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Crystal fields and conduction electrons in praseodymium

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Abstract

The interactions between the crystal-field excitations, the phonons and the conduction electrons in Pr have been studied further. The low-energy satellites to the crystal-field excitations, which are believed to be associated with propagating paramagnon modes in the conduction-electron gas, appear to be quenched by a magnetic field, which also induces a strong hybridization with the phonons.

The rare earth element praseodymium displays a unique magnetic behaviour. The two 4f electrons on each atomic site are localized, making no direct contribution to the transport properties, but with angular-momentum states corresponding to those of the free atom. These localized states 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 the localized 4f states and their interactions constitutes the standard model of rare earth magnetism, which has been extremely successful in explaining the properties of these materials [1].

Even though the 4f electrons on each atomic site have a large uncompensated angular momentum, Pr is paramagnetic at low temperatures, since the crystal-field ground state is a singlet on both the sites with hexagonal and local cubic symmetry in the dhcp structure. However, the exchange is very close to the critical value necessary to induce magnetic ordering. The standard model has been applied with great success to Pr, 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. The crystal-field excitations have also been studied by inelastic neutron scattering and the magnetic interactions thereby derived in great detail [2]. However, the neutron scattering experiments also revealed some unexplained features, notably the quasi-elastic '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 discovered a new propagating mode of magnetic excitation [3], with a very unusual and characteristic behaviour, which we suggested may be associated with the dynamical response of the conduction electrons not included in the standard model. The observations reported earlier and the results presented here were obtained using the cold-source triple-axis spectrometers TAS6 and TAS7, at the DR3 reactor at Risø. The sample was a 6 g single crystal, mounted with an a-direction perpendicular to the scattering plane. Magnetic fields up to 7 T could be applied along this direction by means of cryomagnets.

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

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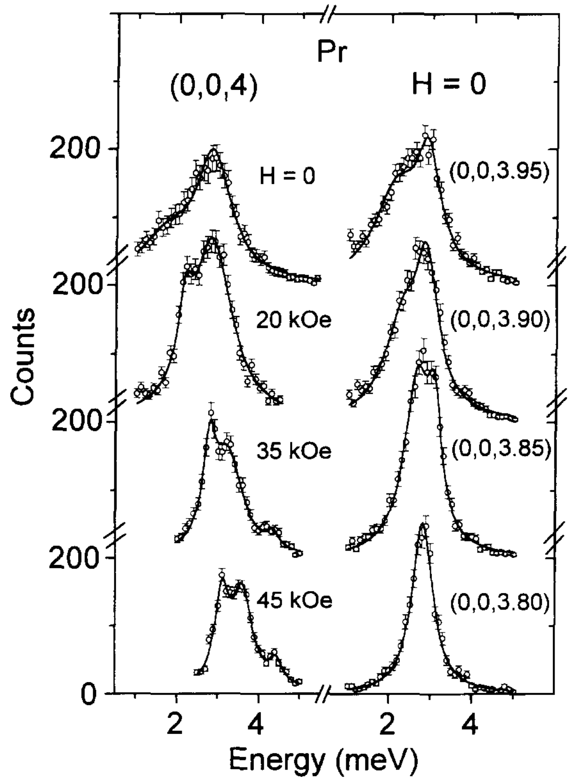

Fig. 1. The energy spectra of inelastically-scattered neutrons in Pr at 4.2 K, for different momentum transfers and magnetic fields. The counting times were about 5 min per point. The full lines are least-squares fits to multiple Lorentzian functions, assuming a negligible background scattering. At (0,0,4) ($\boldsymbol{q}=\mathbf{0}$), 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 illustrate the abrupt and drastic narrowing of the lower peak at $\boldsymbol{q}=\mathbf{0}$ 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 phonons with the magnetic excitations.

dispersion relation is well described by the standard theory. As illustrated in Fig. 2, measurements at 1.5 K reveal a generally similar behaviour to that observed at 4.2 K. Recent measurements on the crystal which was used for the earlier study of the excitations [2] also gave essentially identical results.

As shown in Fig. 1, a magnetic field applied in the a-direction reduces the width of the satellite excitation drastically. At the same time, a magnetoelastic peak 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 [3], although there are still significant residual discrepancies in the positions and relative intensities of the peaks at low q.

