Pressure Dependence of Magnetic Excitations in PrSb

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Inelastic-neutron-scattering studies show triple degeneracy of the Γ_1-Γ_4 exciton along [111] and double degeneracy along [100] with a band-structure—related softening of the longitudinal branch at X. The Γ_1-Γ_4 and Γ_4-Γ_5 transitions decrease with increasing pressure suggesting the occurrence of a pressure-induced soft-mode magnetic transition.

The $4f^2$ configuration of Pr^{3+} in PrSb is a model singlet-triplet system in which to study the interplay of exchange and crystal-field interactions The ninefold degeneracy of the free-ion ground-state $^3H_4$ multiplet is lifted by the crystal field to give with increasing energy a Γ_1 singlet, a Γ_4 triplet, a Γ_3 doublet, and a Γ_5 triplet.[1] At low temperatures, depending on the relative strengths of the crystal-field and exchange interactions, a singlet–ground-state system may or may not exhibit a soft-mode phase transition corresponding to a polarizarion instability of the ground-state wave function.[2] The technique of inelastic neutron-scattering spectroscopy has been used to determine the crystal-field levels in a number of rare-earth intermetallic compounds, and the ionic point-charge model has been used with remarkable success to account for the body of data across the whole rare-earth series,[3,4] with the exception of the nitrides.[5] The pressure variable can be used to provide a critical test of the point-charge model for the crystal-field interaction and to vary the relative strengths of the crystal-field and exchange interaction. In this Letter we report inelastic neutron-scattering measurements on single crystals of PrSb which show that the exchange is highly anisotropic with the degeneracy of the Γ_1-Γ_4 exciton being lifted along the [001] direction. Measurements on single crystals show that the energy of both the Γ_1-Γ_4 and the Γ_4-Γ_5 excitons decreases with decreasing interatomic spacing, a, rather than increasing as a^{-5} as predicted by the point-charge model. These results are in agreement with indirect measurements of the effect of pressure on the Γ_1-Γ_4 transition obtained from the Knight shift[6] and the magnetic susceptibility.[7] Both the symmetry of the excited states and the decrease in the crystal-field levels with increasing pressure are unexpected results which indicate that the theory of crystal-field effects is far from complete. Our results suggest that a pressure-induced soft-mode phase transition to an antiferromagnet will occur as the longitudinal Γ_1-Γ_4 exciton propagating along [001] direction becomes soft at the X point. NdSb with one more $4f$ electron than PrSb is a type-I antiferromagnet at 1 atm.[8,9]

The experiments were performed on a triple-axis spectrometer at the Brookhaven National Laboratory high-flux beam reactor. Pyrolytic graphite crystals were used as monochromator, analyzer, and filter. Most of the data were obtained using constant-Q energy scans with a fixed analyzer energy of 14.8 meV, and various combinations of 20- and 40-min collimation. The measurements at 1 atm were made on a single crystal mounted with the [110] axis vertical in a Cryogenics Associates CT-14 temperature-control cryostat. The measurements at high pressure and low temperature were made in a new apparatus which is based on previous high-pressure cryostats[10] and high-pressure neutron-scattering apparatus.[11,12] The high-pressure die consists of a supported high-density Al_2O_3 (Lucalox) cylinder with tungsten carbide pistons and is cooled by an Air Products closed-cycle He refrigerator. A crystal was cut with the [100] axis vertical into a cylinder 4 mm in diameter and 1 cm high and mounted in a Teflon cell using Fluorinert FC-75[13] as a pressure-transmitting medium. The pressure on the sample was increased until the lattice parameter had decreased $\approx 1\%$ at room temperature and then the sample cooled to 28 K. The fractional change in the lattice parameter, $\Delta a/a_0 = -0.0098$, corresponds to a pressure of ~ 1.6 GPa using a value of the bulk modulus of 51 GPa.[14]

