The true excitations may possibly have a very short lifetime and no well-defined wave number. This would make it more difficult to observe them by means of neutron scattering techniques.

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Neutron Scattering from fcc Pr and Pr_3Tl

R. J. Birgeneau
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
and Danish Atomic Energy Commission Research Establishment Risö, Roskilde, Denmark

and

J. Als-Nielsen
Danish Atomic Energy Commission Research Establishment Risö, Roskilde, Denmark

and

E. Bucher
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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Elastic-neutron-scattering measurements on the singlet-ground-state ferromagnets fcc Pr and Pr_3Tl are reported. Both exhibit magnetic phase transitions, possibly to a simple ferromagnetic state at 20 and 11.6 °K, respectively. The transitions appear to be of second order although that in fcc Pr is clearly anomalous. Additional information on the inelastic scattering studies of the Γ_1-Γ_4 excitons in these systems is presented. dhcp Pr is also briefly discussed.

In a recent paper,[1] we have reported inelastic-neutron-scattering studies of the elementary magnetic excitations, crystal field excitons, in the singlet-ground-state ferromagnets fcc Pr and Pr_3Tl. It was found that well-defined excitons existed in both the ferromagnetic and paramagnetic regimes but with energies which were nearly independent of temperature. This latter result was most surprising in light of our expectations based on the existing theory which predicted both soft-mode behavior at the phase transition and a marked overall temperature dependence of the exciton energies.[2] In this paper we report complementary elastic-neutron-scattering results which elucidate the magnetic structure; we also present additional experimental information on the inelastic studies in order to facilitate any hoped for attempts at a theoretical interpretation of these results. In two accompanying papers by Bucher, Maita, and Cooper[3] and by Andres, Bucher, Darack, and Maita[4] the bulk magnetic properties of the system $(Pr_{1-x}La_x)_3Tl$ as a function of x are presented. In a third paper Cooper[5] discusses an effective boson theory for the excitations of singlet ground state Pr in a cubic environment. This set of papers, therefore, gives a complete exposition of the available experimental and theoretical information on induced-moment ferromagnetism in Pr_3Tl. It is hoped that they will lay an effective groundwork for future studies.

For completeness we briefly review the theory. The Pr^{3+} ion has the configuration $4f^2$ with the free-ion $^3H_4$ multiplet lying lowest. For a cubic system the crystal-field Hamiltonian may be written

$$\mathcal{H}_{CF} = A_4\langle r^4\rangle \chi_4 [O_4^0(J) + 5\,O_4^4(J)] + A_6\langle r^6\rangle \chi_6 [O_6^0(J) - 21\,O_6^4(J)], \quad (1)$$

where the O_n^m are Stevens operator equivalents and the χ_n are reduced matrix elements.[6] The consequent single-ion energy levels for fcc Pr with the

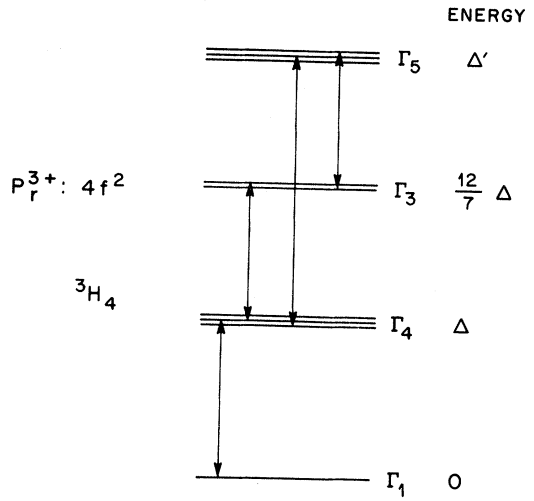

FIG. 1. Crystal-field level scheme for Pr^{3+} in a cubic environment with the Γ_1 singlet the ground state. The arrows indicate nonvanishing magnetic-dipole matrix elements.

