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Quadrupolar interactions in Pr compounds: $PrFe_4P_{12}$ and $PrBa_2Cu_3O_6$

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Abstract

We examine Pr^{3+} crystal field models with near-degeneracy of the two lowest crystal field levels, where interaction-induced quadrupolar and dipolar moments are as important as the permanent moments of the crystal field ground state. We find that the Γ_1–Γ_4 level scheme yields a successful description of the antiferroquadrupolar ordering of $PrFe_4P_{12}$. For $PrBa_2Cu_3O_6$, we argue that quadrupolar interaction is important for understanding the Pr ordering transition at 11 K.

1. Introduction

The highly degenerate f-shells of rare earth and actinide ions support a great variety of local degrees of freedom: magnetic (dipolar), quadrupolar and octupolar. For localized f-electron systems, these (and some of their combinations) are potential order parameters, leading to rich phase diagrams, as for CeB_6 [1]. Field-induced octupoles are known to influence the shape of the phase boundaries for CeB_6 or $PrPb_3$ [12], but it is an outstanding question whether breaking time-reversal invariance with purely octupole order is possible; recent observations on NpO_2 indicate that it may be so [5]. The f-shell multipolar degrees of freedom may also interact and mix with those of other electrons: the unusual heavy fermion behaviour of $PrFe_4P_{12}$ [2], and the exotic superconducting phases of $PrOs_4Sb_{12}$ [3] have been tentatively ascribed to Pr^{3+} quadrupole fluctuations.

Detailed understanding has been achieved for CeB_6 and some other Ce-based systems. The reason is that Ce^{3+} has only a single f-electron, and therefore microscopic analysis is here the easiest. Of particular interest is cubic CeB_6 in which the fourfold degenerate Γ_8 ground state supports the full array of 3 dipoles, 5 quadrupoles, and 7 octupoles [1]. A microscopic analysis [6] indicates that octupole–octupole interactions should not be weaker than quadrupole–quadrupole interactions, which gives rise to close competition between different kinds of order. In fact, if all interactions were exactly equal, the model would be $SU(4)$-symmetrical, which sparked early theoretical interest in the subject [4]. The realistic multipolar model is not fully symmetrical, but the nearness of the $SU(4)$ point is still felt in

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fluctuations [7]. Whether the ground state of an $SU(4)$ model is long-range ordered, or it is rather liquid-like (the $SU(4)$ version of RVB), depends on details like the lattice structure, and the range of the interaction [8]. The approximate realization of high symmetries like $SU(4)$ is of current interest for d- and f-electron systems alike.

We expect that the result that various multipolar couplings are of the same order of magnitude, holds generally for light rare earths. The question arises: what can we say about $4f^2$ systems?

Pr compounds show varied behaviour. A few examples: $PrPb_3$ undergoes an antiferro-quadrupolar transition but it does not order magnetically, though both dipolar and octupolar interactions are thought to be important [12]. PrB_6 has two magnetic phase transitions but the magnetic anisotropy is explained by quadrupolar interactions [11]. $PrBa_2Cu_3O_{7-x}$ is the only member of the group $(RE)Ba_2Cu_3O_7$ (RE = rare earth), which is not a high-T_C superconductor [18]. It is suspected that this is related to the little-understood Pr ordering transition at 17 K, but the connection is not clear. The parent Mott insulator $PrBa_2Cu_3O_6$ has a similar phase transition at 11 K [20].

2. Pr systems

In most compounds, Pr is trivalent. The existence of the dioxide PrO_2 shows that it can also be tetravalent [9], though this is rare. The question of the valence state becomes crucial whenever the nature, or the driving force, of Pr ordering is in doubt. For Pr-filled skutterudites, the formation of a heavy Fermi sea, as seen in $PrFe_4P_{12}$ and in $PrOs_4Sb_{12}$, is most likely to involve the hybridization of Pr f-states with conduction band states, and consequently deviation from strictly integral valence.

These basic doubts notwithstanding, we propose to study the interplay of dipolar and quadrupolar interactions in localized f-electron models, and apply the results to $PrFe_4P_{12}$ and $PrBa_2Cu_3O_6$. We assume the integer valence state Pr^{3+}, and a Hund's rule ground state with $J = 4$. We note that a similar approach was successful in the case of CeB_6 [1], though the system is known to possess the features of a dense Kondo system. We envisage a similar study of Pr systems.

Pr^{3+} is a non-Kramers ion. It follows that a unique ground state can be reached without breaking time-reversal invariance, either by having a singlet Γ_1 crystal field ground state to begin with, or via the ordering of quadrupolar moments.

