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Magnetic Ordering in Single-Crystal Praseodymium Induced by Uniaxial Stress

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Neutron inelastic scattering techniques have been used to examine the dispersion relations for magnetic excitons propagating on the hexagonal sites of double-hcp Pr when uniaxial stress is applied along the $[1\bar{2}10]$ direction. The mode of lowest energy (longitudinal optic) along ΓM was found to exhibit a clear soft-mode behavior with increasing stress. Elastic satellite reflections corresponding to long-range magnetic ordering in a longitudinally modulated structure were observed: at 800 bars the Néel temperature is 7.5 K.

Praseodymium metal has the double-hexagonal close-packed (dhcp) crystal structure. It is well known that the Pr ions ($J = 4$) experience a crystal field which produces singlet ground states at both the locally hexagonal and cubic sites. Pr is a particularly interesting singlet ground-state system since the coupling between the ions on the hexagonal sites is just below the critical value for an induced-moment system.[1] Magnetic ordering may, however, be induced by alloying with small amounts of Nd. Lebech, McEwen, and Lindgård[2] found that $Pr_{1-x}Nd_x$ single crystals exhibited magnetic ordering in a sinusoidally modulated structure with the moments in the basal plane.

Neutron inelastic-scattering studies of Pr have been made by Rainford and Houmann[3] and more recently by Houmann *et al.*[4] They interpreted the majority of the excitations they observed at low temperatures in terms of magnetic excitons, composed of linear combinations of transitions from the ground state $|J = 4, J_z = 0\rangle$ to the first excited states $|4, \pm 1\rangle$ on those sites with local hexagonal symmetry. The lowest energy mode along the Brillouin-zone direction ΓM has a pronounced minimum at approximately the same wave vector (0.25 Å^{-1}) as that describing the longitudinally modulated structure observed in $Pr_{1-x}Nd_x$.

The coupling between the magnetic excitons and the phonons in Pr has been considered by Jensen.[5] This coupling is substantial because of the large orbital angular momentum ($L = 5$) of the Pr ions. From an analysis of the magnetic field dependence of the exciton energies, Jensen deduced a value of 30 meV/ion for the second-order

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magnetoelastic coupling parameter B_{22}; his subsequent predictions[6] of the field dependence of the static magnetostriction and elastic constants of Pr are in excellent accord with recent measurements.[7,8] Jensen also suggested that uniaxial stress applied along an a direction should induce antiferromagnetic ordering of the b-direction components of the magnetic moments on the hexagonal sites. The stress required to achieve this process was predicted to be somewhat less than 1 kbar at 4.2 K. We have therefore examined the stress dependence of the excitations in Pr, with emphasis on the behavior of the incipient soft mode along ΓM.

The crystal was prepared from distilled Pr. Vacuum fusion analysis indicated the major impurities in this material to be 1200 ppm O_2, 140 ppm N_2, and 50 ppm H_2. The metal was additionally purified by zone melting 20 times at 5 cm h^{-1}: Each melt was followed by a mechanical and chemical cleaning of the surface. A melt at 6 mm h^{-1} then produced large grains with a mosaic spread of several degrees. Subsequent zone cycling through the dhcp-bcc transition reduced the crystallinity to an acceptable level. From the resulting ingot a crystal of size $8\times8\times5$ mm was cut by spark machining such that its faces were perpendicular to crystallographic a, b, and c directions. Particular care was taken to ensure smooth, parallel faces; the sample was then electropolished.

The crystal was mounted with its a direction, $[1\bar{2}10]$, vertical in a uniaxial stress assembly comprised of two hardened steel pistons and a thin-walled aluminum-alloy sleeve which retained the applied load. The pistons were coated with Teflon to reduce friction on the sample faces. Loads were generated by a Belleville spring washer system at room temperature and transmitted to the pistons through a steel sphere to compensate for possible misalignment of the sample faces. Deformations under load of the aluminum sleeve were measured by a strain-gauge bridge, and the force applied to the sample was determined directly from the bridge output and the low-temperature elastic constants of Pr.[9] Although the system was calibrated at room temperature, consideration of the temperature dependences of the strain-gauge factor and the mechanical strength of the aluminum alloy indicate that the calibration constant varies less than 10% with temperature.

The stress assembly was contained within a cryostat mounted on the triple-axis spectrometer IN2 at the Institut Laue-Langevin. Measurements were made with graphite monochromator and analyzer crystals in two configurations with fixed incident wave vector: (i) $k_0 = 2.66$ Å^{-1} and a pyrolytic graphite filter, (ii) $k_0 = 1.55$ Å^{-1} and a cooled beryllium filter. Most of the measurements were made around the (0003) dhcp reciprocal lattice point: Some additional measurements were made around (0001).