signs and relative magnitudes of $A_4\langle r^4\rangle$, $A_6\langle r^6\rangle$ estimated from a point-charge model (PCM) are shown in Fig. 1. It should be noted that in the PCM the ground state will always be the Γ_1 singlet provided only that the effective point charge is positive. The arrows in Fig. 1 indicate the levels between which there are nonvanishing magnetic-dipole matrix elements.[7] From specific-heat measurements in fcc Pr Bucher *et al.*[8] estimate $\Delta \sim 69$ °K in reasonable agreement with the exciton dispersion value of ~84 °K. No experimental information is available about Δ' except that it must be $\gtrsim \Delta$. For Pr_3Tl the point symmetry is strictly tetragonal. However, in the PCM if we take $Z(\mathrm{Tl}) \simeq Z(\mathrm{Pr})$ then the symmetry is effectively cubic. Indeed, throughout this paper we shall regard Pr_3Tl simply as an ordered dilute fcc alloy. In Pr_3Tl Bucher *et al.*[3] estimate $\Delta = 78 \pm 10$ °K, in excellent agreement with the exciton dispersion value of 79 °K. Again no information is available about Δ'. It should be noted, however, that in all of the praseodymium pnictides and chalcogenides[9] where explicit spectroscopic values for Δ, Δ' are known, it is found that $\Delta' \simeq 3\Delta$.

In addition to the single-ion term (1), we must also include the exchange term

$$\mathcal{H}_{ex} = -2\sum_{i>j} \mathcal{J}_{ij}\vec{J}_i\cdot\vec{J}_j \,. \tag{2}$$

As has been discussed extensively in the accompanying papers and in the literature[10] for

$$|4\alpha^2\mathcal{J}(\vec{Q})/\Delta| < 1 \tag{3}$$

for all $\vec{Q}$ [$\mathcal{J}(\vec{Q})$ is defined below], the system will remain a Van Vleck paramagnet down to 0 °K. The corresponding elementary excitations at $T = 0$ will be Γ_1-Γ_4 crystal-field excitons with a triply degenerate dispersion relation

$$\hbar\omega_{14}(\vec{Q}) = [\Delta^2 - 4\Delta\alpha^2\mathcal{J}(\vec{Q})]^{1/2} \,, \tag{4}$$

where

$$\alpha = |\langle\Gamma_1|J^z|\Gamma_4\rangle|$$

and

$$\mathcal{J}(\vec{Q}) = \sum_{\vec{r}_j} \mathcal{J}_{ij} e^{i\vec{Q}\cdot(\vec{r}_i - \vec{r}_j)} \,.$$

This dispersion relation, Eq. (4), is identical to that for two singlets.

In the random-phase approximation (RPA) for the singlet-singlet case,[2] Eq. (4) is generalized to finite temperatures by multiplying $\mathcal{J}(\vec{Q})$ by a temperature-dependent renormalization factor $R(T)$, which varies from ~1 at $T = 0$ to ~0 for $k_BT > \Delta$. Thus, as the temperature is raised, the exciton should lose dispersion, ultimately becoming nearly flat for $k_BT > \Delta$. We would expect these temperature effects to be more dramatic in the singlet-triplet case because of the more rapid depopulation of the ground state with increasing temperature.

For situations in which the exchange exceeds the critical value necessary for magnetic order, that is, those for which Eq. (3) is not satisfied, the over-all behavior is rather more complicated. Starting from high temperatures, one anticipates a marked increase in dispersion with decreasing temperature in analogy with the pure paramagnet case. For a ferromagnet this Γ_1-Γ_4 exciton energy should ultimately go to 0 at $\vec{Q} = 0$ at a phase transition temperature defined by $4\alpha^2\mathcal{J}(0)R(T_C)/\Delta = 1$. This softening may occur in either a real or virtual sense depending upon whether the transition is second or first order. In the ordered regime one expects that the triple degeneracy will be removed giving $T = 0$ spectra like those calculated by Cooper.[5] Here the longitudinal mode will be similar to that in the singlet-singlet problem whereas the transverse modes may have quite different behavior. For example, if one ignores the higher-lying Γ_3, Γ_5 levels one finds that the transverse modes go to 0 at $\vec{Q} = 0$.[11] In general, these higher-lying levels play an important role in all aspects of the exchange-induced ordering process because of the sensitivity of the phase transition to any perturbation.

