

Nuclear-induced ferromagnetism below 50 mK in the Van Vleck paramagnet PrCu_5

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In the intermetallic compound PrCu_5 the 3H_4 multiplet of the Pr ion is crystal field split such that the lowest state is a singlet, leading to a nearly temperature-independent Van Vleck susceptibility below 4.2 K. At very low temperatures (below ~ 50 mK) however, we observe ferromagnetic self-polarization of the singlet due to hyperfine and exchange interactions. Specific-heat and magnetization measurements down to 5 mK are presented and discussed in the molecular-field model of a coupled electron-nuclear system.

I. INTRODUCTION

Singlet-ground-state magnetism has been of much interest recently because of the various effects one can expect in a system of singlet-ground-state ions in the presence of both exchange and hyperfine interactions. It has been demonstrated both theoretically and experimentally that if exchange interactions exceed a critical value, the singlet ground state becomes unstable against self-polarization at low temperatures. The transition temperature,^{1,2} the ordered moment^{1,2} (at zero temperature) and even the excitation spectrum^{3,4} (as determined with neutron scattering techniques) of such overcritical induced moment systems have yielded to theoretical analyses.^{5,6} However, some details about the dynamical behavior of induced moment systems, such as the existence or non-existence of a soft mode at the transition temperature, are still controversial and unresolved. Singlet systems with far undercritical exchange interactions have been shown to remain Van Vleck paramagnetic into the mK range of temperature and eventually to undergo spontaneous nuclear magnetic order at very low temperatures. In such systems (e.g., PrTi_3 ,^{7,8} PrPt_5 ,⁹ PrCu_6 ¹⁰) the hyperfine interaction can lead to large enhancements of the local field at the Pr nuclei by a factor of 10 to 20 over the external applied field, a fact that has been utilized successfully in hyperfine enhanced nuclear cooling experiments to reach temperatures down to 1.6 mK. For near-critical exchange interactions, more complex magnetic ordering phenomena¹¹⁻¹⁴ can be expected whereby the self-polarization of the singlet ground state is triggered by the high enhanced susceptibility of the nuclear magnetic moments. The Pr-Cu phase diagram contains several phases which are well suited to the study of these phenomena: PrCu_6 ¹⁰ (which has an orthorhombic crystal structure) is a case of a singlet-ground-state system with weak exchange interactions which is useful for nuclear magnetic cooling down to at least 2.6 mK. In PrCu_2 ¹⁵ (also orthorhombic) the

exchange interactions are close to critical and lead to antiferromagnetic induced moment order below 54 mK. In PrCu_5 (which has the well-known CaCu_5 hexagonal structure) we find ferromagnetic order below about 50 mK, and the exchange interaction again seems to be close to critical in this case. PrCu_5 is the first exchange coupled singlet-ground-state system with near-critical exchange interactions for which we were able to obtain susceptibility and specific-heat data over a temperature interval extending well below its ordering temperature.

II. EXPERIMENTAL

A. Sample preparation

Appropriate amounts of Pr and Cu were arc melted together under a gettered Ar atmosphere. The polycrystalline samples so obtained were subsequently annealed for four weeks at 740 °C and quenched from this temperature. The color is reddish pink and the samples are stable against oxidation in air (in contrast to PrCu_2). X-ray and magnetic analysis showed that the samples were single phase after this heat treatment and had a lattice constant of $a = 5.125$, $c = 4.106$, in good agreement with Buschow and van der Groot¹⁶ and Dwight.¹⁷ Some single crystals were grown from the arc melt by dipping a cold tungsten rod into the melt and slowly pulling a crystal from it under constant rotation. These crystals grew with the c axis along the axis of rotation as evidenced by their perfect hexagonal magnetic anisotropy (see below). Annealing these crystals at 750 °C for three weeks, however, deteriorated them to some extent and made it somewhat difficult to determine their true magnetic anisotropy (see below).

B. Measurements above 1.2 K

Specific-heat measurements between 2 and 30 K were carried out in a heat-pulse calorimeter described earlier.¹⁸ Susceptibility and magnetization measurements were taken both with a pendulum

magnetometer as well as with a flux-gate magnetometer, the principle of which is described below.

C. Measurements below 1 K

The low-temperature data were obtained using a dilution refrigerator which is equipped for adiabatic demagnetization experiments. The refrigerator is of the standard type and is equipped both with a continuous (concentric-tube type) as well as with four-step heat exchangers (of the tubular shape compressed-powder type). The mixing chamber is made out of 1266 Stycast epoxy and contains a bundle of about 3000 No. 42 copper wires for heat exchange. The PrCu_5 sample [of approximately cylindrical shape (0.6 cm diam and 4 cm long)] is mounted below the mixing chamber in the tail section of the vacuum can; it is located in the center of a superconducting solenoid capable of generating 30 kOe. About 15 cm below the PrCu_5 sample, a AuIn_2 probe is located in a second superconducting solenoid. It serves as a nuclear susceptibility thermometer as described before.¹⁹ Thermal contacts are made via soft soldered joints (with indium and cadmium) and a strand of four Cu wires (of 0.1 cm diam each). A superconducting thermal switch (lead, $0.05 \times 0.05 \times 1$ cm) is built between the mixing chamber and the PrCu_5 sample, with a small niobium solenoid around it for its operation. A cerium magnesium nitrate thermometer, as described before,¹⁰ is always thermally connected to the sample. It serves to calibrate the AuIn_2 nuclear thermometer (which is used below 30 mK because of its short thermal relaxation time) as well as for direct temperature and specific-heat measurements above 30 mK. A thermal shield made out of 0.2-mm copper foil (split in order to reduce eddy current heating) surrounds sample and thermometers. It is attached to the continuous heat exchanger and kept at around 0.2 K. The magnetization of both PrCu_5 and AuIn_2