With zero applied stress and using the configuration (i), elastic-scattering scans were made through (0003) parallel to the $[10\bar{1}0]$ direction. At 5 K weak scattering was observed around (0.11, 0, -0.11, 3) with 250 counts/160 s. At 50 K only background, 50 counts/160 s, was detected. In agreement with Lebech, McEwen, and Lindgård[2] this weak scattering had an overall linewidth 5 times larger than the $(10\bar{1}0)$ nuclear Bragg reflection and a peak intensity 4400 times smaller.

With the application of an 800-bar stress, intense magnetic satellites were observed around $(\pm Q, 0, \mp Q, 3)$. The temperature dependences of their magnitude and wave vector were examined. At 2 K the wave vector was $Q = 0.1275$ (0.252 Å^{-1}): A shift to smaller Q of about 1% was observed as the Néel point was approached. Satellites were also observed around (0001) but were absent around $(10\bar{1}0)$. We therefore interpret the magnetic ordering as a sinusoidally modulated structure with the moments confined to the basal plane. From a comparison of the satellite intensities with those of the nuclear peaks, and using a value of 0.44×10^{-14} m for the nuclear scattering length, we estimate the b-direction component of the saturation moment to be $0.5\mu_B$/hexagonal site. The temperature dependence of the satellite peak intensity is shown in Fig. 1: Since the intensity measures the square of the magnetization, the Néel temperature may be deduced (on a mean-field model) via a linear extrapolation as shown. T_N is estimated to be 7.5 ± 0.5 K at this stress. With the spectrometer in the high-resolution configuration (ii), the energy widths of the satellites were examined and found to be identical to the widths of the crystallographic Bragg peaks. Satellites were also observed at 600 bars but were absent on removal of the stress.

However, possibly the most striking changes as a result of the applied stress were observed in the dispersion relation of the magnetic excitons propagating on the hexagonal sites. At a general wave vector in the basal plane, four branches

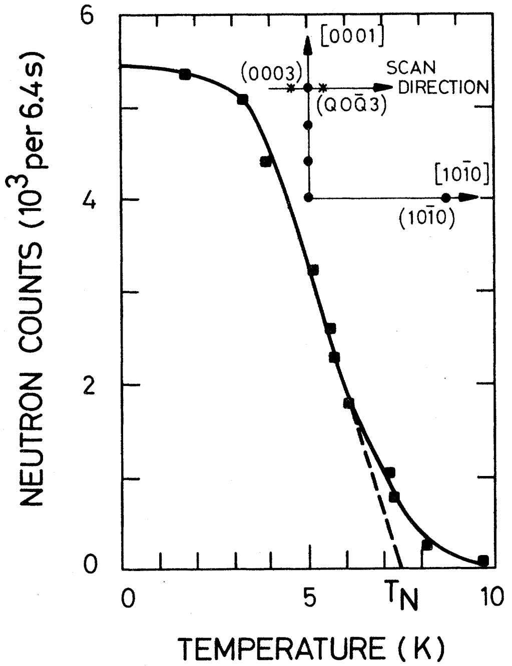

FIG. 1. Temperature dependence of the peak intensity of the $(Q0\bar{Q}3)$ satellite reflection observed in Pr when a uniaxial stress of 800 bars is applied along $[1\bar{2}10]$. The curve through the data points serves to guide the eye, and the dashed line shows the mean-field extrapolation used to determine T_N. The direction of the elastic scans is also indicated.

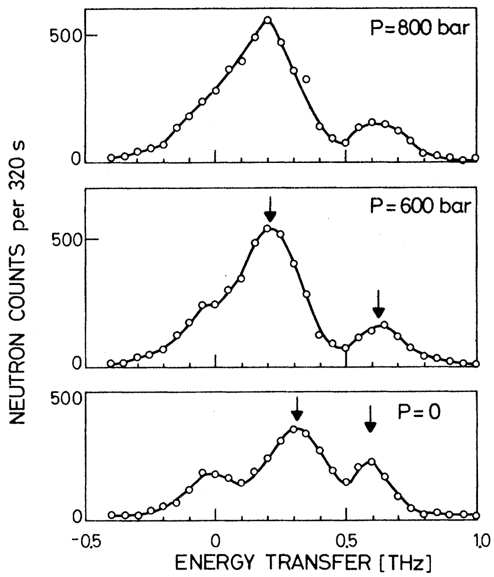

FIG. 2. Constant-Q neutron groups measured at the reciprocal-space position (0.2, 0, −0.2, 3). These measurements were taken in the constant-incident-neutron-energy configuration; the variation of the analyzer crystal efficiency with θ_A for these energy transfers is not particularly significant and so the data have not been modified for this effect. The sample temperature was 5.2 K in each case. The lines are guides to the eye.

exist, as found by Houmann *et al.*[4] These correspond to acoustic and optic excitations: Anisotropic exchange causes the longitudinally polarized modes to have lower energy than the transverse modes. The two lower branches (LO and TO modes) in the ΓM direction were found to be strongly dependent on a perpendicular stress. Figure 2 shows neutron groups obtained at (0.2, 0, −0.2, 3). The three clear peaks at zero applied stress are identified as two excitations and an elastic peak due to incoherent scattering. The energy of the lower mode is substantially reduced on application of the stress and its intensity increases, while the upper mode hardens in energy and its intensity decreases.