We consider first the elastic-neutron-scattering results. These experiments were performed on a triple-axis spectrometer at the DR3 reactor at Risö. The spectrometer was operated both in the double-axis and triple-axis mode, with the latter giving a signal-to-background ratio but with a corresponding loss in over-all intensity. The fcc Pr was in the form of ~20 g of 3-mm pellets in a cy-

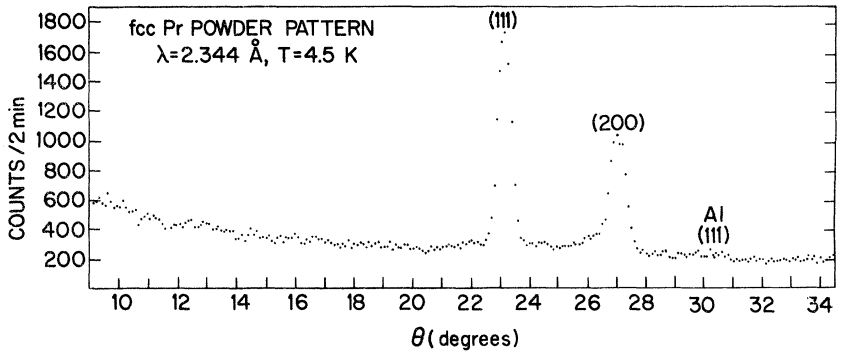

FIG. 2. Two-axis powder pattern for fcc Pr at 4.5 °K.

lindrical aluminum sample holder. The starting material was from lot 2 of the previously reported bulk property studies.[8] As is well known, Pr normally has the dhcp structure at room temperature; however, the high-temperature fcc phase may be retained by quenching from ~1300 °K in an arc furnace. Previous bulk magnetization studies[8] indicated that fcc Pr undergoes a ferromagnetic transition at 8.7 °K with a saturation moment of $0.76\mu_B$. Similar measurements on the sample used in this experiment confirmed this result although it was found that in this and other samples some remanence persisted up to ~20 °K. The purpose of this elastic-neutron-scattering study of fcc Pr was (a) to ensure that our sample was composed of the fcc phase alone, (b) to verify that magnetic ordering does occur and that it is not parasitic, (c) to determine the corresponding magnetic structure, and (d) to determine the saturated moment and the M vs T relationship.

Wide-angle 2θ scans at 293 °K confirmed that our material was indeed pure fcc. All observed peaks could be indexed on the fcc cell with a lattice constant $a = 5.186$ Å. For an elemental fcc structure the observed powder peaks have intensities which are simply related via the relative Lorentz factors and multiplicities. A detailed study of the intensities of the peaks from (1, 1, 1) out to (3, 3, 3), however, showed that in our sample the (h, k, l) even peaks were systematically 14% more intense than those with (h, k, l) odd. This necessitates that there are interstitial impurities in the $(\frac{1}{2}, 0, 0)$ positions, the actual concentration depending on the nature of the impurity. For example, if the principal contributor were nitrogen, this 14% discrepancy would imply a 1.6-at. % impurity concentration. This is somewhat larger than one would have anticipated on the basis of preexisting chemical analysis. It seems likely that such gaseous impurities act as the "glue" which stabilizes the fcc phase at room temperature.

A typical powder pattern at 4.5 °K in the region of the (1, 1, 1) peak is shown in Fig. 2. From the figure it may be seen that there are no new peaks so that if magnetic ordering has occurred it must be at least nearly commensurate with the lattice; alternatively, the noncommensurate component of the moment could be below our limit of detectability (~ $0.2\mu_B$ here). The temperature dependence of the (1, 1, 1) integrated intensity is shown in Fig. 3. Clearly, a magnetic phase transition has occurred at 20 °K. From the ratio of the magnetic to the nuclear scattering the estimated 0 °K moment is $(0.65 \pm 0.1)\mu_B$ in reasonable agreement with the bulk value of $0.76\mu_B$. We note, however, that there is no sign of an anomaly at 8.7 °K, the previously reported ferromagnetic transition temperature. We do not have an unambiguous explanation of this apparent contradiction. One possibility, albeit purely speculative, is that the ordering at 20 °K is to a long-wavelength spiral with a second transition to a simple ferromagnetic state at 8.7 °K. We should also note that, as mentioned previously, the bulk magnetization shows a small remanence persisting up to 20 °K, and in addition, neutron depolarization measurements on fcc Pr in a field of 100 G by Koehler[12] indicate the presence of ferromagnetism to above 20 °K.

