netostatic-mode widths at low frequencies and range from only $\Delta H \simeq 4$ to 9 Oe. This suggests that the broadening of the uniform mode at higher frequencies in a flat disk arises from stronger excitation of magnetostatic modes nearly degenerate with the uniform mode, and might explain why narrow resonance lines were not observed in the original 240-GHz AFMR studies.[6]

The line shape and position of the AFMR in MnF_2 is strongly power dependent at moderately high microwave power levels ($H_{rf} \sim 0.05$ Oe).[14] A detailed account of these effects and the temperature dependence of the linewidths will be published elsewhere.

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Observation of Cooperative Nuclear Magnetic Order in $PrCu_2$ below 54 mK

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Magnetic-susceptibility and specific-heat measurements in Van Vleck paramagnetic $PrCu_2$ down to 30 mK reveal that the Pr nuclei enter an antiferromagnetically ordered state below 54 mK. This high nuclear ordering temperature results from magnetic exchange interactions between the Pr ions, which must be close to the critical value necessary for spontaneous electronic magnetic order in this compound.

In the presence of weak exchange interactions between Van Vleck paramagnetic ions, an indirect exchange coupling between the nuclei of these ions results due to second-order hyperfine effects. The physical mechanism of this coupling can be described as an exchange coupling of $4f$ angular moments $\langle J_{4f} \rangle$ which the hyperfine interaction admixes to the $2I+1$ nuclear substates of the singlet ground state. Alternatively, one can also describe it as a Suhl-Nakamura[1]–type mechanism in which a nuclear spin flip at one site excites a collective crystal-field excitation[2,3] (through the hyperfine coupling) which can be reabsorbed by another nucleus at a neighboring site. This coupling is expected to lead to nuclear ferromagnetism or antiferromagnetism at low temperatures.[4-7] If the exchange interactions between the singlet ground-state ions exceed a critical value, the singlet ground state becomes unstable against spontaneous mixing with the higher excited crystal-field states below some (electronic) magnetic ordering temperature.[8] In this case the nuclear moments will align in the local hyperfine field of the exchange-induced ordered moment at low temperatures. We have found experimentally that the Pr nuclei in the compound $PrCu_2$ order antiferromagnetically below 54 mK. This is the first example of an unusually high cooperative nuclear ordering temperate, and we believe that in $PrCu_2$ the exchange interaction between Pr ions must be less than (but close to) the critical value necessary for electronic magnetic order.

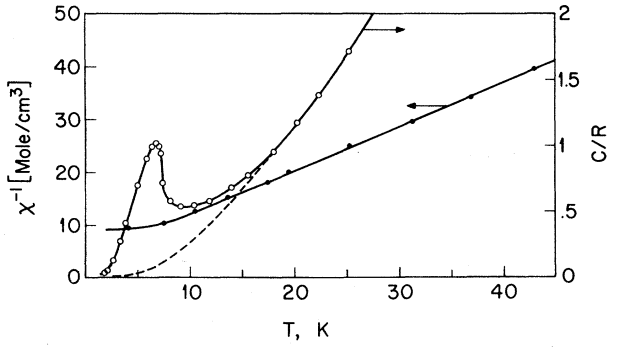

FIG. 1. Molar susceptibility (closed circles) and specific heat (open circles) of $PrCu_2$ above 2 K.

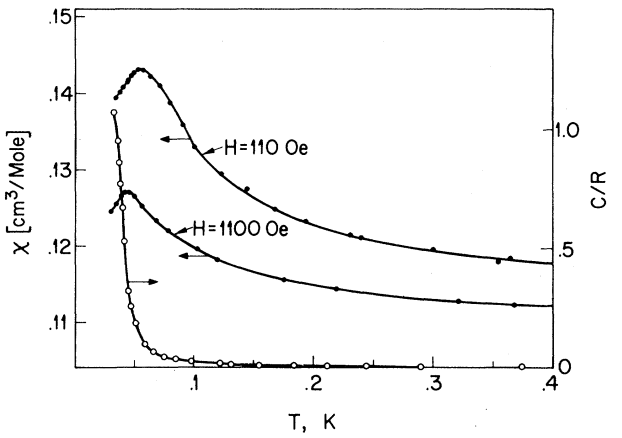

FIG. 2. Molar susceptibility (closed circles) and specific heat of $PrCu_2$ (open circles) below 0.5 K.

