Hyperfine Interactions, Magnetic Impurities, and Ordering in Praseodymium

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The antiferromagnetic ordering in Pr due to the coupling of the $4f$ electronic system to the nuclei and to magnetic Nd impurities has been studied by neutron diffraction. A pure monocrystal of Pr develops true long-range order at about 50–60 mK. The ordering in both this crystal and a *Pr*Nd alloy is, however, presaged by unusually intense and long-range magnetic fluctuations, which are ascribed to the special form of the exchange interactions.

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It is now well established that the exchange interaction between the magnetic ions on the hexagonal sites in Pr is just insufficient by itself to induce magnetic ordering.[1] It is, however, possible to produce a magnetically ordered state fairly readily by external perturbations such as a large magnetic field or uniaxial stress. In this Letter we report studies of the antiferromagnetism which is induced by the internal interactions of the electronic system with the nuclei, through the hyperfine coupling, and with substitutional magnetic Nd ions. The magnetic properties can be semiquantitatively explained in terms of a molecular-field model, using parameters deduced from earlier studies, but the antiferromagnetism is heralded by very strong and long-range magnetic fluctuations which persist over a wide temperature range. These are presumably a consequence of the special form of the magnetic interactions in Pr.

The ground state of the ionic $4f^2$ electron configuration in the crystalline electric field, with z along the hexagonal axis, is the $|J=4, J_z=0\rangle$ singlet, while the first excited state, at about $\Delta = 3.5$ meV, is the $|J=4, J_z=\pm 1\rangle$ doublet. In the molecular-field approximation, the condition for the formation of an antiferromagnetic state with a periodicity defined by the wave vector $\vec{Q}$ along the y $[10\bar{1}0]$ direction and longitudinally polarized is

$$\mathcal{J}^y(\vec{Q})\chi_0{}^y > 1, \tag{1}$$

where $\chi_0{}^y = 2|\langle 1|J_y|0\rangle|^2/\Delta$ is the low-temperature limit of the reduced single-ion Van Vleck susceptibility and $\mathcal{J}^y(\vec{Q})$ is the Fourier transform of the anisotropic indirect exchange interaction. In the random-phase approximation, Eq. (1) is also the condition that the lowest-lying magnetic excitation in the paramagnetic phase should be unstable, leading to a magnetic soft-mode transition. Studies of the magnetic excitations[1] indicate that $\mathcal{J}^y(\vec{Q})$ at the wave vector which corresponds to this minimum excitation energy is about 92% of the value necessary for ordering.

It was first emphasized by Murao[2] that the hyperfine interaction $\sum_i A\vec{J}_i\cdot\vec{I}_i$ between the electronic moments $\vec{J}_i$ and the nuclear moments $\vec{I}_i$ modifies the criterion for magnetism. Instead of Eq. (1) it becomes, to a good approximation,

$$\mathcal{J}^y(\vec{Q})\chi_0{}^y[1+A^2\chi_0{}^y\chi_N] > 1, \tag{2}$$

where $\chi_N = I(I+1)/3kT$ is the reduced nuclear Langevin susceptibility. Even though the hyperfine coupling is small, the temperature dependence of the nuclear susceptibility ensures that a cooperative ordering of the electrons and nuclei must occur at a temperature given by

$$kT_N = (A\chi_0{}^y)^2\mathcal{J}^y(\vec{Q})I(I+1)/3[1-\chi_0{}^y\mathcal{J}^y(\vec{Q})]. \tag{3}$$

The parameters in this equation are all known from earlier studies, and Jensen[3] showed that they imply a Néel temperature of about 40 mK, with a corresponding low-temperature ordered electronic moment of about $0.6\mu_B$/atom. Evidence of nuclear ordering has been observed in the low-temperature heat capacity, and the most recent

measurements by Eriksen, Muirhead, and Young[4] indicate an ordering temperature around 50 mK.

For some years efforts have been made to detect antiferromagnetism in Pr at low temperatures by neutron diffraction. Lebech, Houmann, and Chapellier[5] observed a broad quasielastic "central peak" around $\vec{Q}$ which appears at about 10 K and grows steadily as the temperature is decreased, showing substantial structure by 0.4 K. Because of its form and temperature dependence this central peak was attributed not to ordering but to magnetic fluctuations. McEwen and Stirling[6] extended these studies to lower temperatures and discovered that a sharper peak, which they called "the satellite," emerges from the central peak and continues to grow with decreasing temperature. They interpreted this satellite as a manifestation of long-range magnetic order and deduced a moment of about 0.1 μ_B/atom at their lowest measured temperature of 30 mK.

There are a number of puzzling features about these interesting results. The satellite is already visible at about 1 K, a much higher temperature than would be expected from Eq. (3); the temperature dependence of the deduced moment is very unusual, and its value at low temperatures is much lower than predicted. Since we suspected that these phenomena might be associated with Nd impurities, we decided to repeat the experiments with a crystal containing only about 1 ppm Nd, with a volume of about 0.15 cm^3. It was mounted in a dilution refrigerator and studied by neutron diffraction at the DR3 reactor, utilizing the cold neutron source.

