VOLUME 72, NUMBER 19 PHYSICAL REVIEW LETTERS 9 MAY 1994

New Mode of Magnetic Excitation in Praseodymium

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(Received 3 December 1993)

A novel propagating mode of magnetic excitation has been observed in Pr. It takes the form of low-energy satellites to the crystal-field excitations on both the hexagonal and cubic sites which are very broad at long wavelengths, rise in energy and rapidly narrow with increasing **q**, and disappear beyond the point at which the two excitations would cross. The broadening may be abruptly quenched by a magnetic field. The satellite excitations are believed to be associated with the dynamics of the conduction electrons.

PACS numbers: 75.30.Ds, 75.10.Dg

The nature of the f-electron states in metals has been a topic of discussion and controversy for several decades, and it is by no means yet fully clarified. In heavy fermion systems, which frequently incorporate Ce or U, the $4f$ or $5f$ electrons are itinerant at low temperatures, thus contributing to the conductivity, and have very large and highly enhanced effective masses. In the rare earth elements, on the other hand, the $4f$ electrons are generally localized, making no direct contribution to the transport properties, but with angular-momentum states corresponding to those of the free atom, providing large magnetic moments. These localized moments interact with their surroundings, for example, through the single-ion crystal-field and magnetoelastic forces, and the two-ion indirect-exchange and classical-dipolar couplings. The theory of these local moments and their interactions constitutes the standard model of rare earth magnetism, which has been extremely successful in explaining the properties of these materials [1].

The standard model has been applied with great success to Pr, which has the double hcp (dhcp) structure and is paramagnetic at low temperatures, since the crystal-field ground state is a singlet on both the sites with hexagonal and local cubic symmetry. The crystal-field excitations have been studied by inelastic neutron scattering and the magnetic interactions thereby derived in great detail [2], leading to a very complete theory of the magnetic properties [1], including the prediction, subsequently corroborated experimentally, of the magnetic ordering induced by uniaxial stress or, at very low temperatures, by the hyperfine interaction. However, the neutron scattering experiments also revealed some unexplained features, notably the quasielastic "central peak," observed as a precursor and accompaniment to the low-temperature magnetic ordering, and most plausibly interpreted as due to scattering of the neutrons by the conduction electrons [1]. Furthermore, a pronounced broadening of the excitations occurred at long wavelengths, and was ascribed to the interaction with the electron-hole-pair excitations of the conduction-electron gas [2]. By studying the latter phenomenon under greatly improved experimental conditions, we have discovered a new propagating mode of magnetic excitation, with a very unusual and characteristic behavior, which we suggest may be associated with the dynamical response of the conduction electrons not included in the standard model. The explanation of this mode requires a detailed understanding of the mixing of the $4f$ states and the conduction band, and may therefore elucidate the mechanism by which the former become itinerant at high pressure [3].

It was pointed out [1] that the aforementioned broadening of the crystal-field excitations on the hexagonal sites should be quenched by a magnetic field at the smallest **q** values, resulting in a narrowing of the corresponding neutron peaks, as well as the splitting of the $|\pm 1\rangle$ level by the field. Even though the effect of the field by itself on the conduction electrons is small, it induces a large moment **J** on the ions, if it is applied in the basal plane, and the exchange interaction $-j\mathbf{s}\cdot\mathbf{J}$ with the conduction-electron spins **s** causes a band splitting that measurements of the de Haas–van Alphen effect [4] indicate to be of the order of 10 meV in 10 kOe. The energies of the Stoner modes at low q are thus increased above those of the crystal-field excitations, and the spin-flip scattering is consequently quenched.

Recent technical improvements, particularly in the neutron guide, at the DR3 reactor at Risø have resulted in an increase in the effective neutron flux by an order of magnitude, and allowed a much more detailed study of this phenomenon. The experiments were carried out using the cold-source triple-axis spectrometers TAS6 and TAS7, operated with a constant scattered-neutron energy of 5 meV. The sample was a 6 g single crystal, mounted with an a direction perpendicular to the scattering plane