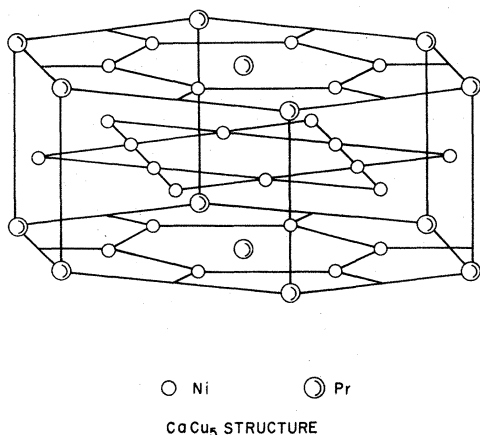


FIG. 1. CaCu_5 crystal structure of PrCu_5 .

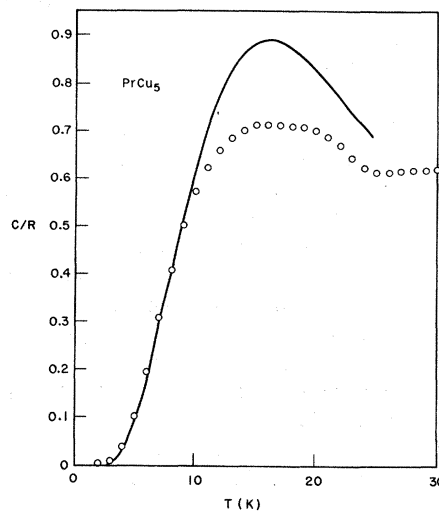


FIG. 2. Difference of molar specific heat between PrCu_5 and LaCu_5 , plotted vs temperature. The solid curve is the computed contribution from a singlet state at 28 K and a doublet state at 46 K above the ground state.

is measured using superconducting flux transformers: niobium pickup coils are wound onto the 0.2-K heat shield around the samples and connected to secondary niobium coils located outside the vacuum can in the 4.2-K liquid helium. These latter coils are well shielded magnetically from the superconducting (S. C.) solenoids. Sample flux changes can then be monitored inside these secondary coils using commercial flux-gate magnetometer probes, as described before.¹⁰ Changes in sample magnetization as a function of temperature in different persistent mode fields can be observed with this arrangement, and a high magnetic field stability is required during measurements. The latter is achieved by inserting one-layer superconducting shielding coils inside the S. C. solenoid bores (as described earlier)¹⁹ in order to shield out any field drifts in the persistent mode (especially after a demagnetization).

III. RESULTS

A. Properties above 1 K

PrCu_5 crystallizes in the hexagonal CaCu_5 structure shown in Fig. 1. All Pr ions are in equivalent positions and experience a crystal field of also hexagonal point symmetry. One can thus anticipate a series of three singlet and three doublet crystal-field levels.²⁰ In Fig. 2 we plot the difference of the molar specific heat of PrCu_5 and LaCu_5 (which should represent the Schottky-type specific heat due to the crystal-field levels of the Pr ions) versus temperature. At low temperatures, where only the ground state and the next excited state are appreciably populated, the molar specific heat (in units

of R) should be given by

$$\frac{C}{R} \cong \frac{g_1}{g_0} \left(\frac{\Delta}{kT} \right)^2 e^{-\Delta/kT}, \quad (1)$$

where Δ is the energy of the excited state and the g 's denote the multiplicity of the states. The analysis between 4.2 and 15 K yields $\Delta/k_B = 32$ K and $g_1 = g_0$. Below 4 K we find deviations from (1), the observed values of C/R being higher than predicted by (1). The origin of this extra contribution is not clear at present. Hyperfine specific-heat measurements (see below) show convincingly that the ground state is a singlet, so that the first excited state must also be a singlet located about 32 K above the ground state.

Starting from this knowledge of the two lowest-lying singlets we then tried to guess at the next higher level by fitting the data to the Schottky specific-heat formula

$$\frac{C}{R} = \frac{\sum_i \tau_i^2 e^{-\tau_i} + \sum_{i \neq j} \tau_i \tau_j (\tau_i - \tau_j)^2 e^{-(\tau_i + \tau_j)}}{(1 + \sum_i e^{-\tau_i})^2}. \quad (1a)$$

Here the indices i and j label the excited states individually (a doublet state being counted as two states with the same energy), and $\tau_i = \Delta_i/kT$. The sums ran over the excited states only, the formula being correct for a singlet ground state. The best computer fit to the data using Eq. (1a) is obtained by assuming the first singlet to lie 30 K and a next higher doublet 55 K above the ground state (solid line in Fig. 2). The fit reproduces properly the location of the Schottky-type peak at 16 K, but overestimates the height of the maximum. We believe that this "smearing out" of the Schottky peak is again due to the ferromagnetic exchange interactions which actually broaden the sharp crystal-field levels into bands of collective excitations. The same behavior was observed in specific-heat measurements of Van Vleck paramagnetic $(\text{Pr}_x\text{La}_{1-x})_3\text{Tl}$ alloys, where the ferromagnetic exchange interactions increase with the concentration x . As we show below, a sequence singlet-singlet-doublet for the lowest levels is indeed consistent with a point-charge crystal-field calculation with reasonable assumptions of the relative strength of second-, fourth-, and sixth-order crystal-field parameters.