$PrCu_2$ crystallizes in the orthorhombic $CeCu_2$ structure. There are four equivalent Pr sites in the unit cell. Each is surrounded by two distorted hexagons of Cu ions and four Pr ions lying at the corners of a distorted tetrahedron.[9] The $^3H_4$ multiplet of Pr^{3+} is split by the orthorhombic crystal field into singlets. Magnetic-susceptibility measurements on polycrystalline $PrCu_2$ (Fig. 1) show nearly temperature-independent Van Vleck paramagnetic behavior below 4.2 K. This confirms that the lowest crystal-field state is a singlet. Specific-heat measurements down to 2 K (Fig. 1) show a large anomaly centered around 6 K. Since there is no susceptibility anomaly around 6 K, the anomaly cannot be due to the onset of magnetic order, but must originate from the first excited singlet state. This assumption is supported first by the amount of entropy associated with the specific-heat anomaly: Using the dashed-line extrapolation in Fig. 1 to subtract the background specific heat (mostly the contribution from higher-lying crystal-field states and lattice specific heat), the entropy under the anomaly is $0.72R$ per mole. This is close to the value $R \ln 2$ ($0.693R$) expected for the entropy of two states. Secondly, we can conclude from hyperfine specific-heat measurements below 1 K (see below) that no ordered moment larger than 4.5% of the full Pr^{3+} moment can exist below 1 K. This again is consistent with the assumption that the Pr^{3+} ions are in a singlet ground state at low temperatures. From an analysis of the tail of the Schottky-type specific-heat anomaly between 2 and 4 K, we estimate that the two lowest singlets are spaced apart in energy by k(13 K).

Measurements of both the specific heat and the magnetic susceptibility down to 30 mK were carried out in a dilution refrigerator. Thermal contact to the $PrCu_2$ sample was made by spot welding Pt wires to it and soft soldering them (with Cd metal) to ca. 3000 No. 40 Cu wires. The Cu wires run into the mixing chamber of the refrigerator through a superconducting thermal switch. The temperatures were measured with a cerium-magnesium-nitrate magnetic thermometer. Magnetic-moment measurements in different applied fields were carried out with a magnetometer described previously.[7] The results are shown in Fig. 2. The susceptibilities plotted in Fig. 2 are the observed magnetic moments divided by the applied fields. It should be noted that the zero of the susceptibility axis is offset in order to show more clearly the hyperfine-enhanced nuclear magnetic contribution which is superimposed on the Van Vleck susceptibility. It can be seen that in an applied field of 110 Oe, the nuclear contribution first rises on lowering the temperature and then shows a drop characteristic of antiferromagnetic order below 54 mK. In order to rule out that this phenomenon might be caused by other rare-earth impurities in the sample, the susceptibility has also been measured in 1100 Oe. If that were true, the ordering phenomenon would be completely wiped out in 1100 Oe because the Zeeman energy would be considerably larger than 54 mK. The fact that the susceptibility shows basically the same feature in 1100 Oe proves that it must be due to the hyperfine-enhanced nuclear moments in the singlet ground state, which order antiferromagnetically. In 1100 Oe, the ordering temperature shifts only from 54 to 42 mK. Some temperature dependence above 54 mK, which in 110 Oe was due to magnetic impurities, is removed and the absolute value of the Van Vleck susceptibility is slightly lower because of its

slight field dependence. Further evidence for nuclear magnetic order below 54 mK comes from specific heat which rises very fast below this temperature (Fig. 2). No appreciable difference in specific heat in fields of 110 and 1100 Oe could be detected below 54 mK. It is clear that this rise reflects the rapid removal of nuclear magnetic entropy below the ordering temperature. In Fig. 3 we plot the specific heat in a $\log(c/R)$-versus-$\log T$ plot. A normal hyperfine specific heat would have a $1/T^2$ dependence at higher temperatures. The solid line in Fig. 3 would be the hyperfine specific heat associated with an ordered moment of only 4.5% of the full Pr^{3+} moment. The observed specific heat above 54 mK must be due to the unusually large nuclear-nuclear interactions in the paramagnetic regime. Another parameter which changes abruptly at 54 mK is the thermal relaxation time in the sample. This time is observed to be fairly short above 60 mK (~30 sec or less), it suddenly increases to about 10 min at 50 mK and lower temperatures.

