in the cases of weak itinerant-electron magnets[6] whose susceptibility changes strongly as a function of temperature though no strong magnetic specific-heat anomaly is found because the total freedom of the fluctuations is smaller than that of the localized moments.

The dc magnetization measurements have been performed on a rod-shaped sample from the same batch of polycrystalline $PrNi_5$ and in the same magnetic field orientation as in the former specific-heat measurements.[1] The measurements cover the temperature range from 50 μK $= 0.12 T_c$ to above 1 K and the field range from -37.6 to $+37.6$ mT. The magnetization was measured with a SQUID magnetometer in two different ways in the experimental space of the Jülich two-stage nuclear demagnetization cryostat.[7] Experimental results are presented in units of the change in the number of flux quanta

φ_0 at the SQUID.

One method is measurement of the dc magnetization changes while varying the sample temperature in small steps and keeping the magnetic field constant. Alternatively the dc magnetization was measured by sweeping the external field at fixed temperatures. At temperatures between 4.2 and 1 K, the field sweep was performed repeatedly in order to calibrate the magnetometer zero, determining the temperature-independent signal proportional to the applied magnetic field which includes both the Van Vleck and Pauli paramagnetic contributions and the signal caused by the mismatch of the astatic pair of windings of the magnetometer. This enabled us to measure selectively the temperature-dependent part of magnetization.

The result of the former type of measurements is shown in Fig. 1 for the indicated magnetic fields and $T \lesssim 1.5$ mK. The field-dependent apparent magnetization at the lowest temperature is mainly the effect of the demagnetization and

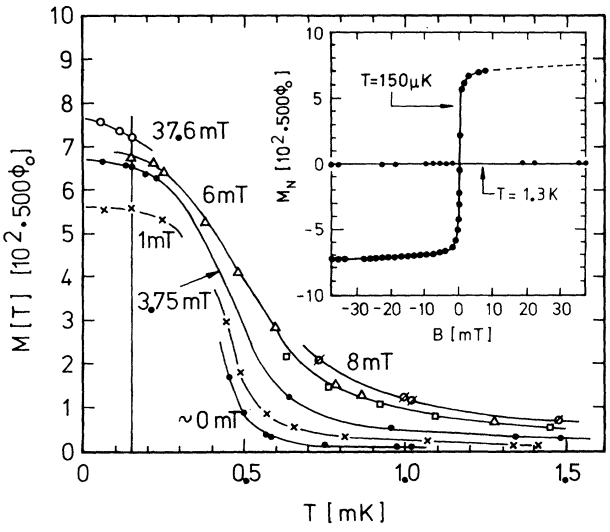

FIG. 1. Temperature-dependent magnetization of $PrNi_5$ at lowest temperatures in the given ambient static magnetic fields, in units of flux quanta at the SQUID. Data from two experimental runs at 6 mT, differentiated by two different symbols, open squares and open triangles, are presented to give some indication of the reproducibility. The symbols at 150 μK, marked by the vertical line, are derived from a field-sweep measurement as indicated by the inset and described in the text. Similar magnetization curves have been observed at 52 and at 60 μK. From these one can obtain $M_s(T=0, B\to\infty) = (778\pm10)\times500\,\varphi_0$. The symbols on a horizontal line are derived from field sweeps at 1.3 K.

anisotropy.[3] Apart from the details of the magnetization curves one can estimate the saturation magnetization in the limit of $T=0$ and $B\to\infty$ with the help of the latter type measurements. Results of such a measurement at 150 μK and 1.3 K are shown in the inset of Fig. 1. The field was swept stepwise and so slowly that the sample temperature did not change more than 5% during the entire sweep. Thermal equilibrium was verified at each step. The whole sweep needed one week. We have performed similar field sweeps at 52 and at 60 μK and found a similar field dependence for the magnetization.

Apart from very low-temperature properties, we found small contributions from ferromagnetic impurity phases with transitions at 6 and at 60 mK. This is consistent with the specific-heat result.[1,3] At temperatures below 4 mK in 0.3 mT and below 60 mK in 37.6 mT field these phases produce a nearly constant saturation magnetization[3] $M_{\mathrm{imp}} = 24\times500\varphi_0$. After subtracting this amount from the field sweep result we obtain the saturation magnetization as $M_s = (778\pm10)\times500\varphi_0$.

The field-sweep results after subtracting M_{imp} are plotted in Fig. 1 with a vertical line. These and the temperature-sweep results are in good agreement which confirms the reliability of the data and the saturation magnetization value. Furthermore, from the specific-heat analysis[1,3] over a much wider field range, one can safely conclude that this is a good estimate for the saturation magnetization.