The inverse low-field susceptibility of a polycrystalline sample below room temperature is shown in Figs. 3(a) and 3(b). It initially follows a Curie-Weiss law down to about 30 K with a slope corresponding to an effective moment of $3.36\mu_B$ and $\theta = +12$ K. The free effective ion moment is $3.58\mu_B$. Below 20 K, the susceptibility flattens out in a manner characteristic of a nonmagnetic ground state (Van Vleck paramagnetism). The

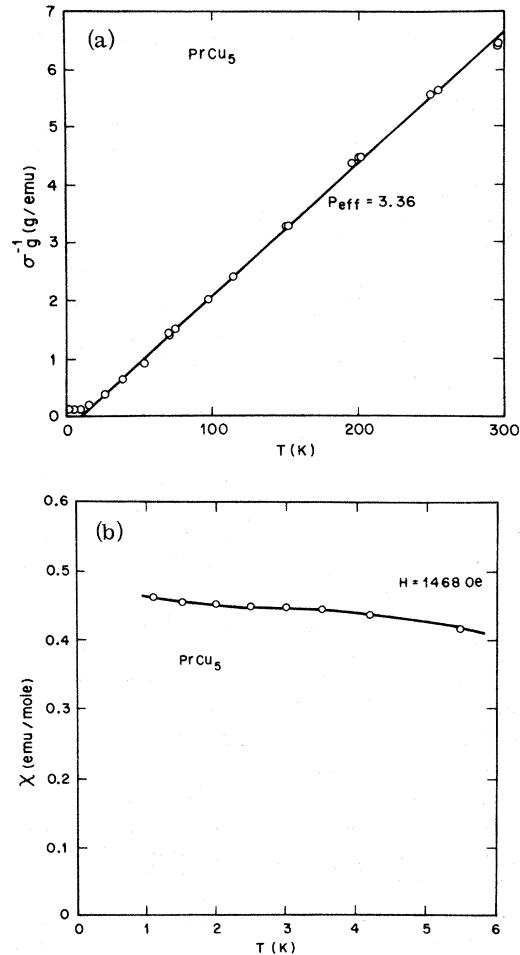


FIG. 3. (a) Inverse magnetic moment of PrCu_5 (observed in 14 240 Oe) plotted against temperature. The slope of the solid line corresponds to the Curie law with effective moments of $3.36\mu_B$ per ion. (b) Low-field susceptibility of PrCu_5 at low temperatures.

value of χ_{VV} at 1 K equals 0.455 emu/mole, which is surprisingly large and again points to a strong ferromagnetic exchange enhancement. Figure 4 shows the magnetization as a function of applied field at 1.2 K. Typical Van Vleck (VV) paramagnetic behavior is observed. The decrease of the VV susceptibility with increasing magnetic field is a crystal-field effect and is enhanced by the exchange interactions (i.e., the susceptibility in high fields is less exchange enhanced than in low fields). In order to compare this polycrystalline value with expectations, it is necessary to know the susceptibility of a single crystal both in the direction of the c axis and normal to it. Single crystals as grown from the arc melt (see above) did indeed show perfect magnetic hexagonal symmetry with the c axis in the pulling direction (probe axis), but with susceptibility values at 4.2 K of 0.503 emu/mole in

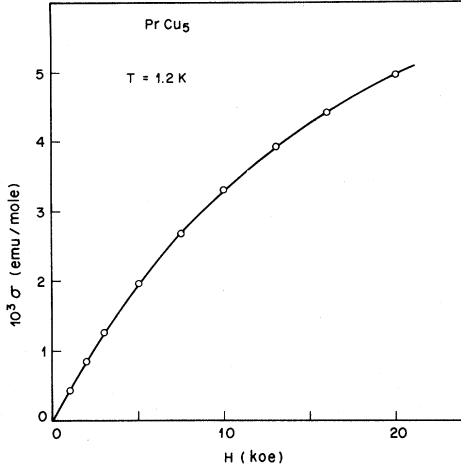


FIG. 4. Magnetization of PrCu_5 at 1.2 K as a function of applied field.

the direction of the c axis and 0.180 emu/mole normal to it. In agreement with this, the unannealed leftover button (polycrystalline) showed a value of χ at 4.2 K of 0.29 emu/mole. X-ray pictures of the material indicated the correct phase, but with somewhat fuzzy Bragg reflections. After annealing both this crystal and the leftover button at 750 °C for three weeks, the button again showed the correct polycrystalline value of 0.455 emu/mole, but the "single crystal" unfortunately no longer showed perfect hexagonal symmetry, indicating more than one preferred orientation. In a particular direction normal to the probe axis, a susceptibility value as low as 0.15 emu/mole was observed, while the probe axis value was as large as 0.7 emu/mole. If the lowest value is indeed the a -axis value, then the true c -axis susceptibility has to be 1.05 emu/mole at 4.2 K in order to agree with the polycrystalline value. The solid lines of Fig. 5 show the observed temperature dependence of the " a -axis" susceptibility as well as of the c -axis susceptibility deduced from it and from Figs. 3(a) and 3(b).

