Nuclear Magnetic Ordering in $PrNi_5$ at 0.4 mK

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The nuclear specific heat of the hyperfine-enhanced Van Vleck paramagnet $PrNi_5$ has been measured from 0.2 to 100 mK in magnetic fields up to 6 T. The ^{141}Pr nuclei order ferromagnetically at 0.40 ± 0.02 mK. Other results reported are hyperfine enhancement factor $1+K = 12.2 \pm 0.5$, enhanced nuclear magnetic moment $\mu = (0.027 \pm 0.004)\mu_B$, internal field $B_0(T=0) = 66 \pm 10$ mT, and nuclear exchange parameter $\Sigma_j J_{ij}{}^N/k_B = 0.20 \pm 0.04$ mK.

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In this Letter we report on the first investigation of the magnetic field and temperature dependence of the nuclear specific heat of a metal through its nuclear magnetic ordering transition. The investigated compound, $PrNi_5$, as well as other Van Vleck paramagnets were investigated above their nuclear ordering temperatures by Andres and co-workers,[1,2] while Babcock *et al.* recently observed a nuclear ordering transition in $PrCu_6$ at 2.5 mK.[3] We have cooled the nuclei and electrons of $PrNi_5$ by adiabatic nuclear demagnetization to 0.2 mK,[4] the lowest temperature obtained for such a material, and have investigated the nuclear magnetic transition, discovered at 0.40 ± 0.02 mK. By applying a magnetic field, we could study the gradual change from spontaneous nuclear ordering to Schottky-like behavior. Analysis of our data has yielded the first detailed information on nuclear ordering in a material where indirect exchange interactions dominate. We have obtained the hyperfine enhancement factor, the internal magnetic fields in the paramagnetic and ferromagnetic range, the saturation magnetization, the enhanced nuclear moment of ^{141}Pr in $PrNi_5$, the Van Vleck susceptibility, and the exchange and the molecular field constants. In addition, we demonstrate purely from thermodynamic data that the order is ferromagnetic.

For rare-earth ions in Van Vleck compounds in an external field B_e, the interactions can be summarized by the Hamiltonian,[5]

$$H = H_{cf} - g_J \mu_B \vec{B}_e \cdot \sum_i \vec{J}_i - \tfrac{1}{2}\sum_{ij} J_{ij}{}^E \vec{J}_i \cdot \vec{J}_j + A \sum_i \vec{J}_i \cdot \vec{I}_i - g_N \mu_N \vec{B}_e \cdot \sum_i \vec{I}_i + H_Q. \quad (1)$$

The crystal field term H_{cf} alone produces an electronic singlet ground state. Together with the electronic Zeeman term it gives a Van Vleck susceptibility which is temperature independent for $T < 2$ K in $PrNi_5$.[2,6] The electronic moments are coupled to each other by indirect exchange interaction and to the nuclei by the hyperfine interaction (with $A/k_B = 52.5$ mK for[7] Pr^{3+}), represented by the third and fourth terms. The last two terms are the nuclear Zeeman and the nuclear electric quadrupole interactions. A model nuclear-spin Hamiltonian can be written as[5]

$$H_N = -g_N \mu_N (1+K) \vec{B}_e \cdot \sum_i \vec{I}_i - \tfrac{1}{2}\sum_{ij} J_{ij}{}^N \vec{I}_i \cdot \vec{I}_j + H_{PQ} + H_Q, \quad (2)$$

where $1+K$ is the hyperfine enhancement factor due to the Van Vleck susceptibility χ and $K = \chi A / g_J \mu_B g_N \mu_N$.

The exchange parameter[1]

$$J_{ij}{}^N = K^2 J_{ij}{}^E (g_N \mu_N / g_J \mu_B)^2 \quad (3)$$

describes the indirect exchange interaction of nuclear moments through electronic exchange and hyperfine interactions. They are believed to cause the magnetic ordering. In Ref. 6 it was shown, from NMR data taken at $T > 1$ K, that the nuclear electric quadrupole term H_Q and the pseudoquadrupole term H_{PQ}, which is a second-order magnetic hyperfine interaction, together give such a small contribution that we can neglect $H_Q + H_{PQ}$ in the following arguments.