The elastic-scattering results for Pr_3Tl are somewhat more straightforward. Here the sample was a 40-g polycrystalline ingot. The Pr_3Tl structure[13] (Cu_3Au) is generated from fcc Pr by replacing corner Pr atoms by Tl. This makes allowed peaks with h, k, l, not all odd or all even. The intensities of these new peaks relative to the "fcc" peaks are calculated to be 1 : 25 using literature values for the nuclear-scattering lengths of Pr and Tl.[14] Nitrogen-temperature powder scans confirm our sample to be the ordered Cu_3Au structure with lattice constant $a(77\ °K) = 4.926$ Å. The nuclear peak intensities are found to be only weakly temperature dependent down to 11.6 °K, at which temperature additional scattering, assumedly magnetic in origin, appears. Results for the (1, 1, 1) peak are shown in the bottom of Fig. 3. Again, the magnetic scattering occurs only at the nuclear positions implying simple ferromagnetism. Some of the weaker peaks [explicitly (1, 1, 0), (2, 0, 1)],

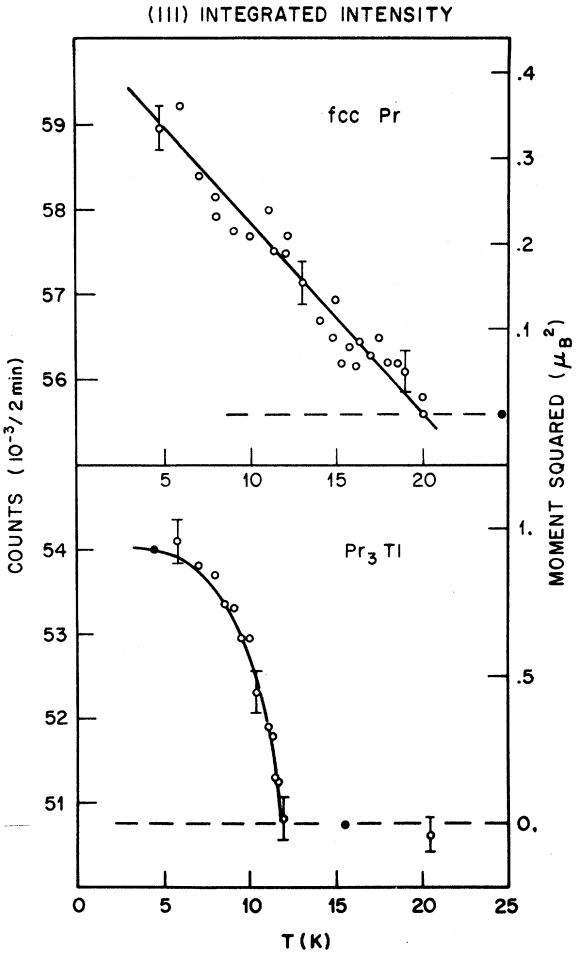

FIG. 3. Integrated intensities of the (1, 1, 1) peaks in fcc Pr and Pr_3Tl. The filled dots are points taken with very high statistics. The dotted line indicates the high-temperature value of the intensity.

however, show an increase in intensity somewhat larger than that calculated on the basis of the magnetic scattering alone. This could indicate that the actual magnetic structure is quite complicated or, more likely, that there are magnetoelastic effects which increase the nuclear component of the scattering for these otherwise very weak peaks. The saturation moment in this case is nearly $1\mu_B$, somewhat larger than the $0.7\mu_B$ estimated from bulk properties while T_C (11.6 ± 0.3 °K) is in good agreement with the bulk value (11.0 and 11.3 °K in two different samples).

There are several final comments of note on these elastic-scattering results. First, because the experiments were done on polycrystalline samples with unpolarized neutrons, our firm conclusions are rather limited in scope. In both cases, we have verified that magnetic ordering takes place, possibly to a simple ferromagnetic state, although there are some remaining difficulties both with fcc Pr and Pr_3Tl. These ambiguities can only be resolved by studies using single crystals and possibly polarized neutrons. For fcc Pr the chances of growing a large single-crystal seem negligible, while for Pr_3Tl there are also some metallurgical difficulties which we have not been able to overcome. For both fcc Pr and Pr_3Tl the magnetic phase transition appears to be continuous (see Fig. 3) so that if either transition is first order it must be only weakly so. However, fcc Pr is clearly anomalous in that the magnetization seems to follow a simple square-root law down to 4.5 °K. Again, these questions can only be resolved by a careful study using single crystals.