A comparison of the results for the dispersion of the two lower modes at 800 bars with the zero-stress results is made in Fig. 3. The longitudinal optic mode propagating along ΓM has a considerably lower energy at 800 bars: The softening is most pronounced near the ordering wave vector. It is not clear whether the mode becomes totally soft at the ordering temperature. A number of high-resolution scans [spectrometer configuration (ii)] were made at 5.2 K (i.e., below

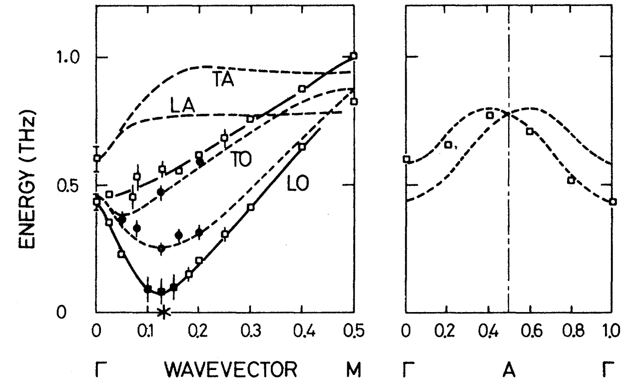

FIG. 3. Dispersion relations for magnetic excitons propagating on the hexagonal sites in Pr, under the following conditions: □ $T = 5.2$ K, $p = 800$ bars, spectrometer configuration (i); ■ $T = 5.2$ K, $p = 800$ bars, configuration (ii); ● $T = 5.2$ K, $p = 0$, configuration (i). The symbol * denotes the satellite position. The dashed lines represent the $p = 0$ data at $T = 6.4$ K of Houmann *et al.* (Ref. 4). The two upper (acoustic) modes were not examined under stress. The double-zone representation is used in the ΓA direction.

T_N). At the satellite wave vector an inelastic peak at 0.08 ± 0.05 THz could just be resolved from the tail of the elastic (satellite) peak. Additional measurements at wave vectors (Q, 0, $\bar{Q}$, $3 \pm \xi$) indicate that the dispersion surface around the satellite position is highly anisotropic. A significant increase, with stress, of the energy of the transverse optic mode along ΓM is apparent from Fig. 3. The dispersion of the degenerate mode along ΓA was also investigated. Slight differences between the results for $p = 0$ and 800 bars are of the same order as the experimental resolution.

After removal of the stress, the exciton dispersion was further examined, at 5.2 K, at a number of wave vectors (including the satellite position). These results, shown in Fig. 3, agree well with those of Houmann *et al.*[4]

Jensen's calculation[5] of the magnetoelastic coupling in Pr used an $S = 1$ model for the crystal-field levels. In a new calculation,[8] the complete level scheme has been considered with a hexagonal site Hamiltonian of the form

$$H = H_{cf} - B_{22}\bar{\epsilon}_\gamma\sqrt{\tfrac{3}{8}}\,O_2^{\,2},$$

where $O_2^{\,2} = \frac{1}{2}\{(J^+)^2 + (J^-)^2\}$ and ϵ_γ is the equilibrium strain. From a fit to measurements[8] of the magnetic field dependence of the elastic constant c_{66}, Jensen deduced $B_{22} = 20.14$ meV, compared with his previous estimate[5] of 30 meV.

By writing the equilibrium strain as

$$\bar{\epsilon}_\gamma = (2c_\gamma)^{-1}(\sqrt{\tfrac{3}{8}})B_{22}\langle O_2^{\,2}\rangle - p_\gamma,$$

a contribution p_γ due to the applied stress may be included. Using $c_{66} = 1.62 \times 10^{10}\ \mathrm{N\ m^{-2}}$ and $c_\gamma = 4c_{66}/\mathrm{N} = 14.0$ eV together with the above value of B_{22}, a Nêel temperature of $T_N = 7.5$ K is calculated[6] at a stress of 770 bars, in excellent agreement with our observations.

In this experiment we have observed directly the soft-mode behavior of the magnetic excitons propagating on the hexagonal sites in Pr. Further experiments will be made at different stresses and temperatures to examine the dynamics of the phase transition in more detail. The response of the ions on the cubic sites will also be investigated: At zero stress the magnetic excitons on these sites are relatively dispersionless with energies of about 2THz. The application of a uniaxial stress along a crystallographic a direction has been demonstrated to produce long-range magnetic ordering in *single-cyrstal* Pr in the perpendicular b direction. There has been a controversy for many years about the existence of magnetic ordering in *polycrystalline* Pr below temperatures of 20 to 25 K.[10] Since the thermal expansion of Pr is highly anisotropic, it is suggested that the cooling of polycrystalline Pr to low temperatures generates internal stresses sufficient to induce magnetic ordering.

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