Theoretical estimates of nuclear ordering temperatures in Van Vleck paramagnetic materials have been given previously following the ideas outlined in the introduction.[5-7,11] The $4f$ angular momentum which the hyperfine interaction admixes to the $2I+1$ nuclear substates of the singlet ground state is given by

$$\langle J_{4f}\rangle = 2I_z A\Lambda_z \tag{1}$$

with

$$\Lambda_z = \sum_{n=1}^{m} \frac{\langle 0|J_z|n\rangle^2}{\Delta_n} . \tag{2}$$

The sum in (2) contains the squares of the off-diagonal matrix elements of the $4f$ angular momentum between ground and excited states, divided by their energy separation from the ground state. Equation (1) neglects anisotropy effects. Previously, we have used the standard molecular-field formula[5-7] to estimate the ordering temperature T_c of the system of moments $\langle J_{4f}\rangle$ coupled by exchange forces $\mathcal{J}_{ij}$. Using (1), one obtains in this way

$$\begin{aligned} kT_c &= \tfrac{1}{3}G|\lambda|\, g_J{}^2\mu_B{}^2\langle J_{4f}{}^2\rangle \\ &= \tfrac{4}{3}G|\lambda|\, g_J{}^2\mu_B{}^2A^2\Lambda_z{}^2I(I+1) , \end{aligned} \tag{3}$$

with

$$\lambda = -2\textstyle\sum_j \mathcal{J}_{ij}/g_J{}^2\mu_B{}^2 .$$

Another estimate for T_c can be obtained from the molecular-field formula for the hyperfine-enhanced nuclear magnetic susceptibility, which is given by

$$\chi_n = \chi_{n,\infty}/(1 - G|\lambda'|\chi_{n,\infty}) , \tag{4}$$

with

$$\chi_{n,\infty} = \mu^2(1+K)^2/3kT \tag{5}$$

being the nuclear susceptibility much above the ordering temperature but still in the regime where the Van Vleck susceptibility is temperature independent. ($\mu = 5.05\mu_N$ is the nuclear moment of ^{141}Pr; μ_N is the nuclear magneton.) $G = 1$ for ferromagnetic coupling ($\lambda > 0$) and can be between 0.5 and 0.2 for antiferromagnetic coupling[10] (depending on the magnetic structure). K is the "Knight shift" of the Pr nuclei and is related to the Van Vleck susceptibility χ_{VV} and the hyperfine interaction constant A by

$$K = \chi_{VV}A/g_N\mu_N g_J\mu_B \tag{6}$$

[$A = k_B(0.0525\ \mathrm{K})$ and $g_J = 0.8$ for Pr^{3+}; $g_N = 1.71$ for ^{141}Pr]. The molecular field constant λ' is related to λ by

$$\lambda' = \lambda[K/(1+K)]^2 \tag{7}$$

since the exchange forces $\mathcal{J}_{ij}$ act only on the hyperfine induced $4f$ moments and not on the bare nuclear moments. The condition $G|\lambda|\chi_{n,\infty} = 1$ in (4) yields for the transition temperature

$$kT_c = \frac{G}{3}|\lambda|\, g_J{}^2\mu_B{}^2\left(\frac{g_N\mu_N}{g_J\mu_B}\right)^2 K^2I(I+1) . \tag{8}$$

