Solid State Communications, Vol.36, pp.861-868.
Pergamon Press Ltd. 1980. Printed in Great Britain.

LOW TEMPERATURE PHASE TRANSITIONS AND MAGNETIC STRUCTURE OF PrB_6

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(Received 8 August 1980 by H. Suhl)

Specific heat, thermal expansion and electrical resistivity measurements on PrB_6 single crystals show that there are two low temperature phase transitions at 6.9 K and 4.2 K, respectively, the latter temperature varying somewhat among different crystals. Neutron diffraction measurements were made on both single and polycrystalline samples of PrB_6. The neutron data indicate a spontaneous incommensurate magnetic ordering at 6.9 K with $Q = (0.23, 0.23, 0.5)\ 2\pi/a_o$. At 4.2 K a commensurate magnetic phase is seen with $Q = (0.25, 0.25, 0.5)\ 2\pi/a_o$ coexisting with the incommensurate phase At 1.74 K, only the commensurate phase remains. A model is proposed for the commensurate antiferromagnetic structure and a profile analysis based on that model yields a magnetic moment of 1.77 Bohr magnetons per praseodymium ion at 1.74 K.

I. Introduction

At the present time the magnetic properties of the rare earth hexaborides are not completely determined or understood. These materials have a cubic crystal structure that can be described as CsCl type with a rare earth ion at each cube corner and a boron octahedron at the body center. X-ray measurements[1] have shown the lattice parameter of PrB_6 to be 4.133 A at room temperature.

Previously only one magnetic transition has been reported for PrB_6. Based on resistivity and susceptibility measurements, Matthias et al.[2] reported antiferromagnetic ordering below 7 K. Hacker et al.[3] reported Curie-Weiss behavior above 100 K with a moment of $3.64\ \mu_B$ and $\theta = -41$ K, and a Néel temperature of 8.3 K. Lee et al.[1] reported a very sharp anomaly in the specific heat corresponding to a transition at 6.9 K. A close examination of this data below 5 K reveals possibly significant deviations between the experimental points and a smoothly fitted curve, although the mesh of data points is not sufficiently fine to distinguish any structure in the data.

Measurements of the low temperature thermal expansion of single crystal PrB_6 which are reported below gave the first clear indication of two low temperature phase transitions at 4 K and 7 K, respectively. Subsequent electrical resistivity and specific heat measurements confirmed this. The neutron scattering measurements reported here were undertaken to examine these magnetic phases of PrB_6 and to determine the specific ordering of the Pr^{3+} moments.

II. Experimental Procedure

A. Specific Heat

The sample material used for specific heat measurements consisted of an assembly of 23 small crystallites with a total mass of 190 milligrams. These crystals were grown using a molten aluminum flux method.

Measurements were made in a He^4 cryo-

*Research supported by the National Science Foundation under Grant No. DMR77-08469.

stat using a differential heating technique with a calibrated germanium thermometer in a manner similar to that discussed earlier.[4] No exchange gas was used. The precision of the measurements, based on run to run repeatability for pure copper, is estimated to be 0.5%. Due to the small size of the sample the accuracy of the measurements reported here is estimated to be near ±2%.

B. Electrical Resistivity and Thermal Expansion

The electrical resistivity was measured by a conventional 4-probe method at 220 Hz. Electrical contact to the single crystal was made via spot-welded 0.002" Pt wire. The temperature of the lower anomaly in the resistivity varied from crystal to crystal. We believe this variation is due to extreme strain sensitivity of the lower transition, and this sensitivity requires that care be taken to attach the leads using as small a discharge as possible.

The thermal expansion measurements were done using a capacitance dilatometer described elsewhere.[5]

C. Neutron Scattering Measurements

Neutron scattering measurements were made on a large polycrystalline sample and on a small single crystal having a mass of 15 mg. The polycrystalline material was prepared by the reduction of Pr_2O_3 by B_4C at about 1770 K under high vacuum. In all cases, both with polycrystalline and single crystal samples, the boron used in the preparations was highly enriched in the isotope ^{11}B (98.5%) in order to minimize the effect of absorption of thermal neutrons by the isotope ^{10}B.

