In recent years, there has been a growing interest towards the role of orbital degrees of freedom in $d$ as well as $f$ electron systems. A number of unusual properties in transition metal compounds have been discussed on the basis of underlying orbital orders. In the case of $4f$ electron systems, the strong intra-atomic spin-orbit coupling forces the magnetic and orbital degrees of freedom to be described in terms of the total angular momentum $J$. For instance, an orbitally degenerate level carries quadrupole moments (rank-2 irreducible tensor operators in $J$). In a cubic ($O_h$) system, up to five independent quadrupole moments are defined (two $\Gamma_3$ type and three $\Gamma_5$ type operators) [1,2]. The orbital ordering in $f$ electron systems, i.e., a spontaneous lifting of the orbital degeneracy by interactions, therefore is a phase transition of quadrupole moments. In reality, active quadrupole moments depend on the low-lying crystalline field levels of the $4f$ ions.

Following magnetic orderings, one refers to uniform magnetic field to examine the quadrupolar ordering. Antiferromagnetic components with $q=\pm(\frac{1}{2}\pm\delta \frac{1}{2}, 0, 0)$, $(\delta \frac{1}{2}00)$ are observed below the transition temperature $T_Q$ (0.4 K at $H=0$) whose amplitudes vary linear with $H$ and vanish at zero field, providing the first evidence for a modulated quadrupolar phase. For $H < 1$ T, a non-square modulated state persists even below 100 mK suggesting quadrupole moments associated with a $\Gamma_3$ doublet ground state to be partially quenched by hybridization with conduction electrons.

Neutron diffraction measurements have been performed on the cubic compound PrPb$_3$ in a [001] magnetic field to examine the quadrupolar ordering. Antiferromagnetic components with $q=\pm(\frac{1}{2}\pm\delta \frac{1}{2}, 0, 0)$, $(\delta \frac{1}{2}00)$ are observed below the transition temperature $T_Q$ (0.4 K at $H=0$) whose amplitudes vary linear with $H$ and vanish at zero field, providing the first evidence for a modulated quadrupolar phase. For $H < 1$ T, a non-square modulated state persists even below 100 mK suggesting quadrupole moments associated with a $\Gamma_3$ doublet ground state to be partially quenched by hybridization with conduction electrons.

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ter, angle-resolved magnetization measurements revealed characteristic field-angular oscillations of $T_Q(H)$, which can be interpreted by assuming $O_2^3$-type AFQ moment and its equivalents to be the OPs at low $H$ ($< 7$ T) [19].

So far, no microscopic verification for an AFQ ordering has been obtained in this system. Our preliminary neutron diffraction measurement in a [110] magnetic field ([110] scattering plane) could not detect any field-induced antiferromagnetic reflection in the AFQ phase below 3 T [20]. In the present work, we have continued the experiment in a magnetic field applied parallel to the [100] direction using a larger crystal of higher quality, and succeeded in observing field-induced superlattice reflections which, as we will discuss below, to our surprise and to the best of our knowledge, provides the first evidence of an underlying AFQ ordering [23]. The present experiment thus confirms the AFQ ordering in PrPb$_3$ and to the best of our knowledge, provides the first evidence of a modulated ($\delta \neq 0$) quadrupolar ordering.

Knowing that the domain population change is negligible, we may estimate the field variation of the staggered component from the intensity of the $(\frac{3}{8} \frac{3}{8} 0)$ reflection. Figure 2 plots the square root of the scattering intensity (background subtracted) at $T=0.32$ K as a function of $H$. Keeping in mind that the peak width is virtually independent of $H$, the square root intensity is proportional to the staggered component. The intensity vanishes at $H=0$, consistent with the previous work reporting the absence of antiferromagnetic scattering in zero field [14]. The important point is that the staggered component develops proportional to $H$ up to 2 T. This fact strongly indicates that the observed superlattice reflections arise from an induced antiferromagnetic moment in the presence of an underlying AFQ ordering [23]. The present experiment thus confirms the AFQ ordering in PrPb$_3$, and to the best of our knowledge, provides the first evidence of a modulated ($\delta \neq 0$) quadrupolar ordering.

At around 2.1 T, we observed a jump in the scattering intensity with an apparent hysteretic behavior, indicat-
ing an occurrence of a first-order transition at this field. Associated with this transition is the 3rd-order harmonic $q'_1$, as shown in Fig. 4. We found that this transition field remains finite ($\geq 1$ T) on cooling down to below 100 mK. It is important to note that no harmonic component is observed in the low field phase.

Figure 3 shows the $H-T$ phase diagram of PrPb$_3$ for $H$ parallel to [001] obtained by the present experiment. The quadrupolar transition line is defined by the onset of the $q_1$ and $q_2$ superlattice reflections. The obtained phase boundary $T_Q(H)$ agrees well with the phase line reported in the specific heat and magnetization measurements [20, 21, 22]. Within the AFQ phase, we observed a first-order phase transition characterized by the appearance of the $q'_1$ and $q'_2$ harmonic reflections. This transition line $T_c(H)$ again agrees with the results of previous thermodynamical measurements [21, 22]. The inset of Fig. 3 shows the temperature dependence of the position of the $q'_1$ and $q'_2$ superlattice reflections in a field of 4 T. In the temperature range $T_c < T < T_Q$, $\delta$ takes a value slightly below 1/8. Upon the first-order transition at $T_c$, $\delta$ exhibits a jump to a value very close to 1/8. Although more careful study would be needed, we expect that the phase below $T_Q$ is an incommensurate state and $T_c$ is a lock-in temperature into the commensurate state with $\delta=1/8$. Noteworthy, the $T_c(H)$ line does not intersect with the abscissa for low $T$ and the modulated phase continues to exist to $T \rightarrow 0$ at low fields below 1 T.