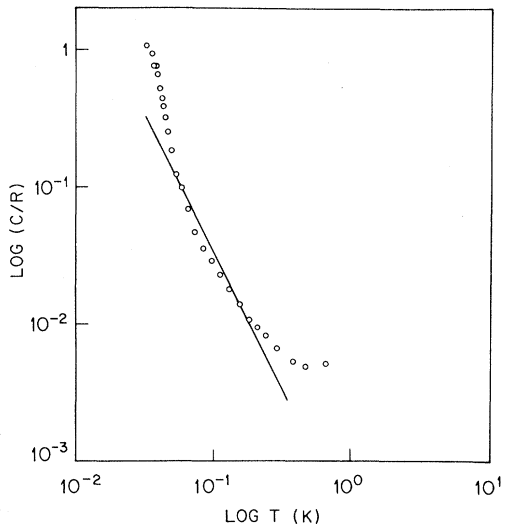

FIG. 3. Molar specific heat of $PrCu_2$ versus temperature below 0.6 K, plotted on logarithmic scales.

Using the relations

$$\chi_{VV} = \chi_c/(1-\lambda\chi_c), \tag{9}$$

$$\chi_c = 2g_J{}^2\mu_B{}^2\Lambda_z, \tag{10}$$

between the Van Vleck susceptibility due to the crystal field only, χ_c, and the exchange enhanced susceptibility χ_{VV}, and using (5) and (6), Eq. (8) can be rewritten in the form

$$kT_c = \tfrac{1}{3}G|\lambda|g_J{}^2\mu_B{}^2\langle J_{4f}{}^2\rangle(1-\lambda\chi_c)^{-2}. \tag{11}$$

The reason that (11) differs from (3) by the factor $(1-\lambda\chi_c)^{-2}$ is that in deriving (11) the exchange forces have been used twice, first to enhance the moments (1) and second to couple the enhanced moments together. Murao[11] has recently calculated the nuclear and electronic magnetic properties of a system of singlet ground-state ions with exchange interactions in the molecular-field approximation. For undercritical exchange interactions, he finds for the ordering temperature of such a system a formula similar to (11), but with the factor $1/(1-\lambda\chi_c)$ to the first power. Experimentally, we find from the observed Van Vleck susceptibility of 0.11 emu/mole a hyperfine enhancement factor of $1+K=22$ from Eq. (6). From an analysis of the nuclear susceptibility in 1100 Oe below 0.5°K, on the other hand, we get $1+K=32\pm10$. This is fair agreement in view of the fact that we have neglected anisotropy effects which always means that $\langle\chi^2\rangle>\langle\chi\rangle^2$ and $\langle(1+K)^2\rangle>\langle 1+K\rangle^2$. Unfortunately, none of the above-mentioned formulas yield good agreement with the observed ordering temperature. Using (8) and the experimental values $T_c=54$ mK and $K=31$, and assuming $G=0.5$, we find that the molecular-field constant would have to have a value of $\lambda g_J{}^2\mu_B{}^2 = k_B(28.6\ \mathrm{K})$ to explain the ordering temperature. This is more than an order of magnitude larger than any possible value, since the critical value $\lambda_{\mathrm{crit}}g_J{}^2\mu_B{}^2 = g_J{}^2\mu_B{}^2/\chi_c$, above which an *electronically* ordered induced moment state exists, is about $k_B(1.2\ \mathrm{K})$. The specific-heat results are also in disagreement with simple molecular field predictions, since we do not observe an ordinary second-order transition. Rather, the specific heat peaks considerably below the susceptibility maximum (around 30 mK). We think that this effect is different from the one discussed by Fisher[12] in the "simple" antiferromagnets MnF_2 or MnO, where it is observed that the specific-heat peak occurs several percent below the susceptibility peak. This latter phenomenon has been explained by Fisher by going beyong the molecular-field approximation and taking spin-spin correlations into account more explicitly. We believe that our observation is related to the "stiffness" of the coupling between the nuclei and the hyperfine-induced $4f$ moments. This "stiffness" decreases with increasing ordering temperature, and the reason why the specific-heat maximum occurs below the susceptibility maximum would then be the rather high nuclear ordering temperature and the fact that the exchange forces must be close to the critical value for an electronically induced-moment state.

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