The investigated $PrNi_5$ is the first nuclear stage of our double-stage nuclear demagnetization refrigerator.[4] It consists of 1.86 kg (4.3 moles) of $PrNi_5$ in the form of sixty rods. For thermometry we used pulsed NMR on Pt wires and the resistance of a 0.1-mm-thick carbon resistor.[4] The temperatures for this experiment were obtained by demagnetization of our $PrNi_5$, starting at a

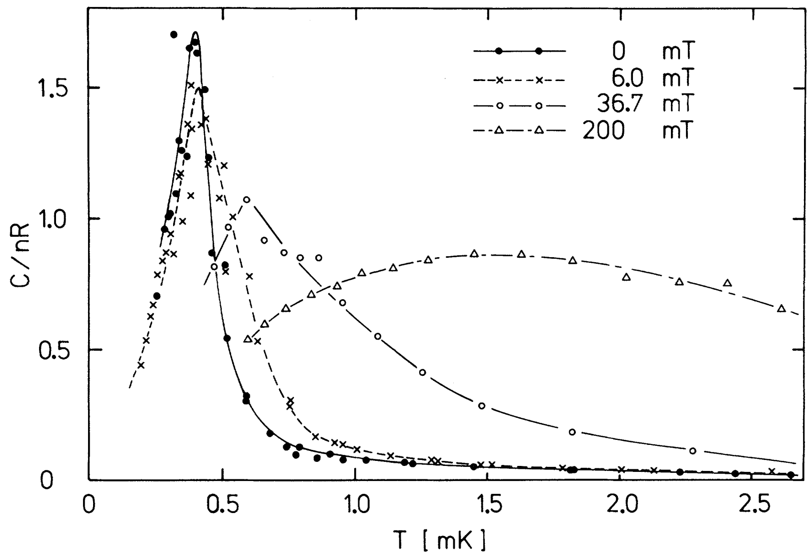

FIG. 1. Low-temperature part of the nuclear specific heat of $PrNi_5$ measured in the indicated magnetic fields. The spontaneous nuclear ordering in zero field occurs at 0.40± 0.02 mK.

field of 6 T and temperatures between 10 and 29 mK. For measurements in external fields, the demagnetization was stopped at the desired fields. The specific heat of addenda and contributions from the background heat leak of about 3 nW were negligible. Thermal relaxation times were up to 2 h near the maximum of the specific heat where they might cause some smearing of the data, but rapidly decreased with increasing temperature. Our $PrNi_5$ shows slightly preferred orientation of the grains typical for hexagonal metals in the as-arc-melted condition. In our analysis we neglect this preference and anisotropy effects, and consider the sample as a polycrystal with random orientations.

The specific heat of $PrNi_5$ measured in small external fields, and below 2.6 mK, is shown in Fig. 1. In zero magnetic field, spontaneous nuclear magnetic ordering is indicated by the sharp peak at 0.40 ± 0.02 mK. Even in rather small magnetic fields this peak decreases, broadens, and shifts to higher temperature, indicating that the order is ferromagnetic.

Figure 2 shows specific heat data for 0.2 T $\leq B_e \leq 6$ T, compared to results in zero field and 0.0367 T. The high-field data show Schottky-like behavior with a field-independent shape and maximum value of $C_{max}/nR = 0.85$, as expected for $I = \frac{5}{2}$, together with $C(x) \propto x^2$ at $x < 0.2$ and $x = g_N \mu_N \times (1+K)B_{eff}/k_B T$. Here B_{eff} represents the effective field seen by the nuclei which results from the externally applied field B_e and from the enhanced nuclear Zeeman and indirect exchange interactions represented in Eq. (2). For further analysis we use $g_N = 1.71$,[7] and treat as parameters the hyperfine enhancement factor, $1+K$, and the effective field, B_{eff}. The data at $B_e = 1.5$, 3, and 6 T were analyzed with $B_{eff} = B_e$, neglecting internal interactions. The fit gives $1+K = 12.2$