Neutron-diffraction scans near the reciprocal lattice point (003) are shown in Fig. 1. The central peak is already clearly visible at 4.2 K and appears to contain structure which presages the emergence of the satellite, which grows as the temperature is reduced. Below about 60 mK this growth becomes dramatic and at the lowest temperature of 40 mK our peak intensity is an order of magnitude greater than that observed by McEwen and Stirling. Following their procedure, we have made a least-squares fit of our results by two Gaussian functions, with a linearly varying background. If the magnetization is along $\vec{Q}$ and varies sinusoidally with amplitude $m\mu_B$/atom, the ratio of the integrated intensity of one of the six magnetic peaks to that of the (hkl) nuclear peak is given by

$$\frac{I_{q03}{}^{m}}{I_{hkl}{}^{n}} = \frac{p_0{}^2 m^2 \cos^2\alpha\, |f(\vec{\kappa})|^2 |F_m(003)|^2}{12 b^2 |F_n(hkl)|^2} \tag{4}$$

with the conventional notation.[6] To facilitate comparison with the data of McEwen and Stirling, we have plotted in Fig. 2 the quantity

$$R = P_{q03}{}^{m} |F_n(103)|^2 / P_{103}{}^{n} |f(\vec{\kappa})|^2 \cos^2\alpha \tag{5}$$

for the peak intensities $P_{q03}{}^{m}$ of both the satellite and central peak, together with an equivalent ratio deduced from their results. The intensities of both the satellite and the central peak are similar in the two studies down to 200 mK, but below this temperature both are much more in-

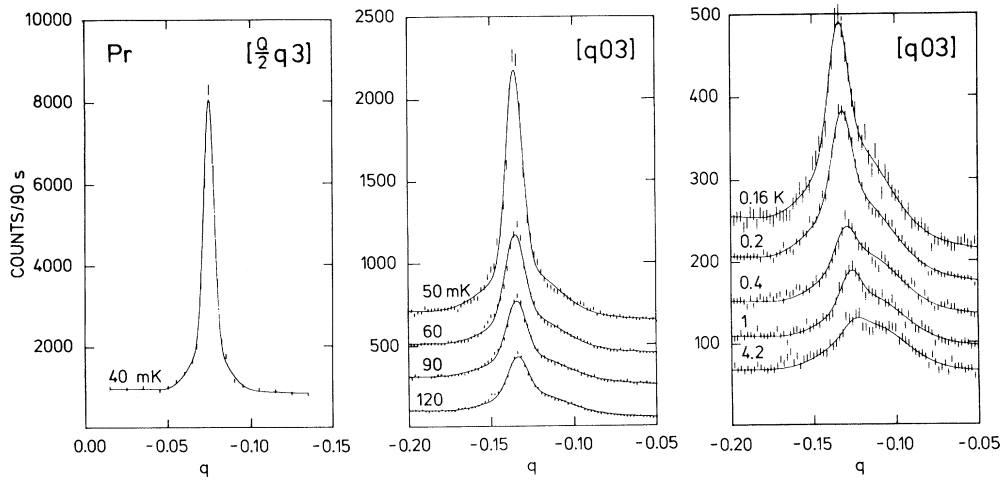

FIG. 1. Neutron-diffraction scans in Pr. The results at 40 mK correspond to a scan precisely through a magnetic peak, but only approximately in the direction indicated. The solid lines show the sum of two Gaussian functions fitted to the data.

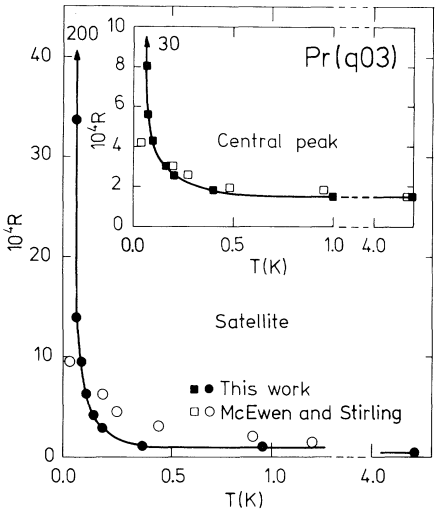

FIG. 2. The suitably normalized ratio of the peak intensities of the two Gaussians in Fig. 1 to that of a nuclear peak, compared with the results of McEwen and Stirling (Ref. 6).

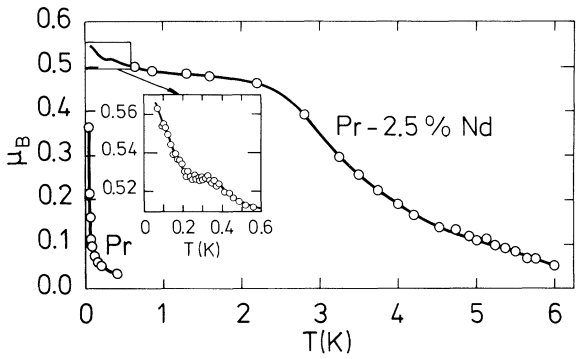

FIG. 3. The effective moments, deduced from the intensity of the satellites as explained in the text, in Pr and a *Pr*Nd alloy.

tense in our measurements.