We can now try to fit these observed susceptibilities as well as the specific heat with a crystal-field-level scheme, taking into account the presence of ferromagnetic exchange interactions in molecular field (MF) approximation. The Hamiltonian for crystal fields of hexagonal symmetry can be written in the form

$$\mathcal{H} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_6^6 O_6^6 \quad (2)$$

in Stevens's operator equivalent notation. Segal and Wallace²⁰ have calculated all eigenvalues and eigenvectors for the point-charge model (where $B_6^0/B_6^6 = \frac{8}{77}$) and for a hexagonal close-packed structure ($c/a = 1.63$), for which the second-order term

B_2^0 vanishes. For pure point charges we have $B_4 > 0$, $B_6 < 0$, and $|B_6| \ll |B_4|$, and the parameter $x = (B_4 F_4 / B_6 F_6) / (1 + |B_4 F_4 / B_6 F_6|)$ (p. 354 in Ref. 20) equals 0.944. The four lowest crystal-field levels in this case, listed in order of decreasing energy, are (see Fig. 11 of Ref. 20)

$$\Gamma_5(\text{doublet}): a_2 | \mp 2 \rangle + a_4 | \pm 4 \rangle,$$

$$\Gamma_3(\text{singlet}): \frac{1}{\sqrt{2}} | -3 \rangle + \frac{1}{\sqrt{2}} | 3 \rangle,$$

$$\Gamma_4(\text{singlet}): \frac{1}{\sqrt{3}} | -3 \rangle - \frac{1}{\sqrt{2}} | 3 \rangle = \text{ground state}.$$

This would indeed be in qualitative agreement with our conclusions from specific-heat measurements. By choosing $x = 0.70$ and the overall crystal-field splitting to be 101 K, the Γ_3 and Γ_5 states, respectively, would be at 30 and 61 K above the Γ_4 ground state, in fair quantitative agreement with our specific-heat result. The low-field susceptibilities can be calculated from the wave functions and their energies by the Van Vleck formula

$$\chi_{\parallel}(\text{per mole}) = \frac{L \mu_B^2 g_J^2}{kT} \frac{\sum_i \langle J_{\parallel, i} \rangle^2 + 2 \Lambda_i kT}{\sum_i e^{-E_i/kT}} e^{-E_i/kT} \quad (3)$$

(and similarly for χ_{\perp}), where L is Avogadro's number, the sum is over all $2J+1$ levels of the multiplet, $\langle J_{\parallel, i} \rangle$ is the expectation value of angular momentum of each level in the c -direction, and $\Lambda_i = \sum_{j \neq i} \alpha_{ij}^2 / (E_i - E_j)$, and $\alpha_{ij} = \langle \varphi_i | J_{\parallel} | \varphi_j \rangle$ is the matrix element of angular momentum between levels i and j . When applying this formula to the above

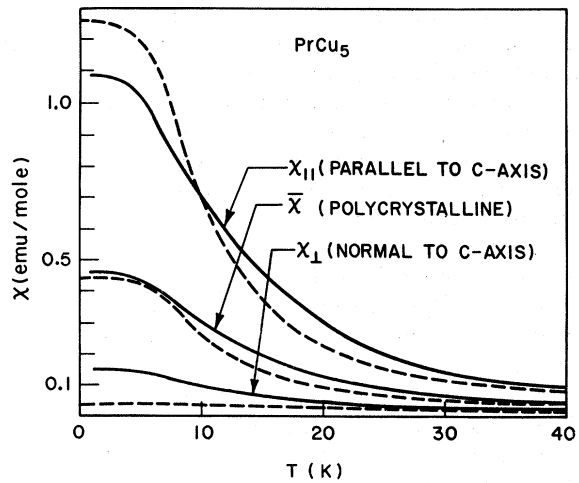


FIG. 5. Anisotropy of the observed low-field susceptibility in a single crystal of PrCu_5 (solid lines). χ_{\parallel} is deduced from χ_{\perp} and $\bar{\chi}$ polycrystalline (see text). The dashed lines are computed using the wave functions in Table I and a molecular field exchange parameter λ of 6.2 mole/emu (see text).

level scheme ($x = 0.70$, overall splitting = 101 K) we find that an appreciable anisotropy in the susceptibility develops only below 25 K, whereas the observed anisotropy persists to much higher temperatures (at 40 K it is still a factor of four). In order to improve the theoretical fit to the observed susceptibility we have included the second-order term in the Hamiltonian (2). Starting from the wave functions and energies given in Ref. 20 we diagonalize the additional perturbation B_2O_2 , which only mixes the two Γ_5 states. Rewriting the Hamiltonian in the form

$$H = W \left\{ (1 - |y|) \frac{O_2}{F_2} + y \left[x \frac{O_2}{F_4} + (1 - |x|) \frac{O_6}{F_6} \right] \right\}, \quad (4)$$

with

$$B_2 F_2 = (1 - |y|) W,$$

$$B_4 B_4 = xy W,$$

$$B_6 F_6 = y(1 - |x|) W.$$

and $F_2 = 1$, $F_4 = 60$, $F_6 = -1260$ being multiplicative factors contained in the respective operators O_2 , O_4 , and O_6 , we obtain a much better fit to the susceptibility with the following choice of parameters: $x = 0.80$, $y = -0.49$, and $W/k_B = -7.88$ K. The corresponding wave functions and energies are tabulated in Table I.

Computer calculations of the crystal-field susceptibilities $\chi_{c||}$ and $\chi_{c\perp}$ in the two principal directions using Eq. (3) and the wave functions in Table I are plotted in Fig. 6. The actual susceptibilities are exchange enhanced over the crystal-field susceptibilities (in MF approximation) by

$$\chi = \frac{\chi_c}{1 - \lambda \chi_c}. \quad (5)$$

A best fit to our experimental data is obtained by assuming $\lambda = 6.2$ mole/emu. This yields the dashed lines in Fig. 5. It is thus apparent that the large observed anisotropy at low temperatures is mostly due to the strong ferromagnetic exchange enhancement, which equals 8.9 along the c axis and 1.17 normal to it. As can be seen, the predicted anisot-

TABLE I. Wave functions and energies of the crystal-field-split 3H_4 multiplet of Pr^{3+} , calculated in the point-charge model for $x = 0.8$, $y = -0.494$, and $W/k_B = -7.88$ K (see text).