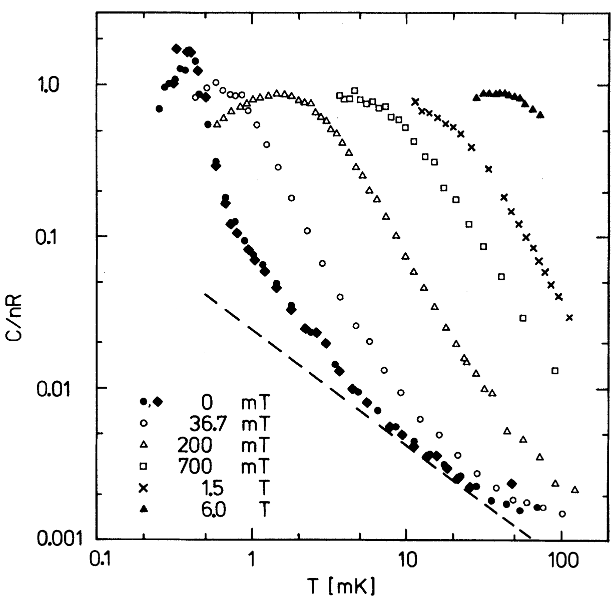

FIG. 2. Nuclear specific heat of $PrNi_5$ measured in the indicated magnetic fields. The dashed line represents the field-independent contribution $\Delta C/nR = 1.4 \times 10^{-4} T^{-0.75}$, which is apparent especially in the low-field data.

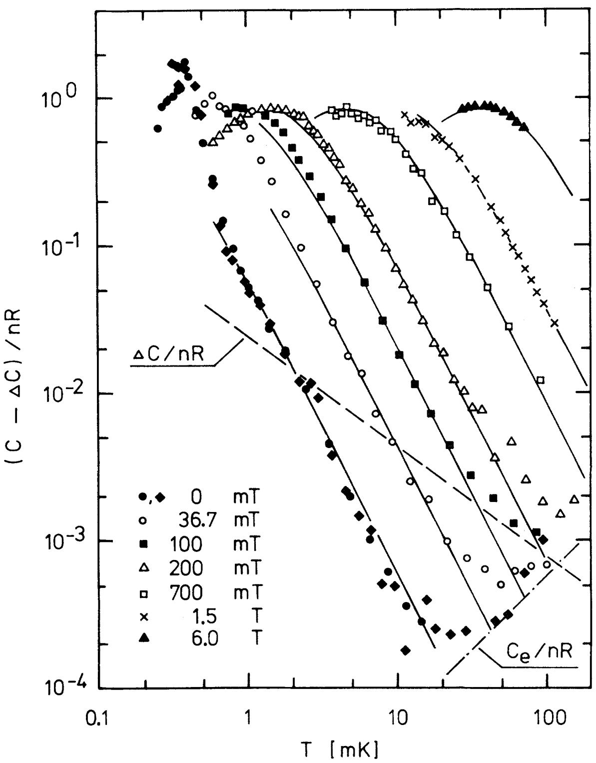

FIG. 3. Measured nuclear specific heat C/nR minus the field-independent contribution $\Delta C/nR = 1.4\times 10^{-4}T^{-0.75}$ (shown as the dashed line) as a function of temperature for the indicated magnetic fields. The dash-dotted line is the electronic contribution, $C_e/nR = 5.9\times 10^{-3}T$, to the specific heat from $PrNi_5$ (Ott *et al.*, Ref. 9), and from the addenda of our calorimeter.

± 0.5,[8] in agreement with the value 12.6 ± 0.5 calculated with $K=\chi A/g_J\mu_B g_N\mu_N$ and with use of $\chi = 0.062\pm 0.003$ emu/mole, the Van Vleck susceptibility measured at $T=3$ K on a 0.3 g sample of our $PrNi_5$.

The data at low fields and at temperatures above a few millikelvin show a contribution proportional to T^{-n} with $n<1$, in addition to the T^{-2} contribution; similar contributions have been observed earlier.[1,2] By plotting CT^2 vs T for all our measurements, we observe that this unexplained contribution is only very weakly field dependent and behaves as $\Delta C/nR = 1.4\times 10^{-4}T^{-0.75}$ (see Fig. 2). After subtracting ΔC from the measured specific heat, we could fit the data at $T>1$ mK in the paramagnetic range for *all* fields with a Schottky function treating $B_{\rm eff}$ as a free parameter; the results are shown in Fig. 3.