Powder samples were encapsulated in a thin wall aluminum sample holder suitably mounted in a helium cryostat. (Our experimental conditions required that measurements above 4.2 K and measurements below 4.2 K be performed in different cryostats.) Diffraction data was obtained on 2XD, a double axis instrument at MURR (Missouri University Research Reactor), using neutrons of wavelength 1.293 A with a flux on sample of 2×10^6 neutrons/cm^2/sec. During the accumulation of data the sample was rotated in order to minimize the effects of preferred orientation.

Guided by the results of the powder data, diffraction scans were performed on a small single crystal in order to determine uniquely the wave vectors associated with the magnetic intensities. The effects of sample absorption, extinction and problems we encountered in orienting the crystal in a sub 4.2 K environment, made it difficult to obtain meaningful relative intensity data for the single crystal; however, it was possible to make precise measurements of the wavevectors associated with these intensities. These measurements were made on a triple axis instrument, 3XE, at MURR which was operated in the constant energy elastic mode, $\Delta E = 0$. Monochromator and analyzer crystals were both Cu(200) and yielded a beam of 1.066 A neutrons on the sample with a flux of 6×10^6 neutrons/cm^2/sec.

III. Results

A. Specific Heat

Figure 1 shows the measured specific heat of PrB_6 as a function of temperature in the range 1.7 K to 15 K. The prominent features are the large peak at 6.89 ± 0.05 K for which the peak value of C was 81.6 Joule/mole-K and a much smaller, but nevertheless distinct, peak at 4.22 ± 0.05 K. The larger peak can be identified with the Néel temperature and was reported earlier by Lee.[1] However, this peak is found to be much higher and sharper in the present work (peak height 81.6 J/mole-K compared to 30 J/mole-K). The peak at 4.22 K appears to be correlated with the anomalies seen in the thermal expansion and the electrical resistivity.

An attempt was made to estimate the entropy change for the transition at 6.9 K. A plot of C/T vs T was extrapolated to give zero magnetic contribution at 20 K and the small peak at 4.2 K was eliminated. Graphical integration of the data then gave the result $\Delta S = R \ln(3.4 \pm 0.2)$. Additional uncertainties in this result remain because of unknown or poorly determined corrections for lattice vibrations, electronic effects and Schottky anomalies. The value found here for ΔS is, however, totally consistent with the expected value for a Γ_5 triplet ground state.

B. Electrical Resistivity and Thermal Expansion

The electrical resistivity at low temperature of a PrB_6 single crystal is shown in Figure 2. Apart from the sharp anomaly at approximately 6.95 K, there is a clear, sharp drop in the resistivity at approximately 4.15 K. During the measurement for which the data is shown, the cooling of the sample was stopped at 4.02 K, and the sample was allowed to warm to 4.35 K, before continuing cooling below 4 K. There is clear hysteresis present, which can be seen in the figure. Above 4.30 K, the warming and cooling data coincide within experimental accuracy.

The thermal expansion data shown in Figure 3 very clearly shows two anomalies, peaking at 6.95 K and 3.95 K, respectively.