The inverse of the temperature-dependent magnetization is plotted in Fig. 2 as a function of temperature for the indicated applied fields. The pure $PrNi_5$ magnetization was obtained simply from the temperature-dependent magnetization for $T \lesssim 3$ mK. Over a wider temperature range the magnetization contributed by the impurity phases is subtracted. The plot shows a Curie-Weiss behavior and the linear relation fits well for all the data for $M^{-1} > 2\times(10^2\times500\varphi_0)^{-1}$. The slope gives a $(T-\Theta)M$ value for data in each applied field. These $(T-\Theta)M$ with $\theta = 0.45$ mK are plotted as a function of nominal applied field from which we again obtain the Curie constant $C = (T-\Theta)\chi = (9.12\pm0.50)\times500\varphi_0$ mK/mT, as the slope of the linear relation over the field range $|B| \lesssim 37.6$ mT. A small amount of offset and nearly identical deviations from the linear relation were observed in the plot and they seem to have their origin in the effective field produced by the magnetization of the impurity phases and in the scat-

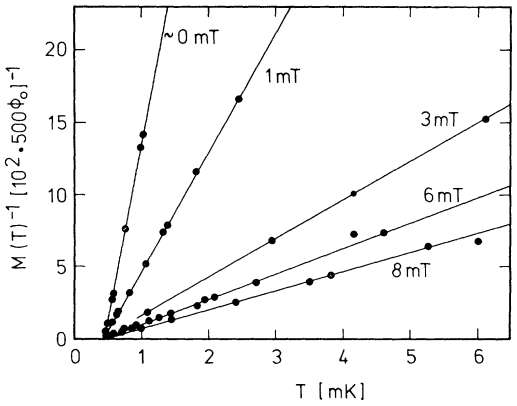

FIG. 2. The inverse of the temperature-dependent magnetization below 6 mK in the given external fields, showing well behaved Curie-Weiss temperature dependence. The slope of each line taken for $M(T)^{-1} > 2\times(10^2\times 500\varphi)^{-1}$ give $M(T)(T-\Theta)$. A plot of $M(T)(T-\Theta)$ vs field is found to be very nearly a straight line for fields up to 37.6 mT, the highest field for these measurements. The slope of the line gives the Curie constant $C = (9.12\pm 0.50)\times 500\varphi_0$ mK/mT.

ter of the thermometry calibrations. This is quite small although measurements were performed over more than one year.

From formulas for the Curie constant and the saturation magnetization for localized HENM moments using $I=\frac{5}{2}$ and $g_N = 1.71$, we expect

$$C/M_s = \frac{Ng_N^2\mu_N^2(1+K)^2 I(I+1)/3k_B}{Ng_N\mu_N(1+K)I}$$

$$= (7.298\times 10^{-4}\ \mathrm{K/T})(1+K). \qquad (1)$$

Taking the values $M_s = (778\pm 10)\times 500\varphi_0$ and $C = (9.12+0.50)\times 500\varphi_0$ K/T from the direct magnetic measurements we obtain the ratio $C/M_s = (1.17\pm 0.08)\times 10^{-2}$ K/T and the enhancement factor $1+K = 16.1\pm 1.1 = (1.32\pm 0.09)\times 12.2$. This is about 30% larger than the result from the specific-heat analysis which is accurate to within 4% and consistent with NMR results.[8] This far exceeds the possible error of the present magnetization measurements as seen below.

The saturation magnetization value is independent of the thermometer and field calibrations. One needs only the extrapolated values for $T=0$ and $B\to\infty$. On the other hand, the Curie constant is obtained from the magnetization change as a linear function of field and inverse temperature. Therefore the C/M_s value is linearly related to the thermometer calibration and inversely to the field calibration.

The same thermometers[7] were used for the former specific-heat experiment and for the present magnetic measurements. The thermometer calibrations were based on National Bureau of Standards fixed-point device[9] down to the Be transition temperature. Therefore the temperatures have been always correct within a few percent in the temperature range between 10 and 100 mK, where both the Curie constant and the enhancement factor were measured with high accuracy in the highest fields with use of a carbon resistance thermometer which was located in a field-free position and calibrated with a help of a cerium magnesium nitrate thermometer. At the lower temperatures our Pt-wire pulsed NMR thermometer was calibrated in the above temperature range against cerium magnesium nitrate and carbon resistance thermometers. We recently found some inconsistencies of a few percent in the Pt NMR calibration method used in the past. These are corrected in the present paper, also for past measurements, causing a change in T_c of about 5%. After the correction we conclude that our thermometer accuracy is better than 3.5%. The field was calibrated at 4.2 K with use of a calibrated Hall probe *in situ* and should be correct to within 4%.