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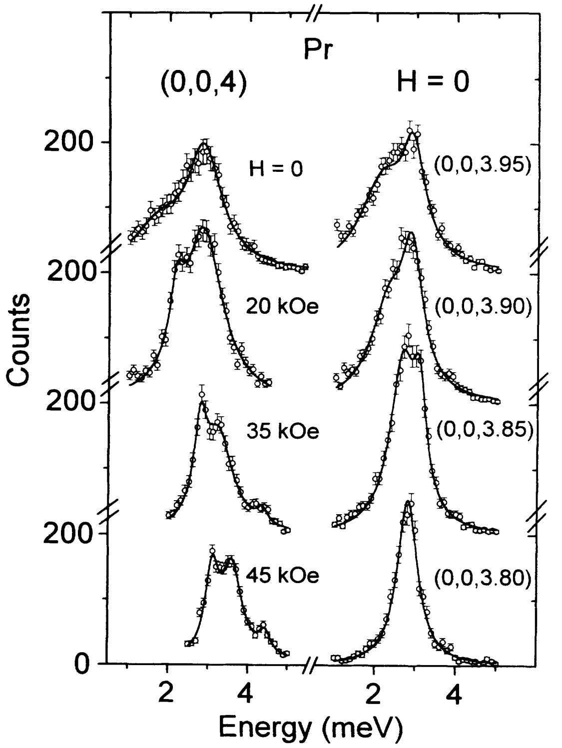

FIG. 1. The energy spectra of inelastically scattered neutrons in Pr at 4.2 K, for different momentum transfers and magnetic fields. The counting times were about 5 min per point. The full lines are least-squares fits by multiple Lorentzian functions, assuming a negligible background scattering. At (0,0,4) ($\mathbf{q}=\mathbf{0}$), there are two peaks at zero field, the lower of which is strongly broadened. As shown in the right column, at zero field this peak rapidly narrows and rises in energy with increasing q, and at (0,0,3.85) ($q=0.15$) both peaks are sharp and well defined. At higher values of q, only one sharp peak is visible. The results in the left column, and in Fig. 3, illustrate the abrupt and drastic narrowing of the lower peak at $\mathbf{q}=\mathbf{0}$ at a field of about 15 kOe. Further increase in the field has little effect on this peak, but the upper one narrows significantly. At the highest fields, a magnetoelastic mode becomes visible at about 4.3 meV, due to the mixing of the transverse photons with the magnetic excitations.

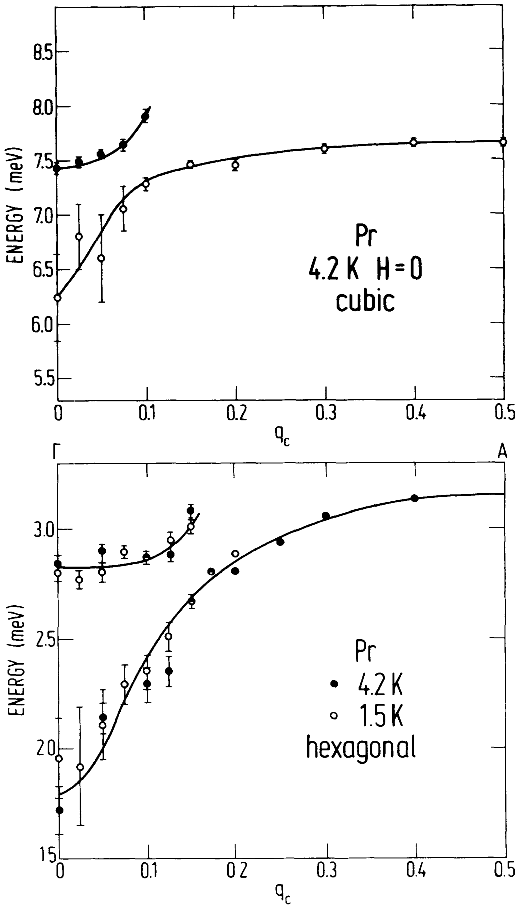

FIG. 2. The energies of the magnetic excitations propagating in the c direction on the hexagonal and cubic sites in Pr in zero field, as a function of q in units of $2\pi/c$. On both sets of sites, the standard model predicts a single branch of crystal-field excitations, but in each case strong hybridization is observed with a low-energy satellite excitation, whose energy increases rapidly with q, and which disappears beyond the nominal crossing point of the two modes. The full lines are intended as guides for the eye.

and along the field direction of an Oxford Instruments 4.5 T cryomagnet.