C. Neutron Diffraction

Neutron scattering measurements made in

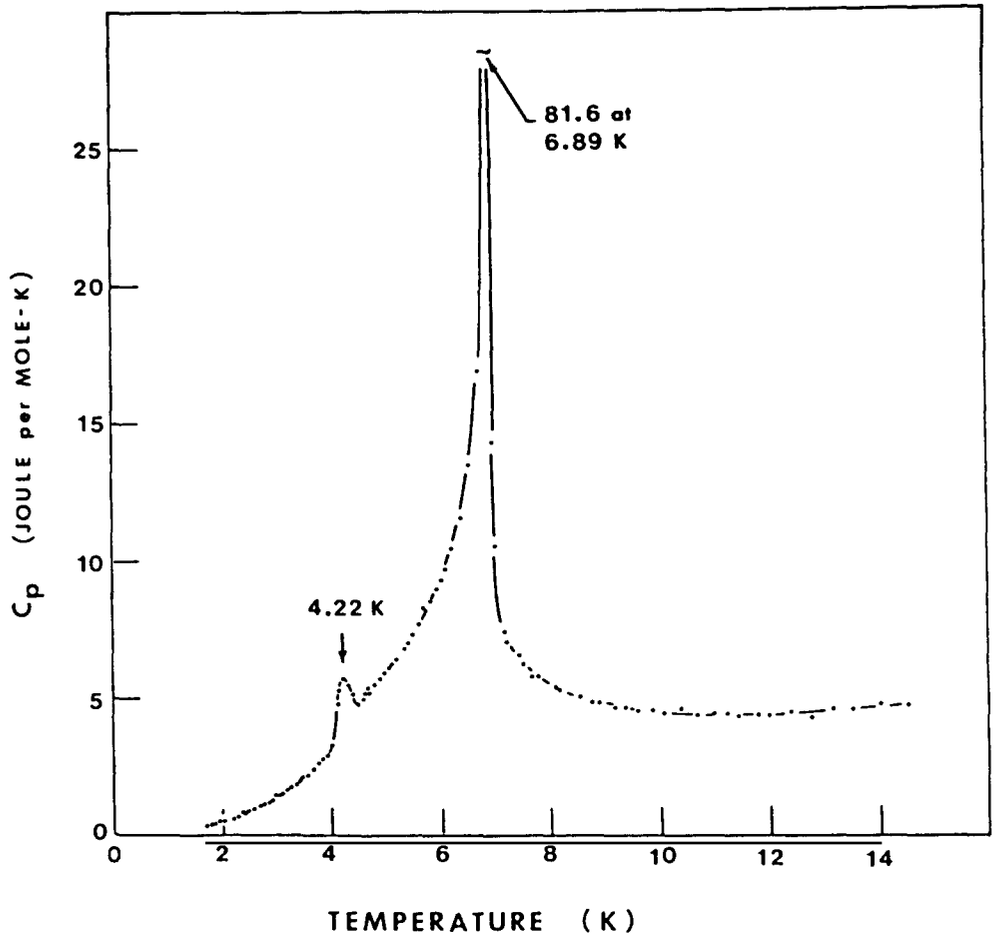

Figure 1. Representative data points for the specific heat C in units of J/mole-K versus the temperature T in units of degrees K for PrB_6.

the $(\bar{1}10)$ plane in the reciprocal lattice of the single crystal of PrB_6 gave intensities arising from the magnetic ordering at positions of the type $(h \pm \delta, k \pm \delta, \ell \pm 0.5)$ where $\delta \approx 0.25$. Scans through these magnetic reflections were made in the triple axis mode, $\Delta E = 0$, and in both [110] and [001] directions. These scans were made at several low temperatures and Figure 4 shows the results. The lower curve, a [110] direction scan at 1.74 K, shows neutron intensity clearly peaked at the point (1/4, 1/4, 1/2), indicating a commensurate antiferromagnetic ordering with the magnetic cell larger than the chemical cell by factors of four in each of two directions and by a factor of two in the third direction. The upper curve in Figure 4, taken at 6.15 K, shows the neutron intensity peaked at the position (0.23, 0.23, 0.5) indicating the antiferromagnetic ordering is either incommensurate or of a very long period. The middle curve, at an intermediate temperature 4.21 K, shows the simultaneous coexistence of both phases. The temperature dependence of the intensity of this peak in the incommensurate phase is shown in Figure 5. This data was obtained by monitoring the intensity as the crystal was warmed from 4.2 K and then the crystal was remounted in a different cryostat and the process repeated on cooling from 4.2 K. Because different cryostats were used a slight renormalization of the data was required in order that the intensities at 4.2 K should coincide.

It should be noted that scans made in the [001] direction indicated that magnetic intensities occurred only for $(\ell \pm 0.5)$ for the third index. Thus, in this (third) direction, the spin ordering remained commensurate with the lattice at all temperatures and corresponds to a reversing of adjacent spins, which was exactly the case with the spin arrangement of NdB_6.[6]

Figure 6 shows the results of a powder diffraction scan at 78 K and the difference between that data and powder data obtained at 1.74 K. Data points were obtained for fixed monitor