As discussed extensively in our previous paper,[1] the Γ_1-Γ_4 excitons in these systems have a temperature behavior entirely different from that anticipated on the basis of the existing theory described earlier in this paper. Well-defined excitons are observed in both the ferromagnetic and paramagnetic regimes but with energies which are nearly independent of temperature. As the temperature is raised, the exciton intensity gradually decreases until at 78 °K in both systems it merges into a broad continuum of scattering extending out to about 10 meV. In our previous publication we showed typical data for a wave vector $Q = 0.6$ Å^{-1} for Pr_3Tl. In Figs. 4 and 5 we present additional data for Pr_3Tl at $Q = 0.4$ Å^{-1} and for fcc Pr at $Q = 0.6$, 1.0 Å^{-1}. These inelastic studies were performed on polycrystalline samples with Q measured from the forward direction, that is, from the

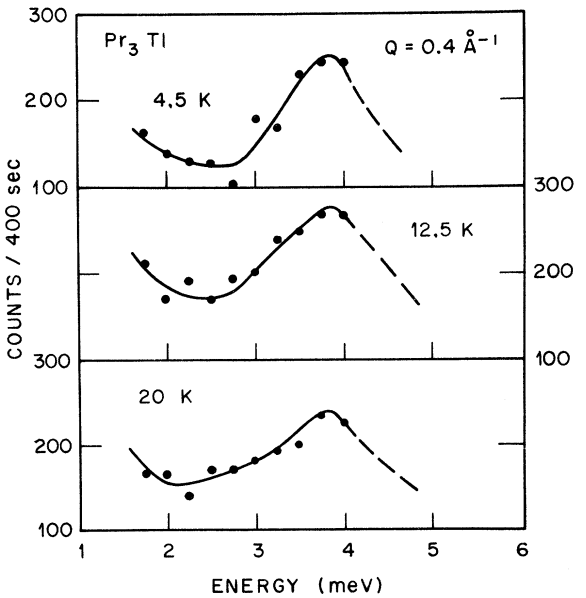

FIG. 4. Γ_1-Γ_4 exciton scans in Pr_3Tl at several temperatures. Here $T_C = 11.6 \pm 0.3$ °K.