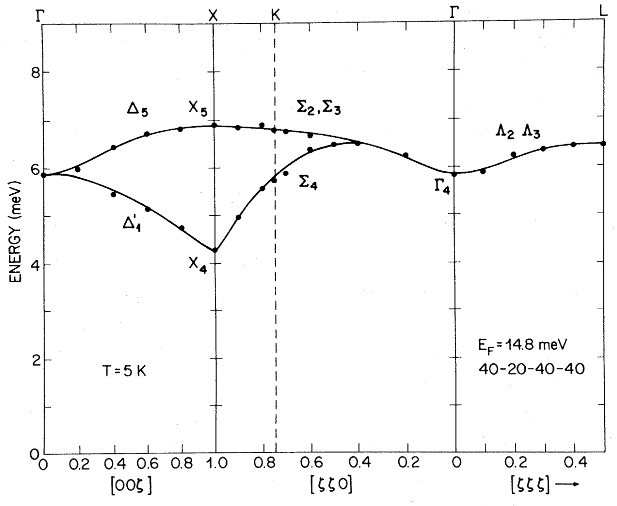

FIG. 1. The lifting of the triple degeneracy of the Γ_1-Γ_4 exciton in the $4f^2$ configuration of Pr^{3+} in PrSb by the anisotropy in the exchange interaction. Note the large splitting along [001] and the absence (within the limits of resolution) of any splitting along [111]. The lines are guides to the eye.

The mosaic spread increased from ~ 0.2 to ~ 0.5 on compression.

For Pr^{3+} ($^3H_4$), the consideration of symmetry and neutron selection rules for magnetic-dipole transitions leads to the result that the energy levels can be completely specified at the zone center by measuring the Γ_1-Γ_4 and Γ_4-Γ_5 excitons.[2] The results obtained at $P = 1$ atm and $T = 5$ K are shown in Fig. 1 for the Γ_1-Γ_4 exciton. The energies were determined by a least-squares refinement of the data assuming a Gaussian line shape. The literature value for this transition is 6.3 ± 0.3 meV[2] and this is in agreement with the data in Fig. 1. In order to determine the symmetry of the modes, both longitudinal and transverse scans were made in the three principal directions. From the variation with Q of the intensity, the upper branch along $[0,0,\zeta]$ was identified as the doubly degenerate Δ_5 mode. Scans taken with higher resolution (20-20-20-40) along Σ give linewidths of 0.65, 0.92, and 0.65 for $\zeta = 0$, 0.25, and 0.5, respectively, which suggests that Σ_4 separates from Σ_2 and Σ_3 and then crosses them at $\vec{q} = \frac{1}{2}$.

The effect of pressure on the (Γ_1-Γ_4) triplet exciton is shown in Fig. 2. In the inset is a typical scan obtained at $P = 1.6$ GPa and $T = 28$ K. The Δ_5 and Σ_2, Σ_3 modes decrease more or less uniformly by 0.7–0.9 meV which corresponds to $d\ln E(\Gamma_1 - \Gamma_4)/d\ln a = 13 \pm 1$ at $\vec{q} = 0$.