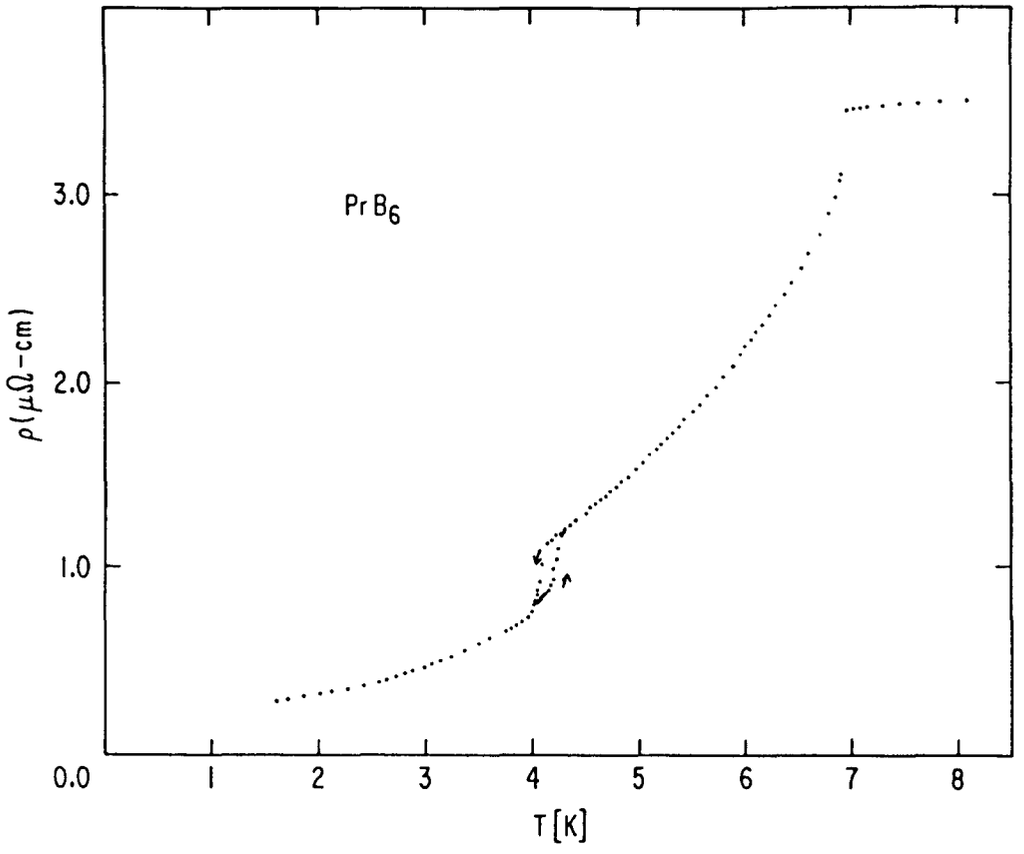

Figure 2. Low temperature electrical resistivity of single crystal PrB_6. Absolute value obtained from comparison of data with that of ref. 8.

counts (approximately 2.5 min per point) in equal angular increments, $\Delta 2\theta = 0.1°$. The nuclear cell parameters were obtained from the 78 K data and the results of a least squares fit[7] to the data are shown in the figure by the solid line. This fit gave a lattice parameter of 4.120 ± 0.001 A and the boron positional parameter u = 0.301 ± 0.001. (Boron atoms are located at (1/2 ± u, 1/2, 1/2), (1/2, 1/2 ± u, 1/2) and (1/2, 1/2, 1/2 ± u).) R factors obtained for this fit were R_{TOTAL} and R_{NUC} = 1.39 and $R_{PROFILE}$ = 5.02.

The lower portion of Figure 6 is due only to the magnetic scattering from the commensurate phase since it is a direct subtraction of the 78 K data from the 1.74 K data. All of the data points in the background regions are not plotted in the figure; rather a single point representative of a 10-point average is shown. The magnetic intensities are quite small compared to the nuclear intensities-note that the scale of the magnetic intensities is expanded by a factor of 8 in the figure. Statistical accuracy for the magnetic data is therefore rather poor, particularly so for peaks like (3/4, 1/4, 3/2) which lie in the wings of a nearby nuclear peak. The solid line presented with the magnetic data is the calculated line profile refined on the basis of an antiferromagnetic model as represented by Figure 7. In this refinement the nuclear parameters were held at the values obtained from the 78 K fit and only magnetic parameters were allowed to vary. Figure 7 shows only the Pr ions in a (100) plane. The individual moments in a 2 × 2 square array of ions are oriented parallel to each other and in (110) directions. Adjacent (2 × 2) arrays are oriented antiparallel to the first as shown. The next layer of Pr ions is arranged with moments antiparallel to those in the layer shown. Therefore the resulting magnetic cell (tetragonal) contains 32 Pr ions. In the data of Figure 6 all peaks are indexed on the basis of the cubic chemical cell rather than this expanded magnetic cell. Many other models were considered, but