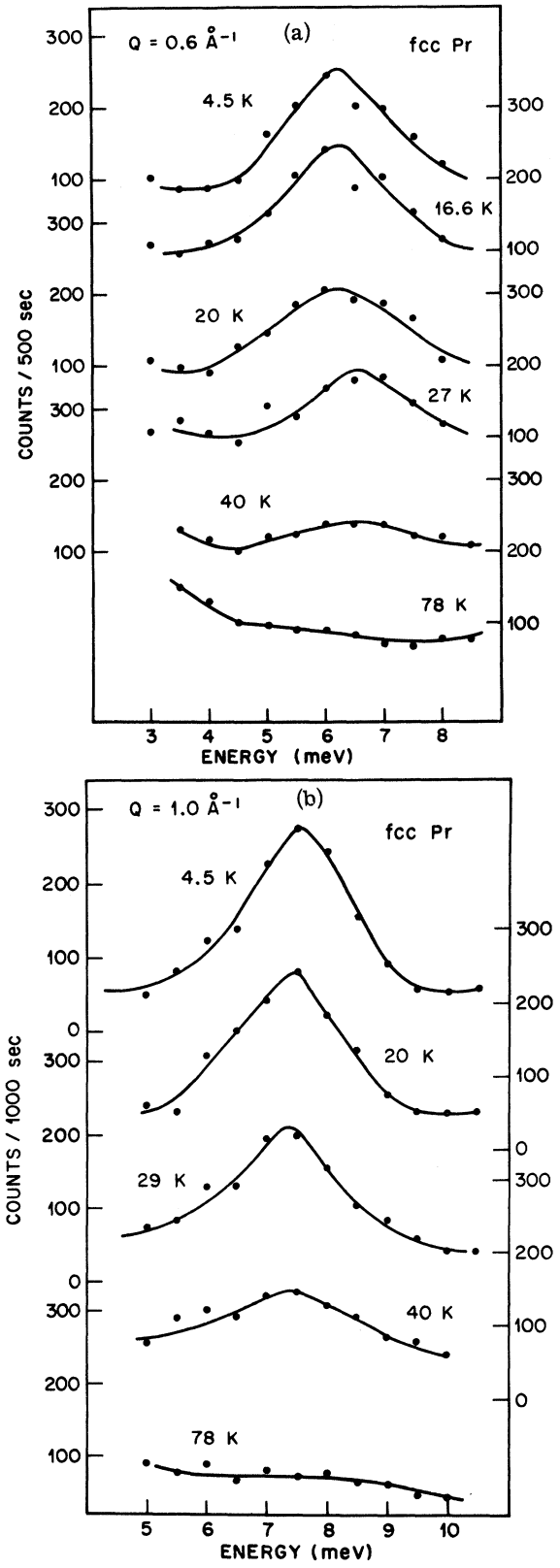

FIG. 5. Γ_1-Γ_4 exciton scans in fcc Pr at several temperatures. Here $T_C = 20 \pm 1$ °K. (a) $Q = 0.6$ Å^{-1}; (b) $Q = 1.0$ Å^{-1}.

(0, 0, 0) reciprocal-lattice position. This corresponds to measuring a spherically averaged dispersion relation. In an fcc structure with dominant nearest-neighbor interactions, such a measurement is quite close to single-crystal measurements along the (1, 1, 0) axis over most of the Brillouin zone. The major disadvantage of this technique is that the region around $Q = 0$, which is perhaps of the most interest physically, is not experimentally accessible because of contamination from the direct beam. This effect may be seen in Fig. 4. Here the upper half of the exciton peak is dominated by the forward scattering, and we have only been able to draw in an estimated curve. Nevertheless, if the predicted soft-mode behavior at wave vectors accessible to us did occur, then it would have been readily observable in our experiment. However, if the softening was confined to long wavelengths, that is, $Q < 0.2$ Å^{-1}, it would not have manifested itself in our spectra. In short, the existing predictions for the over-all temperature dependence of the exciton dispersion relation are incorrect; however, we cannot make any definitive statement about the existence of a soft mode except that it must be confined to long wavelengths if it occurs at all. It should be emphasized that soft-mode behavior of this sort is not contained in the existing theory which predicts that at T_C the exciton dispersion relation should vary linearly with Q, going to 0 at $Q = 0$. It is this latter type of soft-mode behavior which we can definitively rule out.

Finally, we should relate these results to those of Rainford and Houmann[15] and others[16–19] in dhcp praseodymium. In this structure the packing sequence along the c axis is $ABAC$; the A layers have a local environment of approximately cubic symmetry, while in the B and C layers the atoms have a hcp arrangement of nearest neighbors. Both the A and B, C sites have crystal fields such that the ground state is a nonmagnetic singlet. Neutron-diffraction measurements on polycrystalline dhcp Pr indicate a transition to antiferromagnetic long-range order at ~ 25 °K, and it has been suggested that this order is associated exclusively with the hexagonal sites. However, similar measurements on single crystals down to 1.7 °K show no evidence for a magnetic phase transition.[18] Rainford and Houmann[15] have studied the elementary excitations from 4.2 to 30 °K. They observe a complex array of crystal-field excitons which may be assigned separately to the cubic and hexagonal sites. The cubic site Γ_1-Γ_4 exciton branch is rather flat with an energy of 8–9 meV. This is in good agreement with the Γ_1-Γ_4 crystal-field splitting in fcc Pr of 7.2 meV, especially considering that the nearest-neighbor spacing in fcc Pr is about 1% larger than that in dhcp Pr. The hex-

agonal site excitons in dhcp Pr are much more complex, indicating the presence of appreciable anisotropic interaction effects.[19] From our point of view, however, the important feature is that Rainford and Houmann do see a slight softening of the exciton at the zone boundary perhaps indicating an incipient phase transition. This is in contrast with our results where no apparent softening at all is observed.

In an attempt to resolve the single crystal vs polycrystalline ordering dilemma in dhcp Pr, we have reexamined the Bragg scattering in a polycrystalline sample using triple-axis techniques. It seemed to us that the strong inelastic exciton scattering might mimic an antiferromagnetic Bragg peak in a two-axis powder scan. Accordingly, we examined the Bragg scattering in a good-purity polycrystalline rod of dhcp Pr using a triple-axis spectrometer with an energy resolution of ~ 0.4-meV half-width. The result, very briefly, is that the relative intensities of the "antiferromagnetic" and nuclear peaks are unaffected by energy analysis of the outgoing neutrons, implying that the system has true antiferromagnetic long-range order. The dhcp praseodymium dilemma, therefore, remains unresolved.

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