We now discuss possible magnetic and quadrupole structures of PrPb$_3$ in a [001] field. While the field-independence of the relative intensity of the $q_1$ and $q_2$ reflections favors a double-$q$ structure, we cannot rule out the possibility of a single-$q$ structure with two equally populated $Q$ domains. The direction-independent scattering intensity within the ($h0k$) plane leaves two possibilities regarding the polarization of the field-induced antiferromagnetic component $\mu_{AF}$: $\mu_{AF}$ is either parallel to [001] or rotating in the (001) plane. Although the latter structure cannot be excluded from the present neutron scattering data alone, it is incompatible with the quadrupole OPs in the $\Gamma_3$ doublet state and therefore we will not discuss this possibility here [2]. In the former case, the alignment of $\mu_{AF}$ along the [100] axis is given in Figure 4 by the thick arrows, where we assume $\delta=1/8$ for simplicity. The observed superlattice reflections below $T_Q$ (AFQ I) is best described by a sinusoidally modulated antiferromagnetic structure as shown in Fig. 4(a). The amplitude of the staggered moment is determined to be $|\mu_{AF}|=0.48\pm 0.17$ $\mu_B$ at 4 T and 0.5 K assuming a single-$q$ structure. Below $T_c(H)$, this state undergoes a first-order transition into an antiphase structure (AFQ II) as shown in Fig. 4(b) which is accompanied by third harmonic reflections at $q'_1$ and $q'_2$. The polarization of $\mu_{AF}$ || [001] (angular momentum operator $J_z$) is compatible with the quadrupole moment $Q_0^2$ [2], being consistent with the analysis of the recent angle-resolved $T_Q(H)$ measurement [12]. Since the field-induced $\mu_{AF}$ is proportional to the AFQ OP [22], it is concluded that

![FIG. 3: $H-T$ phase diagram of PrPb$_3$ in a [001] magnetic field. Open and closed triangles denote the transition points determined from the $T$- and $H$-scan measurements, respectively. For both cases, the upward and downward triangles represent the increasing and decreasing $T(H)$ scans, respectively. AFQ I denotes the possible incommensurate structure with the wave vectors $q=(\frac{1}{2} \pm \delta \frac{1}{2} 0)$ and/or $(\frac{1}{2} \pm \delta \frac{1}{2} 0)$, ($\delta \sim \frac{1}{8}$). AFQ II denotes the antiphase structure as discussed in the text. The inset shows the temperature dependence of the center position of the magnetic reflection at around $q=(\frac{1}{2} \pm \delta \frac{1}{2} 0)$ in a field of $H=4$ T, obtained on cooling below 0.75 K as shown by the arrow.]

- The $O^0_2$ moment should show a similar sinusoidal oscillation in this phase as schematically illustrated in Fig. 4(a) where the solid line represents the amplitude of the $O^0_2$ moment. Below $T_c$, the $O^0_2$ moment would also take the antiphase structure as shown in Fig. 4(b).

Recalling that PrPb$_3$ is a $\Gamma_3$ non-Kramers doublet ground state system, it is reasonable that the system undergoes a phase transition from the sinusoidal to the antiphase structures at low $T$. In general, the sinusoidal structure is stable only at a high temperature region below $T_Q$ where thermal fluctuations are dominant, and gives way to the antiphase (square) structure in the ground state to reduce the entropy, as is often seen in magnetic ordering systems. Calling back the phase diagram in Fig. 4, however, we find that the non-square modulated phase persists down to the experimental accessible temperature of 100 mK in low fields below 1 T, without any indication of further transition. This observation is hardly understood within the framework of a localized $f$ electron model in which the (pseudo) degeneracy with respect to the $\Gamma_3$ doublet would remain in a part of Pr sites. Similar phenomena of non-antiphase modulated structures persisting toward $T \rightarrow 0$ have also been reported in magnetic Kramers compounds, in which a Kondo screening effect is considered to be relevant for stabilizing such states at $T=0$ [24, 25]. The analogy to those magnetic systems strongly suggests that...
FIG. 4: Field induced antiferromagnetic moments and the possible quadrupole structures along the [100] axis (y=0) in a (001) field. (a) sinusoidal structure with $q=(\frac{1}{2} \pm \delta \frac{1}{2} 0)$, and (b) antiphase structure with $q=(\frac{1}{2} \pm \delta \frac{1}{2} 0)$ and $(\frac{1}{2} \pm 3\delta \frac{1}{2} 0)$. We assume that $\delta=\frac{1}{2}$ for simplicity. Uniform components are not included. The solid lines denote the amplitude of the staggered components, whose phase factor is arbitrarily chosen.

the local quadrupole moment in PrPb3 should be partly quenched in the modulated phase at very low T due to the quadrupole Kondo effect. Possibility of the Kondo effect associated with the orbital degeneracy has been discussed in several U- and Pr-based systems, but is still not well established experimentally. Very recently, it has been recognized that the strong hybridization effect between Pr 4f and conduction electrons does exist in some of the Pr-based skutterudites, leading to heavy fermion behavior and unconventional superconductivity. The present results on PrPb3 would provide another piece of evidence for the Kondo effect in Pr (4f2) systems. It would be interesting to examine the low energy excitation of this system at very low temperatures.

In summary, neutron diffraction experiment in a magnetic field has revealed a modulated quadrupole structure in PrPb3 which persists as $T \rightarrow 0$ at low field. The results suggest a Kondo screening of the quadrupole moments of Pr3+ in the ground state.

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