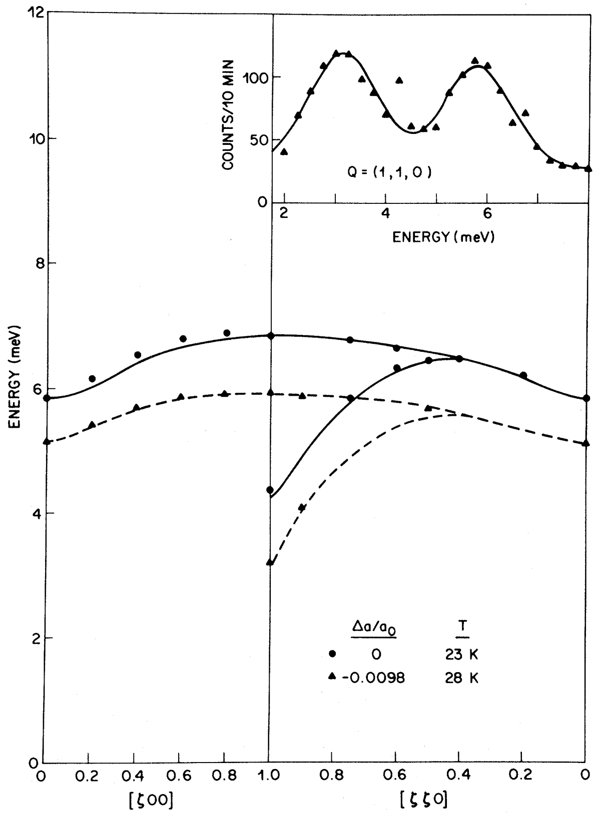

FIG. 2. The effect of pressure on the crystal-field levels. The results suggest that a soft-mode magnetic transition will occur at higher pressures. The 1-atm line is from Fig. 1. The inset shows typical data obtained at $P = 1.6$ GPa (16 kbar) and $T = 28$ K.

The intensity of the Γ_4-Γ_5 transition is substantially weaker than that of the Γ_1-Γ_4 transition as a result of population-factor and matrix-element effects. A larger powder sample was studied at $P = 0.5$ GPa ($\Delta a/a_0 = -0.003$) and $T = 298$ K using a pressure die made of a high-strength Al alloy (7075-T6). The results are shown in Fig. 3. The measurements at high pressure were made at several different values of Q with similar results and the average of data collected at $Q = 1.3$ and 1.35 Å^{-1} is plotted in the figure. The data at 1 atm correspond to the sample out of the pressure cell with $Q = 1.5$ Å^{-1} and $E_1 = 30$ meV. It is clear that the energy of the Γ_4-Γ_5 transition has decreased with decreasing lattice spacing. The position at 1 atm[2] and the position expected if the Γ_4-Γ_5 transition were to scale with the Γ_1-Γ_4 transition are indicated at the top of the figure. The observed spectra are not inconsistent with this scaling.

The Knight shift and the magnetic susceptibility

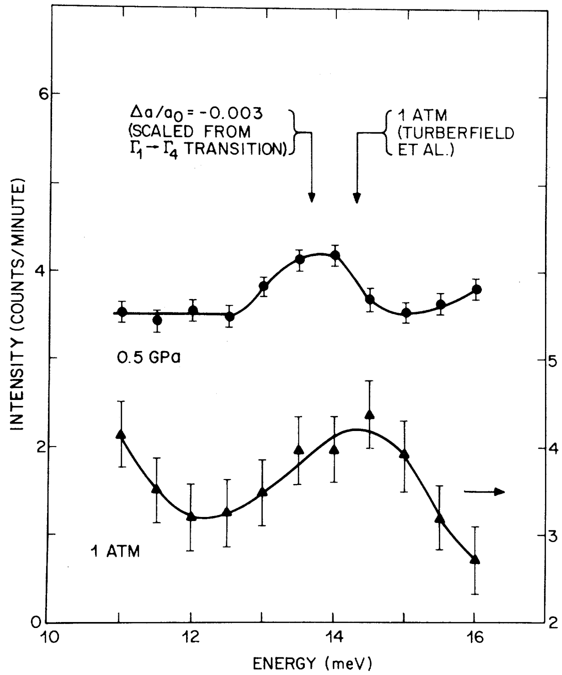

FIG. 3. The effect of pressure on the Γ_4-Γ_5 transition. Data taken on a powder sample at $P = 0.5$ GPa and $T = 298$ K. The transition decreases in energy with increasing pressure. The shift expected, if the pressure dependence of the Γ_4-Γ_5 transition were to scale with that of the Γ_1-Γ_4 transition, is indicated by arrows.