As may be seen in Fig. 1, the predicted splitting and narrowing of the neutron spectrum indeed occurs but, even in the absence of the field, novel and unexpected effects are observed. As shown in Figs. 1 and 2, the dispersion relation for the modes propagating predominantly on the hexagonal sites in the c direction at 4.2 K in zero field, which according to the standard theory should comprise only a single branch, splits into two at low q, giving rise to a low-energy "satellite" to the crystal-field excitations. This satellite excitation is very broad at the longest wavelengths, but narrows rapidly as it rises in energy with increasing q and approaches the nominal crossing point with the crystal-field excitations, which also narrow significantly. The two modes hybridize strongly over the whole range and, beyond the crossing point, the upper one rapidly disappears. At higher q values, the width of the neutron peak is limited by the experimental resolution, and the dispersion relation is well described by the standard theory. As illustrated in Fig. 2, measurements at 1.5 K reveal a generally similar behavior to that observed at 4.2 K.

As shown in Figs. 1 and 3, a magnetic field applied in the a direction has little effect below 10 kOe, but over the next 10 kOe the width of the satellite excitation falls drastically. Thereafter, this width remains essentially unchanged and resolution limited as the field is increased further, but the higher mode becomes increasingly narrow with field. At the same time, a magnetoelastic peak

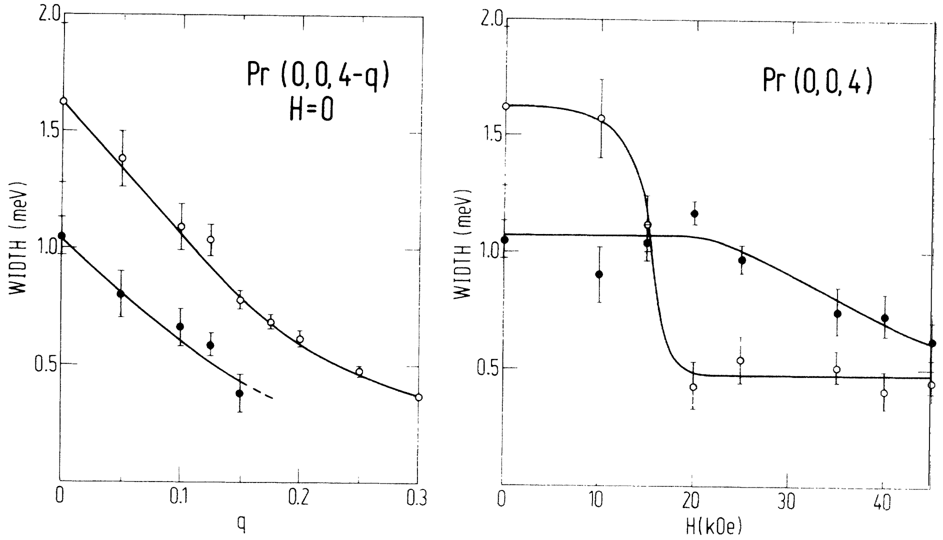

FIG. 3. The widths of the hexagonal excitations as a function of q and magnetic field in Pr at 4.2 K. The open circles correspond to the lower branch in Fig. 2, and the closed circles to the upper branch. The results have not been corrected for the energy resolution of the spectrometer, which varies from 0.25 meV at zero energy transfer to 0.55 meV at 9 meV.

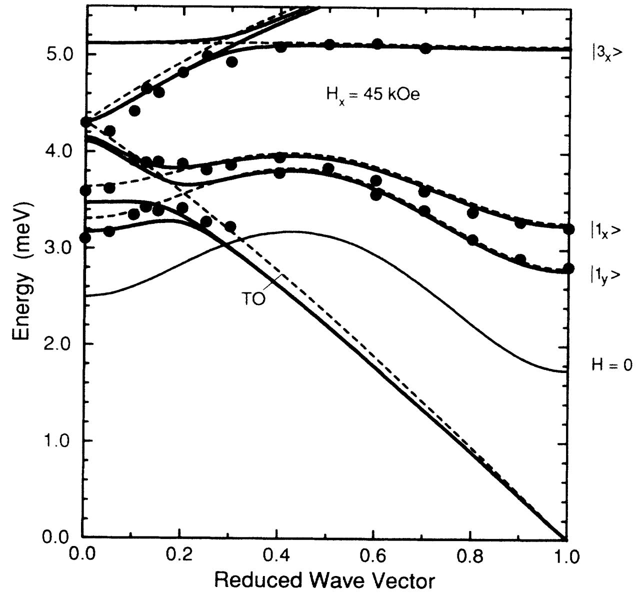

FIG. 4. The dispersion relations for excitations propagating in the c direction in Pr at 4.2 K in a field of 45 kOe. The circles are the experimental results, the dashed lines the theory in the absence of magnetoelastic coupling, and the full lines the standard theory when this interaction is taken into account. The magnetic field splits the $|\pm 1\rangle$ state and mixes it with the $|3_x\rangle$ level. The magnetic excitations also hybridize strongly with the transverse optic phonons in a field. The theory gives an accurate account of the observations at larger q values, but is less satisfactory at long wavelengths, where the influence of the satellite excitation is still noticeable. In addition to the discrepancies in the energies, the intensity of the low-energy mode is greater than predicted.

appears, which is due to the interactions between the $|1_{x,y}\rangle$ states, the higher-lying $|3_x\rangle$ level and the phonons, which are induced by the field, and absent in zero field.