The same general behaviour is observed in the b-direc-

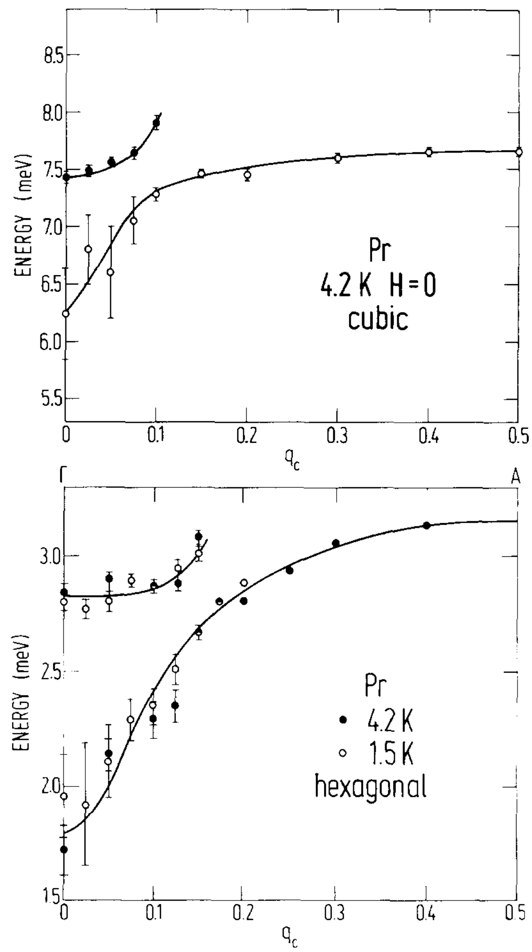

Fig. 2. The energies of the magnetic excitations propagating in the c-direction on the hexagonal and cubic sites in Pr in zero field, as a function of q in units of $2\pi/c$. On both sets of sites, the standard model predicts a single branch of crystal-field excitations, but in each case strong hybridization 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.

tion, as illustrated in Fig. 3. The crystal-field and satellite excitations observed in zero field evolve with field into modes whose dispersion relations can be accounted for by the standard theory, provided that the interaction with the phonons, which is a consequence of the induced moment, is taken into account.

The total magnetic scattering from the hexagonal sites, approximated by simply summing the appropriately normalized scattered intensity between 1 and 5 meV, is shown as a function of magnetic field in Fig. 4. Even though the *energy-dependence* of the magnetic scattering at small q and fields is highly anomalous, the decrease in the *total* scattering with field is well described by the standard theory, as is the q-dependence at different fields.

The predominantly cubic-site excitations, which have been less thoroughly studied, show a qualitatively similar behaviour 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.

The unusual and characteristic behaviour of the satellite excitations is presumably associated with the response of

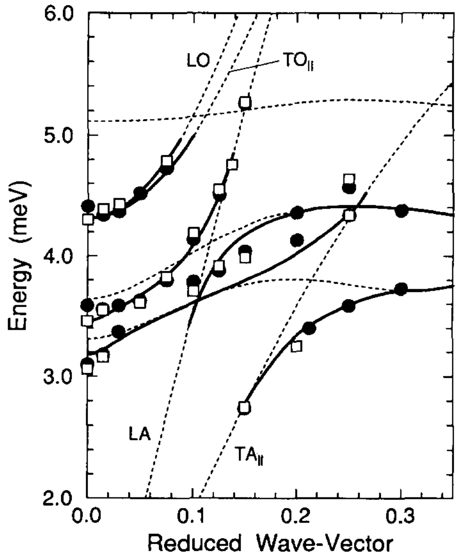

Fig. 3. The dispersion relations for excitations propagating in the b-direction in Pr at 4.2 K in a field of 45 kOe. The ● denote the experimental results obtained in the vicinity of the (0,0,4) reciprocal-lattice point, while the □ were measured around (0,0,2). The dashed lines represent the results of the standard theory in the absence of magnetoelastic interactions, while the full lines indicate the modification expected when these couplings are taken into account. The magnetic excitations polarized longitudinally and transversely relative to q hybridize respectively with the transverse and longitudinal phonons in a field, in accordance with the theory.

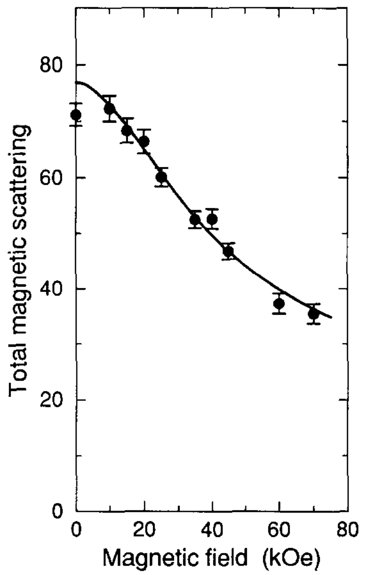

Fig. 4. The total inelastic magnetic scattering in the low-energy region at (0,0,4) as a function of magnetic field in the a-direction, compared with the standard theory. The experimental points were obtained by summing the intensities in scans analogous to those shown in Fig. 1 between 1 and 5 meV. The theoretical curve includes a single scale parameter. The low value of the point at zero field is consistent with the observation that the scattering extends below 1 meV under these conditions, as shown in Fig. 1.

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 [4]. Such behaviour cannot be accounted for by the standard model, in which the conduction electrons appear only through their static susceptibility $\chi(q)$. 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 $\chi(q,\omega)$, 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.

In order to further elucidate the nature of the satellite excitations, it would be useful to try to determine their form factor by measurements of the intensity of the inelastically scattered neutrons around different reciprocal lattice vectors. The excitations on both the hexagonal and cubic sites, and the central peak, should also be studied in higher fields, applied in different directions, and at lower temperatures. We hope that such measurements, together with a further attempt to explore the behaviour of the electrons in Pr through calculations and complementary experiments, will result in a significant improvement in our understanding of its 4f states.

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