In units of $\vec{\tau}_{100}$ the width of our satellite peaks in the $[q03]$ scans is about 0.014 from 200 to 60 mK, which is substantially greater than the resolution width of 0.009, and then falls to 0.011 at 50 mK. The fitted width in the $[Q/2\,q\,3]$ scan at 40 mK is close to the resolution width. The conclusion from these observations is that the satellite at higher temperatures does not reflect the presence of true magnetic long-range order, but rather very intense fluctuations with a range of some hundreds of angstroms, which presumably vary slowly in time. Below about 100 mK signs of a narrow diffraction peak begin to appear, but it is only at around 50–60 mK that a significant amount of long-range order develops. As we shall see, similar phenomena were observed in a *Pr*Nd crystal.

It is necessary to say a few words about the cryogenic difficulties which beset these measurements. Within the constraints of a neutron-diffraction experiment, it is not easy to establish adequate thermal contact between the cryogenic bath and the sample below about 100 mK. In addition, because of the very large heat capacity associated with the magnetic ordering, the sample cools very slowly in this temperature range. To reach our lowest sample temperature of about 40 mK, we attached the crystal by silver paint to a Cu cradle in contact with the cryogenic bath and allowed it to cool for about a week while the reactor was shut down. After the neutron beam was switched on, it heated the sample with a time constant of some hours to a temperature so high that the diffraction peak disappeared. When the thermal contact was established by surrounding the sample with liquid ^{4}He, similarly to the method used by McEwen and Stirling, the intensity of the diffraction peak was much lower even after a week of cooling. The sample temperature was measured by a Ge resistance thermometer, but its sensitivity fell drastically below about 70 mK, so that our measurements are uncertain by as much as ±10 mK at the lowest temperatures. In view of these observations it seems likely that the large discrepancy between our results and those of McEwen and Stirling at the lowest temperatures are due to a substantial difference between the bath and sample temperature in their experiments.

The magnetic moment corresponding to the integrated intensity in the satellite can be calculated by using Eq. (4). The results of this calculation are shown in Fig. 3. As emphasized earlier, only at the lowest temperatures does the indicated moment correspond to true magnetic long-range order. The ordered moment at 40 mK is $0.36\,\mu_B$/atom. It is noteworthy that, interpreted in the same way, the integrated intensity of the central peak at 40 mK corresponds to a moment of about $0.25\,\mu_B$/atom.

Analogous results for a crystal of Pr containing 2.5% Nd are also shown in Fig. 3. The temperature dependence of the scattered intensity follows qualitatively the behavior observed in pure Pr. The central peak appears at around 10 K, a satellite which is broader than the experimental resolution emerges from it around 6 K, and a diffraction peak, signifying true long-range order, de-

velops below about 3.5 K. As in Pr the central peak grows with the magnetization, and its integrated intensity at the lowest temperatures corresponds to about $0.4\mu_B$/atom.

The rise in magnetization below about 0.2 K is ascribed to the polarization of the nuclei and their hyperfine interaction with the magnetic system. The decrease in the magnetization when the crystal is heated from 0.2 to 1 K is believed to be due to the increasing population of the upper level of the doublet ground state, which is split in the molecular field by roughly 1 K. Evidence for this conjecture is contained in inelastic scattering studies of the crystal-field levels of the Nd ions, details of which are presented elsewhere.[7]

Pr thus displays a remarkable duality. On the one hand, the magnetic ordering and properties, their dependence on field, temperature, and stress, and the excitation spectrum can all be explained at least semiquantitatively in terms of a self-consistent set of exchange, crystal-field, and magnetoelastic parameters.[3] On the other hand, the critical magnetic fluctuations, which are not encompassed by molecular-field or random-phase theories, are both very unusual and much more difficult to account for.

Many attempts have been made to explain the central peak in terms of extraneous factors, but it now appears that it is a genuine bulk property of pure Pr. It seems very likely that its shape and temperature dependence reflect the detailed form of the exchange. In the paramagnetic phase there is a pronounced minimum in the energy of the crystal-field excitations, whose locus traces a roughly circular path in the basal plane of the zone, over which the energy varies by only a few kelvins. There is therefore simultaneously a very strong tendency towards magnetic order and a great ambiguity in the ordering wave vector. Indeed, if the degeneracy were perfect along this circle, the system would be unable to display long-range order.[8] It appears that the magnetic fluctuations in Pr reflect the presence of a large number of excited states of very low energy at wave vectors close to that which characterizes the antiferromagnetic state. The properties of such an exceptional system clearly deserve further exploration.

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