At low fields, the results cannot be explained by the standard theory. The splitting of the peaks at 20 kOe, shown in Fig. 1, is, for example, far too great to be accounted for by the splitting of the $|1_{x,y}\rangle$ states in this modest field. On the other hand, increasing the field improves the agreement with the theory. Provided that the interaction with the phonons is taken into account, both the overall form of the dispersion relations and the scattering intensities in the c direction at 45 kOe can be fitted quite well by the standard theory, as illustrated in Fig. 4, although there are still significant residual discrepancies in the positions and intensities of the peaks at low q. We anticipate that, as the field is further increased, the standard theory will become increasingly satisfactory, and we are planning experiments to examine this question further.

The dispersion relations in the b direction, which will be presented elsewhere, also display the satellite excitation at low q and a strong perturbation due to interactions with both longitudinal and transverse phonons at high fields.

The predominantly cubic-site excitations, which have been less thoroughly studied, show a qualitatively similar behavior to those on the hexagonal sites. The strongly broadened satellite excitation in zero field again rises in energy with q, as shown in Fig. 2, and narrows rapidly, hybridizing with the crystal-field excitation and disappearing beyond the nominal crossing point. The satellite peak is also narrowed by a magnetic field, but still has a substantial width at 45 kOe.

We have thus observed a new mode of magnetic excitation, with a very unusual and characteristic behavior, on both the hexagonal and the cubic sites in dhcp Pr. It is noteworthy that this phenomenon depends crucially on the special properties of Pr, which is paramagnetic, so that the conduction electrons are unpolarized in zero field, but has well-defined collective excitations of the $4f$ system. In Tb, for example, analogous behavior would be quenched by the internal field at low temperatures. The abrupt quenching, by a magnetic field of about 15 kOe in the a direction, of the broadening of the satellite excitation on the hexagonal sites indicates that this field may produce a spin splitting of some energy band which is equal to the excitation energy. A similar quenching is observed on the cubic sites, but it appears to be more gradual and is not complete at 45 kOe. The higher-lying excitations are also narrowed by the field, but more gradually.

It is natural to associate the satellite excitation with the response of the conduction electrons to the spatially and temporally varying fields accompanying the magnetic excitation of the $4f$ electrons. It may thus bear some relation to the paramagnons which occur in nearly ordered magnetic systems, but with the important difference that it is a genuine propagating, though highly broadened mode, rather than the diffusive response which may be observed in transition-metal systems [5]. Such behavior cannot be accounted for by the standard model, in which the conduction electrons appear only through their static susceptibility $\chi(\mathbf{q})$. It may, however, be explicable in terms of a natural extension in which the time dependence of the conduction-electron response is taken into account by a perturbation-theory calculation of $\chi(\mathbf{q},\omega)$, beyond the first-order term which gives rise to the simple broadening of the crystal-field excitations. On the other hand, the fact that a satellite seems to be associated with each crystal-field level may indicate that hybridization between the $4f$ and conduction-electron states must be taken explicitly into account, involving the full electronic potential rather than the exchange alone, so that the former are partly delocalized. As mentioned earlier, it is believed that the $4f$ electrons in Pr become delocalized at high pressure, and, in the neighboring element α-Ce, the $4f$ states form bands.

We plan to extend this study, in the first instance, by measuring the excitations on both the hexagonal and cubic sites in fields up to 90 kOe and at much lower temperatures. We hope that this work, together with a further attempt to explore the behavior of the electrons in Pr through calculations and complementary experiments, will result in a significant improvement in our understanding of the $4f$ states in this intriguing metal.

The experiments reported in this paper were supported by the Commission of the European Community, through the Large Installations Plan, and by the UK Science and Engineering Research Council. We have benefited greatly from discussions with Roger Cowley, Leo Falicov, Jørgen Kjems, and Ole Krogh Andersen. Steen Aagaard Sørensen has kindly helped with some of the measurements and their analysis.

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