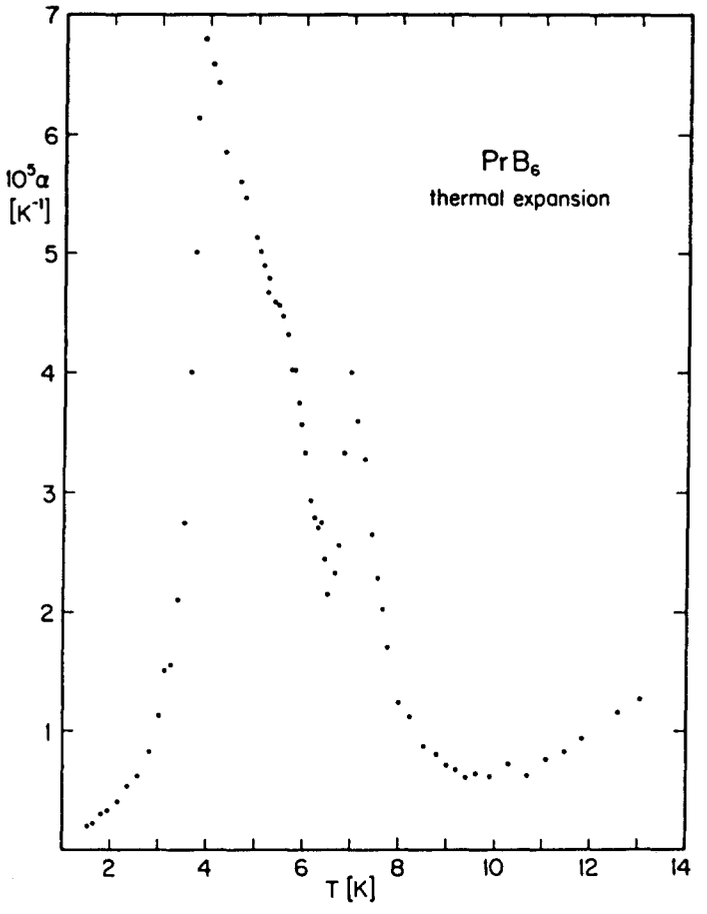

Figure 3. Low temperature linear thermal expansion coefficient of single crystal PrB_6.

only the model shown in Figure 7 gave reasonable intensities without incorrect vanishings.

In the fitting procedure each of the 32 Pr positions was treated as a unique position. No equivalent position rotation or translation matrices and no magnetic rotation matrices were used for this calculation. The results of the fitting process gave a magnetic moment of 1.77 ± 0.05 μ_B per ion at 1.74 K with R factors of $R_{TOTAL} = R_{MAG} = 34.2$. This relatively large R factor for the magnetic scattering is due to the low intensity of the magnetic scattering compared to the nuclear scattering and the large experimental uncertainty that therefore resides in the data[7] (note the error bars in Figure 6).

The magnetic moment of 1.77 μ_B is considerably less than the saturation moment expected for the free ion, $gJ\,\mu_B = 3.20\,\mu_B$. Much of this difference can be ascribed to the quenching of the orbital contribution to the moment by the crystalline electric field. The ground state of Pr in PrB_6 is a well separated Γ_5 triplet, as shown in ref. 8, and for a pure Γ_5 triplet the maximum ordered moment is 2.0 μ_B.

According to the strong thermal expansion anomaly and the temperature dependence of the electrical resistivity it is quite possible that the lower transition is a quadrupole induced structural ordering. The magnetic ordering at 6.9 K splits the Γ_5 triplet ground state into three singlets. The non-vanishing quadrupolar matrix element $\langle |O_2^2| \rangle$ between the ground state singlet and another of these singlets and the previously found strong aspherical Coulomb charge scattering of the conduction electrons[8] may lead to a quadrupolar ordering.[9] The further splitting of the two singlet states involved accounts for the small anomaly in the specific heat. A quadrupolar ordering of this type should lead to a rhombohedral distortion of the cubic lattice, a feature which could not be established in our experiments, but the symmetry of the low temperature magnetic phase gives some support for this interpretation. Furthermore we should like to mention, that structural ordering is often only seen in single crystalline samples of a material[10] and the lack of observation of this