Wave function ($H=0$)	E/k_B (K)
$\Gamma_1 = 0\rangle$	241.7
$\Gamma_6 = \pm 1\rangle$	218.1
$\Gamma_5^2 = -0.1404 \pm 2\rangle + 0.8834 \mp 4\rangle$	138.0
$\Gamma_5^3 = 0.8834 \mp 2\rangle + 0.1404 \pm 4\rangle$	55.1
$\Gamma_3 = \frac{1}{\sqrt{2}} -3\rangle + \frac{1}{\sqrt{2}} 3\rangle$	30.0
$\Gamma_4 = \frac{1}{\sqrt{2}} -3\rangle - \frac{1}{\sqrt{2}} 3\rangle$	0.0

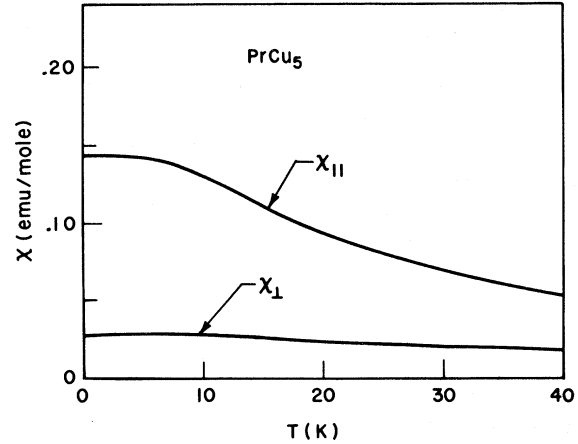


FIG. 6. Crystal-field susceptibilities along and normal to the c axis computed from the wave functions in Table I.

ropy at 1 K is appreciably larger than observed, which may again reflect the fact that we did not have a perfect single crystal for our measurements (see above). The calculated polycrystalline value, however, is in fair agreement with our observations.

It should be pointed out that the value of λ is very sensitive to the calculated value of $\bar{\chi}$ for polycrystalline material at low temperatures (~ 1 K). Also, the value of $\chi_{c||}$ at 1 K is insensitive to the choice of the crystal-field parameters x and y , as $\chi_{c||}$ arises only through the mixing of the Γ_3 and Γ_4 wave functions. A first approximation for the value of λ can thus be obtained by setting $\chi_{c\perp} = 0$ (i. e., by neglecting the states above the Γ_3 state) and using the equation

$$\bar{\chi} = \frac{1}{3} \chi_{c||} = \frac{1}{3} \frac{\chi_{c||}}{1 - \lambda \chi_{c||}}. \quad (6)$$

With $\bar{\chi} = 0.455$ emu/mole and $\chi_{c||} = 0.144$ emu/mole we obtain from Eq. (6) $\lambda = 6.21$ mole/emu, a value practically identical to the one deduced above on the basis of the complete level scheme.

We can thus say that both the thermal and magnetic properties of PrCu_5 above 1 K are rather well explained with the crystal-field-level scheme in Table I which was calculated from a point-charge model, when at the same time ferromagnetic exchange interactions are assumed. The largest critical parameter is observed in the c axis and is equal to $\lambda \chi_{c||} = 0.89$ (using $\lambda = 6.2$ mole/emu), rather close to the critical value of 1 for spontaneous induced moment order.

B. Properties below 1 K

Only polycrystalline samples were used for the very-low-temperature experiments. Because of

the large Van Vleck susceptibility of PrCu_5 , large hyperfine fields (of order 86 times the applied field, see below) can be induced at the Pr nuclei with moderate applied fields, and the technique of hyperfine enhanced nuclear magnetic cooling can be effectively used to cool the material to very low temperatures. If the Van Vleck susceptibility is temperature independent, the local field at the Pr nuclei is given by

$$\begin{aligned} H_{\text{loc}} &= H_{\text{ext}} + h_f \chi_{\text{VV}} H_{\text{ext}} \\ &= H_{\text{ext}}(1 + h_f \chi_{\text{VV}}) = H_{\text{ext}}(1 + K) \end{aligned} \quad (7)$$

and is thus enhanced by $1 + K$ over the external applied field. Here h_f is a hyperfine coupling constant defined by

$$h_f = \frac{A}{g_N \mu_N g_J \mu_B L} = 187.7 \text{ mole/emu}, \quad (8)$$

where we have used the values $g_N = 1.71$, $g_J = 0.8$, and $A/K = 0.0525 \text{ K}$. In our polycrystalline sample $\bar{\chi}_{\text{VV}} = 0.455 \text{ emu/mole}$, and we thus get an average hyperfine enhancement factor

$$(1 + K)_{\text{av}} = 86.4, \quad (9)$$

which is the largest one observed to date in an intermetallic praseodymium compound. It leads to a very large enhancement of the nuclear magnetic susceptibility, which is superimposed on the Van Vleck susceptibility and given by

$$\chi_N = \frac{C_N}{T} \langle (1 + K)^2 \rangle_{\text{av}}. \quad (10)$$

Here C_N is the bare nuclear magnetic Curie constant of Pr^{3+} , which is equal to $9.50 \times 10^{-7} \text{ emuK/mole}$. Now in a magnetically anisotropic material like PrCu_5 , the average of the square of the susceptibility is not equal to the square of the average susceptibility, and likewise for the hyperfine enhancement factor. If we denote the magnetic anisotropy by $a = \chi_{\perp} / \chi_{\parallel}$, it is easily shown that the two averages are related by

$$\langle \chi^2 \rangle_{\text{av}} = (\bar{\chi})^2 \frac{9}{5} \frac{\frac{8}{3} a^2 + \frac{4}{3} a + 1}{4a^2 + 4a + 1}, \quad (11)$$

where the bar means average over all directions. Our measurements above 1 K indicate $a = 0.143$; from our calculated and exchange enhanced susceptibilities at 1 K we would deduce $a = 0.019$. Since our anisotropy measurements were done on an imperfect single crystal (see above) we adopt the latter value and obtain

$$\langle \chi^2 \rangle_{\text{av}} = 1.71 (\bar{\chi})^2 \quad (12)$$

and likewise

$$\langle (1 + K)^2 \rangle_{\text{av}} = 1.71 (1 + K)_{\text{av}}^2. \quad (13)$$

