Neutron diffraction study of the high magnetic field phase diagram of La-doped PrB$_6$

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Abstract. The high magnetic field phase diagram of lanthanum-doped PrB$_6$ was investigated by single-crystal neutron diffraction. In this compound, a peculiar incommensurate phase denoted IC2 was observed in magnetic fields applied along directions close to [111]. Unlike the double-k IC1 phase $[k_{IC1} = (1/4 - \delta, \pm 1/4, 1/2)]$ for field below $T_N = 7$ K, IC2 is characterized by a propagation vector with two incommensurate components, $k_{IC2} = (1/4 - \delta', 1/4 - \delta', 1/2)$ ($\delta' \approx 0.03$). The field and temperature evolutions of domain populations further indicate that, contrary to the low-field phases C and IC1, the magnetic structure in phase IC2 is single-k.

1. Introduction
In rare-earth compounds, orbital degrees of freedom, involving different active multipole moments within the crystalline electric field (CEF) ground state, give rise to a number of interesting phenomena. Among these systems, the rare-earth hexaborides RB$_6$ ($R$: Ce, Pr, Nd, ...) have attracted special attention because of their complex phase diagram ascribed to the competition between exchange dipolar and higher-rank multipolar interactions. A wide variety of ordered phases has been reported in previous works [1, 2, 3]. In this series, the compound CeB$_6$ was extensively studied because of its archetype antiferro-quadrupolar (AFQ) order setting in below 3.2 K, and further evolving into a complicated noncollinear "2-k-k" magnetic order at lower temperatures [1]. Octupolar interactions have been shown to play a major role in this system [4].

PrB$_6$, on the other hand, has only three dipole and five quadrupole moments, but no octupole moment, in its $\Gamma_5$ CEF ground state. Its phase diagram, first studied by Burlet et al. [5], shows two successive phase transitions at zero magnetic field. A second-order transition first takes place at $T_N = 7$ K from the paramagnetic state to an incommensurate (IC) magnetic phase denoted IC1. This phase originates from long-range RKKY-type exchange interactions [6, 7] and is characterized by two IC propagation vectors $k_{IC1} = (1/4 - \delta, \pm 1/4, 1/2)$, producing a noncollinear magnetic structure (Fig. 1 (c)). Recent nonresonant x-ray diffraction measurements [8] showed that, in the solid solution Ce$_{0.7}$Pr$_{0.3}$B$_6$, the magnetic (dipole) order in phase IC1 is accompanied by an incommensurate quadrupole order involving $O_{xy}$-type quadrupole moments, with a propagation vector $k_{Q}^{IC1} = 2k_{1}^{IC1}$. At lower temperature ($T_C = 4.2$ K), one observes a first-order lock-in transition into a 2-k commensurate ordered phase (C-2k), involving both
Figure 1. \((H, T)\) phase diagrams of diluted Pr\(_{0.9}\)La\(_{0.1}\)B\(_6\) for different field directions \((H \parallel [001], [110] \text{ and } [111])\) obtained from resistivity measurements in Ref. [7]: (a) high-field 1-\(k\) commensurate magnetic structure ; (b) low field 2-\(k\) commensurate magnetic structure; (c) low-field 2-\(k\) IC magnetic structure [5]. The phase diagrams for pure PrB\(_6\) [2] (not shown here) have a similar shape except for slightly higher transition temperatures and magnetic fields. Note that the dashed line separating phases C-1\(k\) and C-2\(k\) is not well-defined for the diluted sample.

magnetic dipole \((k_{1,2}^C = (1/4, \pm 1/4, 1/2))\) and electric quadrupole \((k_{Q}^C = (1/2, 1/2, 0))\) order parameters (Fig. 1 (b)).

Previous studies have shown that the different types of orders in the \(RB_6\) series are very sensitive to the application of a magnetic field, which strongly affects the phase diagram and gives rise to new ordered phases, whose pattern depends on the field direction. This is particularly true for the compound PrB\(_6\), in which the C-2\(k\) phase transforms, for \(H \parallel [110] > 2\) T, into a C-1\(k\) collinear structure with magnetic moments aligned along \([1−10]\), thereby minimizing the Zeeman energy (Fig. 1 (a)) [5]. More recently, magnetization and magnetoresistance measurements have shown that, at higher temperatures, phase IC1 is also suppressed in high fields, leaving place to a new incommensurate phase (IC2). The latter phase was observed both for \(H \parallel [111]\) in pure PrB\(_6\) and in Pr\(_{x}\)La\(_{1-x}\)B\(_6\) [2, 7], and also for \(H \parallel [110]\) in the Ce\(_x\)Pr\(_{1-x}\)B\(_6\) solid solutions for several compositions [9, 10].

In order to gain more insight into the above magnetic field effects, and to characterize the so far unknown magnetic structure in phase IC2, we have performed neutron diffraction measurements on a Pr\(_{0.9}\)La\(_{0.1}\)B\(_6\) single crystal. The purpose of substituting a weak amount of nonmagnetic lanthanum was to reduce the lowest critical field of the IC1-IC2 transition from 9 T in pure PrB\(_6\) to 5 T in the diluted compound, making it possible to explore all regions of the phase diagram using a standard 7 T cryomagnet. This minor doping is not expected to alter the nature of the order in the different phases significantly, as also suggested by the smooth and limited changes observed in magnetization and electrical resistivity measurements [7].