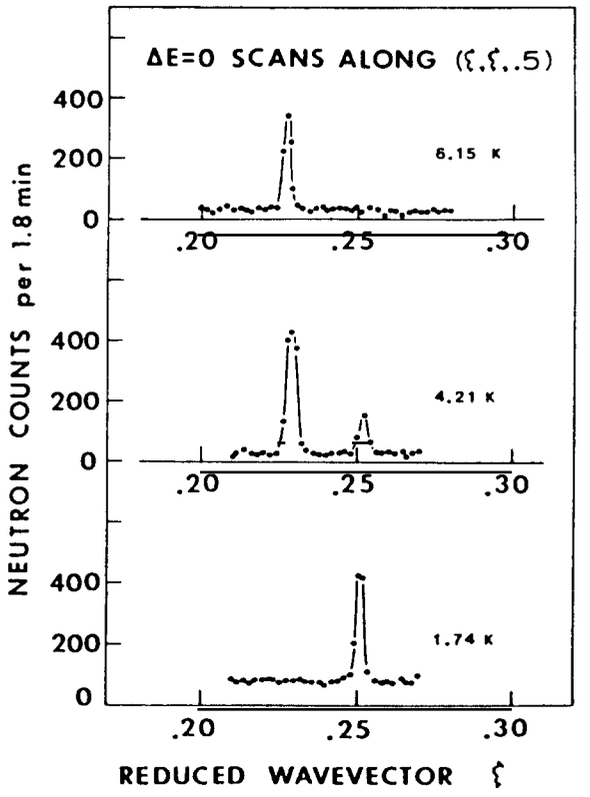

Figure 4. Constant E scans with $\Delta E = 0$ along the [110] direction. The upper curve (6.15 K) shows the incommensurate phase while the lower curve (1.74 K) shows the commensurate phase. The middle curve (4.21 K) shows the coexistence of the two phases.

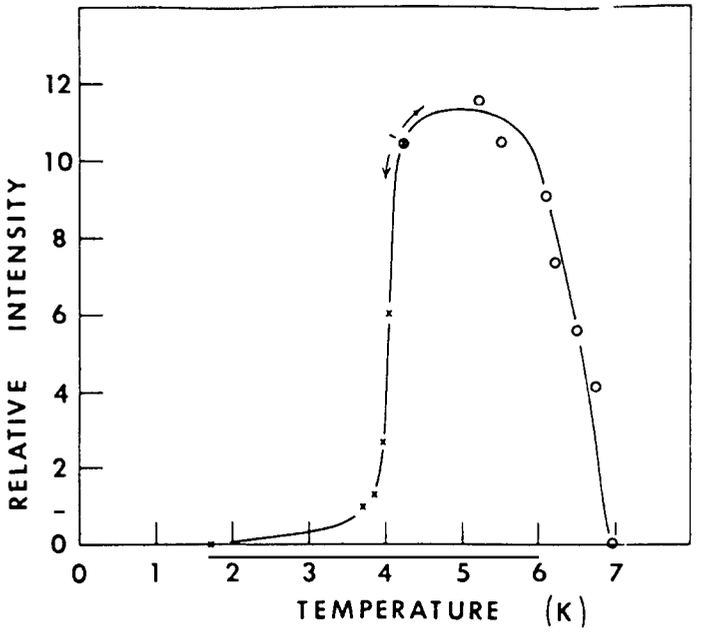

Figure 5. Temperature dependence of the intensity of the PrB_6 (0.23, 0.23, 0.5) incommensurate magnetic reflection. The manner in which measurements were made is described in the text.