Using the value 86.4 obtained from Eq. (8), for

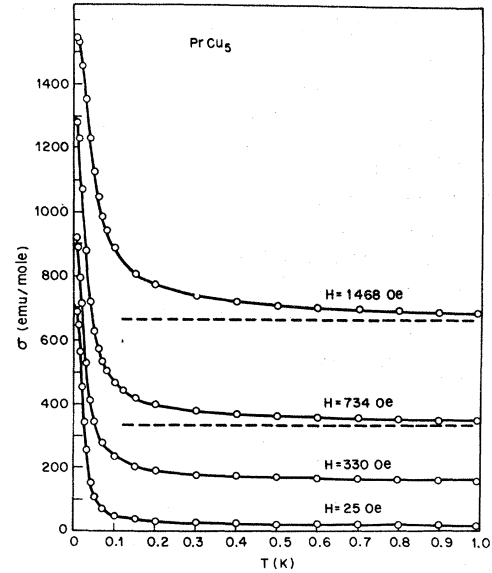


FIG. 7. Molar magnetic moments of polycrystalline PrCu_5 in different fields at temperatures below 1 K.

$(1 + K)_{\text{av}}$, the expected enhanced nuclear susceptibility would then be

$$\chi_{N \text{ theor}} = 1.21 \times 10^{-2} \text{ emuK/mole}. \quad (14)$$

Magnetization and specific-heat measurements below 1 K were carried out as follows: The sample was first precooled in a field of 25 kOe to around 40 mK with the dilution refrigerator. It was then demagnetized to a fixed field, and the change in magnetization was observed on warming the cold sample up to 1 K. Demagnetization to 25 Oe resulted in a lowest end temperature of 4.5 mK. Measurements were carried out in four fields, namely 25, 330, 734, and 1468 Oe, and the results are shown in Fig. 7. The hyperfine enhanced nuclear susceptibility which is superimposed on the Van Vleck susceptibility (dashed lines) is clearly visible already at 1 K. It can further be seen that an additional moment, more or less independent of field, develops below 0.1 K. Magnetization curves at constant temperature deduced from Fig. 7 are shown in Fig. 8. There is clear evidence of an ordered ferromagnetic moment at zero degrees of magnitude:

$$\sigma_{\text{sat}} = 940 \text{ emu/mole}. \quad (15)$$

According to Fig. 7, the ordered moment disappears above about 40 mK. However, even in a field as low as 25 Oe there is no clear evidence of a sharp phase transition in this vicinity. In Fig. 9 we plot the inverse of the difference between the observed susceptibility and the Van Vleck susceptibility for two different fields versus temperature

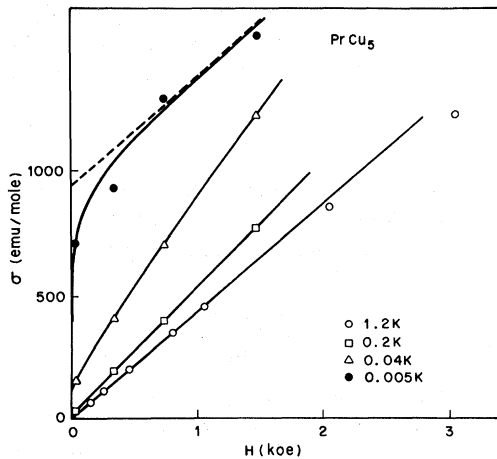


FIG. 8. Magnetic moment of polycrystalline PrCu_5 vs applied field at four different temperatures below 1.2 K.

below 1 K in the paramagnetic regime. The Van Vleck susceptibilities in 1468 and 734 Oe have been evaluated by fitting the data to the equation

$$\sigma T = \sigma_{\text{VV}} T + \chi_N H,$$

and the values found for these two fields are 0.455 and 0.459 emu/mole, respectively. We observe indeed a Curie-Weiss law with a mean Curie constant of 1.6×10^{-2} emuK/mole and a Curie-Weiss temperature of 10 ± 10 mK. This is considerably larger than the theoretical value 1.21×10^{-2} emuK/mole deduced above and casts some doubt on this method of analysis. While it has been demonstrated before¹³ in a number of cases that for smaller exchange interactions (and lower ordering temperatures), the susceptibility is indeed separable into a (temperature independent) Van Vleck part and a "nuclear" part, this may no longer apply for PrCu_5 where the exchange interactions are closer to the

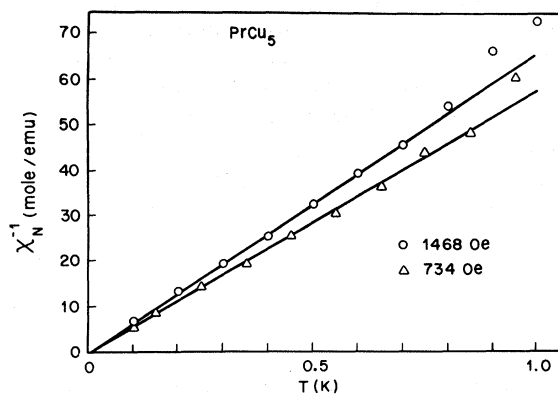


FIG. 9. Plot vs temperature of the inverse of the difference between the observed and the Van Vleck susceptibility for two different applied fields (see text).