are sensitive only to the energy difference between the Γ_1 singlet and Γ_4 triplet at $\vec{q} \to 0$, and the interpretation of the pressure measurements is further complicated by the problem of separating exchange and crystal-field effects. The diagonalization of the crystal-field Hamiltonian as a function of W (a scale factor) and x (the ratio of the fourth-order to sixth-order terms) shows that a decrease in the energy of the Γ_1-Γ_4 transition could result either from a decrease in W or from x becoming more negative. At $P = 0.5$ GPa the energy of the Γ_4-Γ_5 transition should decrease 0.5 meV or increase 0.2 meV for changes in W or x, respectively. The data in Fig. 3 are more compatible with a decrease in the scaling factor W with decreasing interatomic spacing (increasing pressure). In a point-charge model W varies directly as the effective charge Z of the ligands and the average $4f$ radial wave function, $\langle r^4 \rangle$, and inversely as the fifth power of the interatomic spacing. The negative pressure dependence of W suggests that the screening of the effective charge dominates over the a^{-5} dependence on interatomic spacing. There must be a cancellation of competing chemical effects which results in the crystal-field parameters increasing with increasing atomic number (and decreasing interatomic spacing)[4] but decreasing with increasing pressure.

Turning to a discussion of the dispersion curve, we shall call attention to two principal points: the lifting of the degeneracy and the depression of the longitudinal mode at X. Many related materials have exciton spectra which are consistent with the hypothesis of isotropic exchange which implies triple degeneracy at all $\vec{q}$. In the case of Pr metal, exchange which is axially symmetric about the line between the sites is indicated.[15] The present results, with triple degeneracy along Λ and double degeneracy along Σ, are unusual and indicate that a typical exciton can be described as an excitation to a Γ_4 state oriented along one of the cubic axes, which hops between sites without change of orientation. (The Γ_4 representation is that to which axial vectors belong.) At any point in $\vec{q}$ space, the modes are labeled x, y, or z. Along (110), x and y are degenerate; along (111), all three. This labeling is also appropriate for isotropic exchange, but it is surprising that it applies when the degeneracy is lifted.

The minimum in the longitudinal mode at X is so sharp as to be indistinguishable from a cusp in our data. Such behavior cannot be reproduced by models involving interactions with only a few near neighbors. It should be emphasized that the depression cannot be due to interactions with phonons, as the phonons and excitons have opposite parity at X. Moreover, while the X_5' phonons have almost the same energy as the X_5 excitons, examination of the phonon dispersion in LaSb,[16] PrSb,[16] and NdSb[17] shows no evidence for anomalous behavior in PrSb.

A plausible explanation of the observed dispersion is found in the band structure, which has been calculated neglecting spin-orbit coupling.[18] There are a pocket of holes at Γ and three pockets of electrons at the X points, the latter being elongated in the Δ direction. There are a number of processes by which the electron can be scattered from X to Γ, while an exciton in an f shell is deexcited, and then scattered back as the exciton is created again at another site. These processes involve the electrostatic couplings between the f-shell and outer electrons ($\vec{J}_1 \cdot \vec{l}$ or $\vec{J}_1 \cdot \vec{s}$) and appear to give the proper sign for the splitting of the exciton levels at X. Although we cannot at present claim that either the magnitude of the splitting or the sharpness of the structure at X is predicted, the observed lifting of the degeneracy via interaction with the conduction electrons is certainly feasible and warrants further theoretical study.

The softening of the longitudinal exciton at X and the decrease in the crystal-field splitting with pressure suggests that at higher pressures a soft-mode magnetic transition will occur. This raises the possibility of studying the evolution of the exciton as a function of pressure near the critical pressure. Preliminary experiments performed in a clamp device at the Institut Laue-Langevin suggest that the critical pressure for the stabilization of a magnetic ground state is $P \approx 3.5$ GPa. Experiments are in progress to determine the phase boundary and the evolution of the excitons near the critical pressure.

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