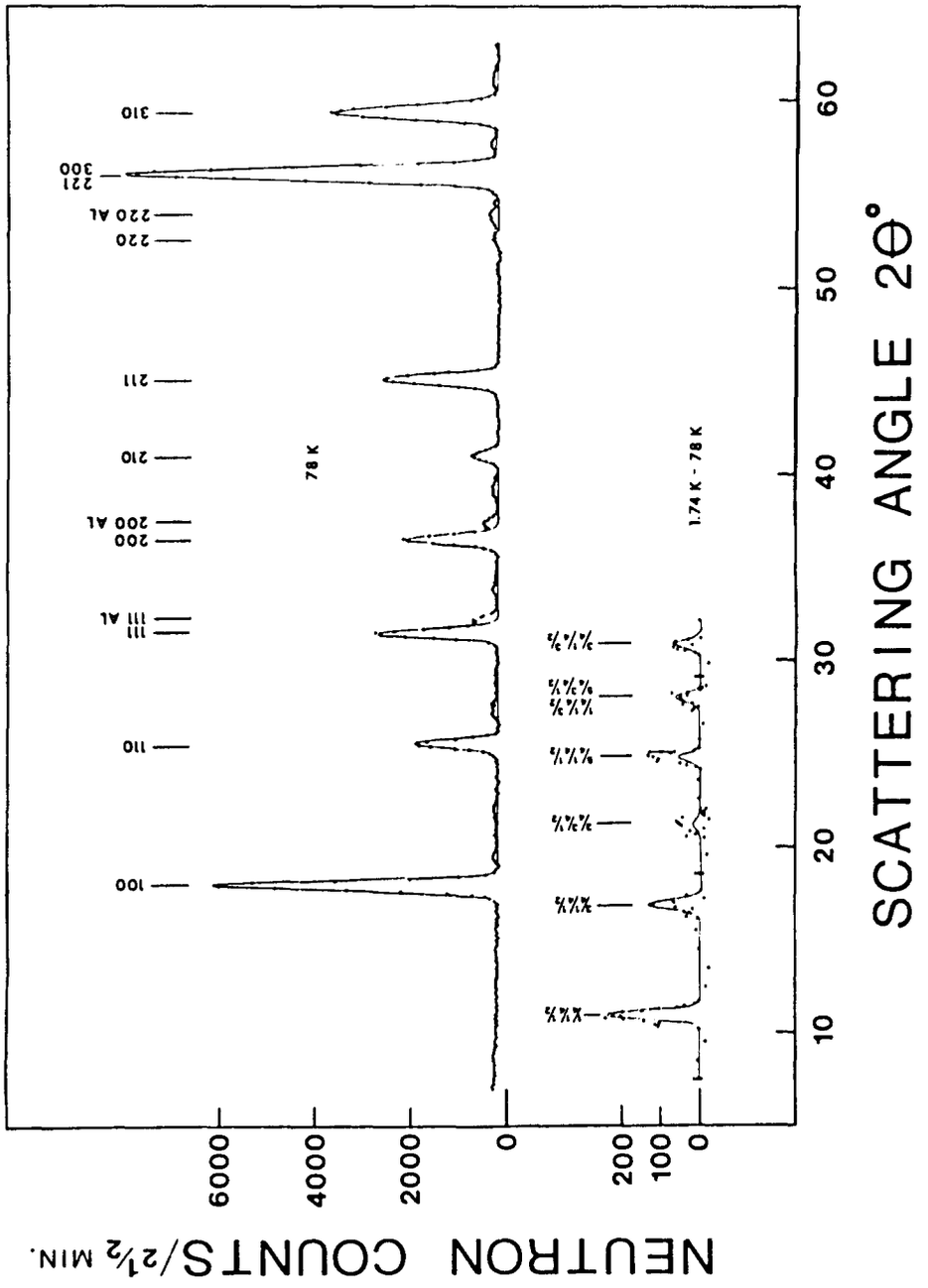

Figure 6. Neutron diffraction diagram of PrB_6 powder at 78 K (TOP) and the difference pattern (BOTTOM) of 1.74 K - 78 K. Points are actual data while the solid line is a profile analysis fit. All indices refer to the original chemical unit cell. Al refers to aluminum peaks from the sample cell.

Figure 7. Low temperature commensurate magnetic structure proposed for PrB_6. Only the Pr ions in a (100) plane are shown. The next layer of Pr ions, which represents the other half of the magnetic unit cell, is arranged with moments antiparallel to those in the layer shown.

lower transition in earlier work may be ascribed to this fact. The quadrupolar ordering and the locking of the commensurate magnetic structure is probably a first order transition. Strain effects between the upper and lower transition temperature account for the rather broad anomaly in the thermal expansion coefficient.

Acknowledgments-The neutron scattering studies were made possible by the support of the University of Missouri Research Reactor. The support of the Alumni Development Board and of the Research Council of the University of Missouri is also gratefully acknowledged.

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