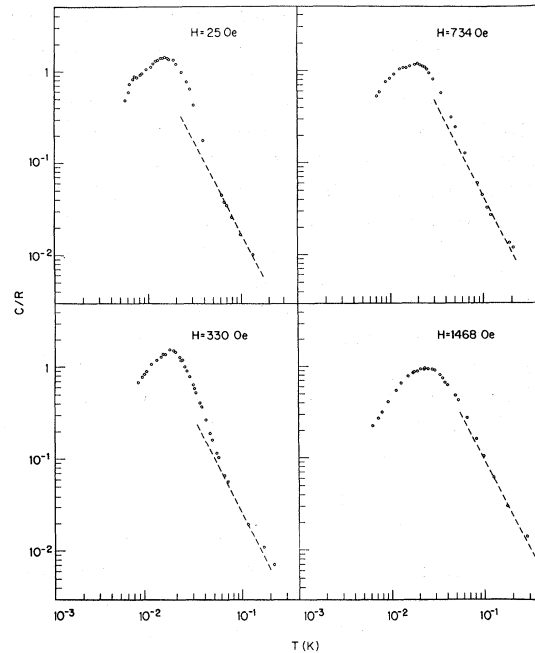


FIG. 10. Observed molar specific heat of PrCu_5 in four different applied fields at very low temperatures.

critical value for induced moment order. In other words, the hyperfine enhanced nuclear susceptibility may eventually no longer be treated as a second-order effect, and one should rather consider the total susceptibility of the combined electron-nuclear system. However, we show below in the discussion that when doing this in MF approximation one recovers an expression for the temperature-dependent part of the susceptibility which is very similar to (10), even for near-critical exchange interactions. The second-order estimate of the ordered moment at zero temperature is given by

$$\sigma_{\text{max}} = \frac{A}{g_J \mu_B} \chi_{\text{VV}} I = 1111 \text{ emu/mole.} \quad (16)$$

Surprisingly, this is in rather good agreement with our observation [Eq. (15)].

The specific-heat measurements in the four fields are shown in Fig. 10. Again it can be seen that there is no sharp transition. Instead, we observe an initial $1/T^2$ rise which corresponds to the hyperfine enhanced nuclear Zeeman splitting in the applied field, then below about 70 mK a more rapid rise to a maximum centered at about 17 mK in 25 and 330 Oe and shifted to 20 and 25 mK, respectively, in 734 and 1468 Oe is observed. In the two higher fields, these specific-heat anomalies look qualitatively like nuclear Schottky-type anomalies. In lower fields, they look like sharpened-up Schottky-type anomalies and can be interpreted as arising from a temperature-dependent hyperfine field which (in

25 Oe) starts developing rapidly below about 50 mK and attains its full value around 10 mK. It is thus obvious that no long-range order exists among the Pr nuclei close to T_c . However, long-range order must be developing in the system of the 4f electrons of the Pr ions. It is obviously present below, say, 10 mK and gradually develops below about 50 mK. We have evaluated graphically the entropies between 0 and 400 mK by extrapolation and obtain the values $\Delta S/R = 2.03, 2.05, 1.95,$ and 1.75 for the four fields 25, 330, 734, and 1468 Oe. These values are reasonably close to the ideal value of $\ln 6 = 1.792$ and are consistent with the assumption that the specific-heat anomalies are entirely due to the six nuclear substates in the Pr singlet ground state.

IV. DISCUSSION

The data presented above show that PrCu_5 is a Van Vleck paramagnet with exchange interactions about 0.89 times the critical value necessary for spontaneous induced moment order. Thus PrCu_5 is a near-critical singlet-ground-state system which orders magnetically below ~ 20 to 50 mK only because of hyperfine interactions. Such coupled electron-nuclear magnetic systems have been treated theoretically for the first time by Murao in the molecular field (MF) approximation.^{11,12} He was the first to point out that when hyperfine interactions are included, the transition temperature of an induced moment system is a continuous function of the critical parameter $\lambda\chi_c$ across the critical value of 1, with T_c showing the characteristic rapid drop into the nuclear ordering regime at $\lambda\chi_c$ just below 1. The electron-nuclear Hamiltonian to be considered has the form

$$\mathcal{H} = \mathcal{H}_c - 2K_0(\vec{J})\vec{J} - A\vec{J} \cdot \vec{I}, \quad (17)$$

where $\langle J \rangle$ is the total temperature-dependent expectation value of 4f angular momentum and $K_0 = \sum_{j>i} K_{ij} = \frac{1}{2} \lambda g_j^2 \mu_B^2$ (K_{ij} = exchange interaction between ions i and j , λ = molecular field exchange constant). \mathcal{H}_c is the crystal-field Hamiltonian which in our case leads to the eigenfunctions and energies tabulated in Table I. If one acts with (17) on these eigenfunctions and their nuclear substates and diagonalizes the Hamiltonian, one gets a self-consistent equation for $\langle J \rangle$ which can generally be solved only by iteration on a computer. Triplet and White¹⁴ have presented solutions for $\langle J \rangle$ as a function of T and the critical parameter $\lambda\chi_c$ for the case of Pr^{3+} , assuming two singlet states (having only a matrix element of \vec{J}_z equal to 2.582 (in units of \hbar). For our energy separation of $k_B \times 30$ K and our critical parameter $\lambda\chi_c = 0.89$ (the largest one, observed along the c axis), the computer plots of Ref. 14 would suggest a transition temperature of about 35 mK, in fair agreement with what we ob-

serve. We have shown before¹³ that a good approximation for the transition temperature can also be obtained from the MF formula for the susceptibility,

$$\chi = \frac{\chi_0}{1 - \lambda\chi_0}, \quad (18)$$

provided that χ_0 is now taken to be the sum of the (crystal-field) Van Vleck susceptibility and the hyperfine- (but not exchange-) enhanced nuclear susceptibility:

$$\chi = \frac{\chi_{c||} + (C_N/T)(1 + K_{c||})^2}{1 - \lambda\chi_{c||} - \lambda'(C_N/T)(1 + K_{c||})^2}. \quad (19)$$