2. Experiments and results

Single crystals of Pr\(_{0.9}\)La\(_{0.1}\)B\(_6\), prepared from 99.5% enriched \(^{11}\)B isotope, were grown by a floating-zone technique in pressurized, high-purity Ar gas [11]. Neutron diffraction measurements were performed on the two-axis lifting detector neutron diffractometer 6T2 (LLB) at an incident wavelength \(\lambda = 2.354\) Å. Second-order contamination was suppressed by a PG filter inserted on the incident beam. A Soller collimator was placed before the counter to both reduce background and improve Q resolution. Magnetic fields up to 6.5 T were applied vertically along the [111] crystallographic direction in an Oxford Instruments cryomagnet.

Measurements were first performed at low fields \((H < 4\) T\) and the results agree with those
reported previously for PrB$_6$ by Effantin et al. [1], confirming the similarity between the pure and weakly diluted compounds. Scans along the [010] direction at different temperatures show that the 2-k phases C-2$k$ and IC1, both corresponding to noncollinear magnetic orders, are respectively characterized by the propagation vectors $(1/4, ±1/4, 1/2)$ and $(1/4−δ, ±1/4,1/2)$, with $δ ≃ 0.044$ at $H = 0$, and therefore nearly identical to those reported for PrB$_6$ ($δ ≃ 0.050$ [5]).

At higher fields ($H > 4$ T), the structures changes with increasing temperature from IC1 to IC2. The temperature evolution of the magnetic satellites through this transition is presented in Fig. 2 (left) for $H = 6.5$ T. Scans performed along the $(-h,1/2,−0.44+h)$ direction, shown in Fig. 2 (right), provide evidence for the two types of satellites. The IC1 reflections at $(-1/4+δ,1/2,−1/4)$ and $(-1/4,1/2,−1/4+δ)$ vanish around $T = 5.3$ K, while new satellites, corresponding to a propagation vector with two incommensurate components $\mathbf{k}_{IC2} = (-1/4 + δ',1/2,−1/4 + δ')$ ($δ' ≃ 0.030$) appear.

The star of the propagation vector $\{\mathbf{k}_{IC2}\}$ is characterized by six inequivalent branches $\mathbf{k}_{x}^± = (1/2,±[1/4−δ'],1/4−δ')$, $\mathbf{k}_{y}^± = (1/4−δ',1/2,±[1/4−δ'])$, $\mathbf{k}_{z}^± = (±[1/4−δ'],1/4−δ',1/2)$. Figure 3 displays $Q$ scans of reflections associated with these different domains for $T = 5.6$ K and $H = 6.5$ T. When the magnetic field is applied along [111], only the $\mathbf{k}_{y}^+$ with $i = x$ (a), $y$ (b) and $z$ (c) are observed. This information alone is not sufficient, in principle, to distinguish between a 1-k structure, in which the three reflections $\mathbf{k}_{y}^+$ originate from different single domains, from a multi-k structure in which each domain contributes to several reflections. However, one sees on Fig. 3 that the peak intensities differ significantly ($127±7, 250±6$, and $162±4$ counts/5s for $i = x$, $y$, and $z$, respectively). Whereas geometrical effects may play a role in view of the absorption coefficient from residual $^{10}B$, they are unlikely to produce such large discrepancies. Both a 2-k structure of the type observed in phase IC1, which would couple $\mathbf{k}_{y}^+$ and $\mathbf{k}_{z}^-$ components within the same domain, and a 3-k structure coupling all three $\mathbf{k}_{y}^+$ components, can be safely ruled out. A 1-k collinear structure, with one propagation vector $\mathbf{k}_{IC2} = (1/4−δ',1/4−δ',1/2)$ and moments oriented perpendicular to the field (apart from a uniform canting component) thus seems the most likely. Differences in intensities may then result from a minor deviation of the
Figure 3. Scans through magnetic reflections associated with different components of the \( k^{IC2} \) star: (a) \( k_x^+ \), (b) \( k_y^- \), (c) \( k_z^+ \) and (d) \( k_y^- \). The large difference in the widths of peak scanned along different \( Q \)-space directions results from the resolution of the lifting-detector diffractometer.

field direction from the [111] axis.

Thermal expansion and magnetostriction measurements carried out both in PrB\(_6\) [12] and Pr\(_{0.9}\)La\(_{0.1}\)B\(_6\) [7] indicate that the magnetic anisotropy that might be produced by an underlying quadrupolar order is very weak, and that a “\( \chi_\perp \)” configuration, in which the magnetic moments orient perpendicular to the field in order to minimize the Zeeman energy, is realized in phase IC2. Such a behavior is in line with the above assumption of a collinear 1-\( k \)-sine-wave structure.

In conclusion, we have investigated the high-magnetic-field phase diagram of PrB\(_6\) at low lanthanum doping using single-crystal neutron diffraction. The measurements, made for several magnetic satellites associated with different domains, strongly suggest that the field-induced magnetic order in phase IC2 is primarily collinear, and can be described by a single propagation vector having two incommensurate components \( k^{IC2} = (1/4 - \delta', 1/4 - \delta', 1/2) \) (\( \delta' \simeq 0.030 \)).

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