Using $1+K=12.2$, we find that in the paramagnetic range and for $B_e\le 0.2$ T, $B_{\rm eff}$ increases linearly with external field. The relation $B_{\rm eff}^2 = B_e^2+B_i^2$ does not give a constant internal field B_i; $B_i=18$ mT at $B_e=0$ and then increases with external field. For $B_e>0.2$ T, the difference between $B_{\rm eff}$ and B_e becomes too small to distinguish them reliably. A field dependence has also been observed for the NMR linewidth of Van Vleck paramagnets.[6,10] Well above the ordering temperature and at $B_e=0$, $CT^2\propto B_i^2\propto\sum_j J_{ij}^{N2}$. We then obtain $(\sum_j J_{ij}^{N2})^{1/2}/k_B = 0.066$ mK and $(\sum_j J_{ij}^{E2})^{1/2}/k_B = 0.39$ K for the exchange parameters in the paramagnetic range. The latter result is in reasonable agreement with the value 0.24 K derived from NMR data for $T>1$ K.[6]

The nuclear magnetic entropy of ^{141}Pr in $PrNi_5$ was reduced by up to 90% in our experiments.[4] We can therefore perform a new analysis of the specific heat by integrating it at each field down to 0 K, and then separate into a field-dependent part and into the field-independent internal nuclear magnetic energy at $T=0$,

$$-E_0=\int_0^\infty C\,dT=\int_0^{M_s}(\alpha M+B_e)\,dM$$

$$=(\tfrac{1}{2}\alpha M_s+B_e)M_s=(\tfrac{1}{2}B_0+B_e)M_s, \quad (4)$$

where M_s is the saturation magnetization and B_0 is the internal exchange field at $T=0$. For the integration, ΔC was subtracted from the measured specific heat above the temperature where the specific heat began to deviate from T^{-2} behavior. Subtraction of ΔC also at the low-temperature end would only change the results within the given error bars.

As shown in Fig. 4, E_0 is a linear function of B_e, even at fields smaller than the internal field, which means M_s is constant. We find from the intercept the internal field at saturation magnetization, $B_0=66\pm 10$ mT,[11] in agreement with the value of 65 ± 5 mT obtained from our analysis of the nuclear demagnetization behavior of $PrNi_5$.[4] M_s is constant and the results for B_0 confirm that the nuclei order ferromagnetically in $PrNi_5$. The slope of the line in Fig. 4 is the saturation magnetization, $M_s=0.15\pm 0.01$ J/T mole, from which we get for the enhanced nuclear magnetic moment $(0.027\pm 0.004)\mu_B$. This value agrees with $g_N\mu_N(1+K)I=0.028\mu_B$ for $1+K=12.2$.

If the internal interaction is due to indirect exchange, then B_0 is related to the exchange parameters by

$$\sum_j J_{ij}^N = g_N\mu_N(1+K)B_0/I,$$

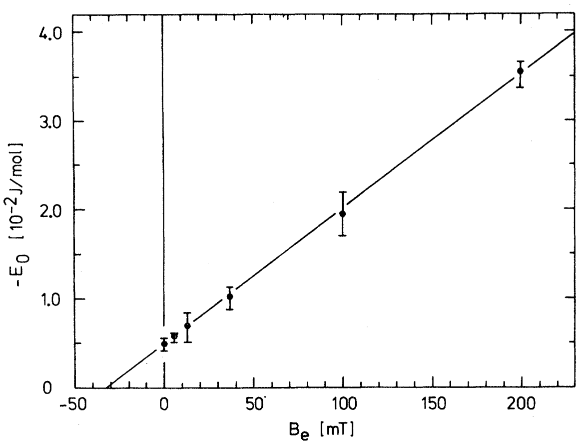

FIG. 4. The nuclear magnetic energy of $PrNi_5$ at $T = 0$ K obtained by integrating its specific heat as a function of applied magnetic field. The data indicate that an internal field of $B_0 = 66 \pm 10$ mT adds linearly to the applied field and that the order is ferromagnetic (see text).

giving $\sum_j J_{ij}^N/k_B = 0.20 \pm 0.04$ mK. This value and Eq. (3) give $\sum_j J_{ij}^E/k_B = 1.0 \pm 0.2$ K and a molecular field constant $\lambda = \sum_j J_{ij}^E/Ng_J^2\mu_B^2 = 4.2$ mole/emu.[6]

We have observed that the nuclear moments of ^{141}Pr in $PrNi_5$ order ferromagnetically at 0.4 mK and have shown that detailed, quantitative information about the interactions causing nuclear ordering phenomena in Van Vleck compounds can be obtained by studying the magnetic field and temperature dependence of the specific heat. Our data show the transition from spontaneous nuclear ordering to Schottky-like behavior when a magnetic field is applied. The interactions originate from the nuclear moments but are mediated by electrons; therefore the electronic exchange parameters can be determined. Because the ordering occurs at extremely low temperatures, the measured specific heat is not contaminated by electronic or lattice specific heat which usually have to be subtracted to reveal the magnetic contribution.

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