We have also sought other possible explanations for the observations. Crystallographic anisotropy is one of them. Micrographic examination shows that the c axis of the crystallites is nearly perpendicular to the axis of the rod-shaped samples as is typical for arc-melted hexagonal metals. The NMR Larmor frequency of $PrNi_5$ depends on the time-averaged hyperfine field at each ^{141}Pr nucleus and should depend on the localized HENM fields. NMR measurements on a single crystal of $PrNi_5$ at liquid-He temperatures yielded the anisotropic enhancement factors $1+K_{\parallel} = 6.29$ and $1+K_{\perp} = 12.59$.[8] The enhancement factor $1+K = 12.2\pm 0.5$ from our analysis of the specific heat lies between the values for $1+K_{\parallel}$ and $1+K_{\perp}$ obtained in the NMR experiments and very close to the latter value as expected from the orientation observed in the micrographic examination. If the sample were not in the same orientation as for the specific-heat measurements, the observed value $1+K = 16.1$ could only increase the discrepancy compared to the value from the specific heat beyond the given error.

Therefore we can conclude that we have observed evidence for extra fluctuating magnetic moments which have long wavelength and do not give large contributions to the specific heat at

low temperatures.

An additional independent observation which confirms the importance of the moment fluctuations in $PrNi_5$ is the difference between the Weiss temperature calculated from the measured exchange parameter[1] with the formula[10] $\Theta = I(I+1) \times \sum_j' J_{ij}{}^N/3k_B$ and the 30% smaller value, $\Theta = (0.45 \pm 0.02)$mK, obtained from the susceptibility measurements taken sufficiently above the ordering temperature.

Though these measurements cannot determine the origin of moment fluctuations, there is a reasonable explanation for them in a metallic Van Vleck paramagnet. $4f$ moments are induced in the singlet ground state by the exchange and dipole-dipole interactions in addition to moments induced by the hyperfine interaction.[2,11] In the case of metallic HENM substances, the exchange interaction alone is not strong enough to cause magnetic ordering among the exchange induced moments unless there is a further contribution from the HENM moments. The long-range exchange interaction should give rise to moment fluctuations in addition to the well localized HENM moments. Long-wavelenth magnetic fluctuations have, in fact, already been observed in single-crystal Pr metal samples, which is also a metallic, singlet–ground-state Van Vleck paramagnet that currently receives considerable attention.[12] Such singlet–ground-state systems may present us with another class of materials showing spin (moment) fluctuations besides the itinerant-electron magnets.[5] Furthermore, metallic HENM systems offer a new category of magnetic materials which simultaneously have well localized HENM moments and various moment fluctuations. Dynamics of such a system should be an interesting subject.[13]

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[1]M. Kubota, H. R. Folle, Ch. Buchal, R. M. Mueller, and F. Pobell, Phys. Rev. Lett. 45, 1812 (1980); M. Kubota, Kernforschungsanlage, Jülich, Report No. 1688, 1980 (unpublished).

[2]T. Murao, J. Phys. Soc. Jpn. 39, 50 (1975); K. Andres, Phys. Rev. B 7, 4295 (1973); B. Bleaney, Physica (Utrecht) 69, 317 (1973).

[3]M. Kubota, G. Kraaij, R. M. Mueller, Ch. Buchal, H. Chocholacs, J. R. Owers-Bradley, and F. Pobell, to be published.

[4]M. Kubota, H. R. Folle, Ch. Buchal, R. M. Mueller, and F. Pobell, Physica (Utrecht) 108B, 1093 (1981); the Curie constant obtained from the specific-heat data analysis is given as the inverse slope of χ^{-1} vs T plot and consistent with $1 + K = 12.2 + 0.5$.

[5]T. Moriya, J. Magn. Magn. Mat. 31–34, 10 (1983).

[6]K. A. Gschneider, Jr., and K. Ikeda, J. Magn. Magn. Mat. 31–34, 265 (1983).

[7]R. M. Mueller, Ch. Buchal, H. R. Folle, M. Kubota, and F. Pobell, Cryogenics 20, 395 (1980).

[8]N. Kaplan, D. L. Williams, and A. Grayevsky, Phys. Rev. B 21, 899 (1980); we have used $g_N = 1.71$ as before instead of 1.64 given in this reference.

[9]National Bureau of Standards fixed-point device (SRM 768 series), National Bureau of Standards, Washington, D.C. 20234.

[10]J. S. Smart, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. 3, Chap. 2.

[11]G. J. Bowden, private communication; B. Bleaney, G. J. Bowden, and R. G. Clark, J. Phys. C 15, 1663 (1982).

[12]H. Bjerrum Møller, J. Z. Jensen, M. Wulff, A. R. Mackintosh, O. D. McMasters, and K. A. Gschneidner, Jr., Phys. Rev. Lett. 49, 482 (1982); E. M. Forgan, Physica (Utrecht) 107B, 65 (1981); R. M. White and P. Fulde, Phys. Rev. Lett. 47, 1540 (1981); K. A. McEwen, N. G. Stirling, and C. Vettier, J. Magn. Magn. Mat. 31–34, 599 (1983).

[13]M. Kubota, Ch. Buchal, R. M. Mueller, and F. Pobell, J. Magn. Magn. Mat. 31–34, 739 (1983).