The transition temperature T_c then would be the temperature for which the denominator of (19) is zero. With $K_{c||} = \hbar_f \times \chi_{c||} = 27.03$ [Eq. (7)], we again take the maximum values of χ and λ along the c axis to be the crucial ones for determining T_c , the denominator in (18) is zero for (we have set $\lambda \approx \lambda'$)

$$T_c = \frac{\lambda C_N (1 + K_{c||})^2}{1 - \lambda\chi_c} = 42.1 \text{ mK} \quad (20)$$

which is similar to the result of Ref. 14. [Equation (20) applies if we can neglect the temperature variation of χ_c below T_c .] Previously,¹³ we have argued that in other Pr singlet-ground-state compounds with smaller exchange interactions (and hence lower ordering temperatures), better agreement with observed (or extrapolated) ordering temperatures is obtained when the actual observed value of K rather than the crystal field value K_c (which is not enhanced by exchange interactions) is used in (20). However, using $K_{||}$ instead of $K_{c||}$ in (20) yields a T_c of 2.10 K, which is much too high [roughly $(1 - \lambda\chi_c)^{-2} = (\frac{1}{0.11})^2$ higher than 37.9 mK]. Thus the simple MF estimate for T_c seems to work rather well for PrCu_5 , especially in view of the fact that our measurements can pinpoint T_c no closer than being between 20 and 50 mK (see below).

We now discuss the susceptibility above T_c in the light of formula (19). In a polycrystal, we would have to average (19) over all crystalline directions, which would be rather difficult to do analytically. Instead, we first separate out the temperature-independent parts and write (for a particular crystal orientation)

$$\chi - \chi_{vv} = \frac{\chi_c + (C_N/T)(1 + K_c)^2}{1 - \lambda\chi_c - \lambda'(C_N/T)(1 + K_c)^2} - \frac{\chi_c}{1 - \lambda\chi_c}, \quad (21)$$

with

$$\chi_{vv} = \frac{\chi_c}{1 - \lambda\chi_c}.$$

$\chi - \chi_{vv}$ is the quantity which we called the hyperfine and exchange enhanced nuclear susceptibility χ_N (see above and Fig. 9). With the approximation $\lambda' \cong \lambda$ and some simple algebra we can rewrite (20)

in the form

$$\chi_N = \chi - \chi_{VV} = \frac{C_N[(1+K_c)/(1-\lambda\chi_c)]^2}{T-\theta} = \frac{C_N(1+K)^2}{T-\theta}, \quad (22)$$

$$\theta = \lambda C_N(1+K_c)^2/(1-\lambda\chi_c). \quad (23)$$

Thus we see that the exchange enhancement of χ_c at very low temperatures [which arises because of the term $\lambda'(C_N/T)(1+K_c)^2$ in (19) as well as the exchange enhancement of the hyperfine enhanced (crystal field only) nuclear susceptibility] can be summed up into the hyperfine *and* exchange enhanced nuclear susceptibility which was derived before from the local nuclear field point of view [Eq. (10)]. θ in Eq. (22) is again the ordering temperature T_c [similar to (20)]. As pointed out recently by Murao,²¹ T_c must be proportional to $(1-\lambda\chi_c)^{-1}$ in strict MF approximation, in contrast to the $(1-\lambda\chi_c)^{-2} \times (1-|\lambda|\chi_c)^{-1}$ dependence with which we have tried to explain electron-nuclear ordering phenomena in PrTl₃, PrCu₆, and PrCu₂.¹³ Much above T_c , the nuclear susceptibility χ_N is now easy to average over all directions, and by doing so we recover Eq. (10). As pointed out above, the agreement of (10) with our observation is somewhat less satisfactory, in that our experimental nuclear susceptibility (Fig. 9) is consistent with an average hyperfine enhancement factor $(1+K)_{av}$ of 99.2 while the value deduced from the observed and crystal-field Van Vleck susceptibilities is 86.4. In spite of that, we can still say that both the observed susceptibility

above T_c and the ferromagnetic saturation moment much below T_c are in fair agreement with MF estimates of the coupled electron-nuclear system. On the other hand, MF theory predicts a sharp second-order transition at about 37 mK, which is not obviously borne out by the data. We may not expect to see an anomaly in the specific heat at T_c since we are still in the regime of electronic induced moment order where the hyperfine splitting of the singlet ground state just below T_c is still smaller than kT_c ,¹³ (and hence no appreciable lowering of the nuclear entropy can be expected at T_c). However, we would have expected to see a sudden increase of χ at T_c in our lowest field of 23 Oe, but this is not observed. Thus it may be that the nuclear induced ferromagnetic polarization of the singlet ground state happens inherently in a continuous fashion without any sharply defined transition temperature and has to be explained by going beyond MF theory and taking short-range correlations between ions into account. The rather high values of the nuclear specific heat even above T_c support this assumption and indicate that there are already small ferromagnetic polarizations between neighboring ions in this temperature range that are longer lived than inverse nuclear precession times.

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