2.1. The Γ_1–Γ_4 scenario for $PrFe_4P_{12}$

$PrFe_4P_{12}$ undergoes a second-order transition at $T_{tr} = 6.51$ K, which is manifested in a susceptibility spike, and a λ-shaped anomaly of the specific heat [2]. Though at first thought to be antiferromagnetic, the ordered phase is now known to be antiferroquadrupolar. Upon switching on a magnetic field, the transition temperature decreases. The character of the transition switches to first order at the tricritical point $T_{tri} \approx 5$ K, $H_{tri} \approx 2$ T, and the ordered phase is completely suppressed at $\sim$4 T [2]. These parameters depend on the direction of the applied field. However, here we consider only the case of a field applied along the (100) direction.

The question whether the f-states are itinerant or localized can be posed again. $PrFe_4P_{12}$ is one of the few Pr-based heavy fermion systems [2]. Although having an even number of f-electrons per site makes the distinction between large and small Fermi surfaces difficult, we take the view that the large Fermi sea of heavy f-electrons competes with a state in which the conduction electrons build a small Fermi sea, and multipolar inter-shell interactions are switched on [13–15]. This is supported by inelastic neutron scattering finding that the crystal

field excitations become sharply defined when the temperature is lowered below T_{tr}. It follows that we may use a localized f-electron model to describe the ordered phase and the vicinity of the phase boundary. We use the crystal field states of the octahedral group O_h. We note that the icosahedron of the 12 P atoms surrounding a Pr site gives a novel tetrahedral component to the crystal field potential [16], but we assume that using cubic symmetry labelling is an acceptable approximation.

Since the local order parameter is one of the quadrupolar moments, it may look evident that the crystal field ground state should carry a (spontaneous) quadrupolar moment. However, an analysis of the high-T behaviour of the magnetization curves shows that the level scheme (ground state)–(first excited state) may be either of the following three: Γ_1–Γ_4, Γ_1–Γ_5, or Γ_3–Γ_4 [2]. Only the last, with the Γ_3 ground state, carries an unfrozen quadrupolar moment which can be ordered by switching on (arbitrarily small) intersite interactions. It was also shown that this choice is consistent with a symmetry analysis of the structural distortion accompanying the antiferroquadrupolar ordering [10]. This latter argument relies only on the assumption of the Γ_3 ground state, and does not refer to the nature of the first excited state.

Here we show that the alternative Γ_1–Γ_4 scheme is also capable of accounting for most of the observed static properties of $PrFe_4P_{12}$. We list the crystal field states

$$\begin{aligned}\Gamma_1 &= \sqrt{5/24}(|4\rangle + |{-4}\rangle) + \sqrt{7/12}|0\rangle \\ \Gamma_4^{\pm} &= (1/4)(|3\rangle \pm |{-3}\rangle + \sqrt{7}[\pm|1\rangle + |{-1}\rangle]) \\ \Gamma_4^0 &= \sqrt{1/2}(|{-4}\rangle - |4\rangle)\end{aligned} \tag{1}$$

where we use the quadrupolar eigenstates $\Gamma_4^{\pm}$ in the representation Γ_4. Since the ground state carries no kind of moment, the ordered quadrupolar moment must be interaction-induced, implying that the interaction has to exceed a threshold value of the order of the Γ_1–Γ_4 splitting. Taking for granted that intersite interactions mix the Γ_4 states with Γ_1, the possible local order parameters are those appearing in the decomposition

$$(\Gamma_1 \oplus \Gamma_4) \otimes (\Gamma_1 \oplus \Gamma_4) = 2\Gamma_1 + \Gamma_3 + 3\Gamma_4 + \Gamma_5. \tag{2}$$

The system is capable of either Γ_3- or Γ_5-type quadrupolar ordering, or any (dipolar or octupolar) kind of Γ_4 order. In principle, we have to allow for all the corresponding intersite interactions. However, we neglect the octupoles. We assume Γ_3-type quadrupolar order and, recalling that the pair interaction has only tetragonal symmetry, and so $\mathcal{O}_2^2$ and $\mathcal{O}_2^0$ are not equivalent, we arbitrarily keep only the $\mathcal{O}_2^2 = J_x^2 - J_y^2$ term. The following mean-field-decoupled Hamiltonian also includes a dipole–dipole coupling:

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{CF} + \mathcal{H}_{Zeeman} + \mathcal{H}_{quad} + \mathcal{H}_{dipole} \\ &= \Delta \sum_{n=0,\pm} |\Gamma_4^n\rangle\langle\Gamma_4^n| - g\mu_B \boldsymbol{H}\boldsymbol{J} - zQ\langle\mathcal{O}_2^2\rangle_{B(A)}\mathcal{O}_2^2 - zI\langle\boldsymbol{J}\rangle_{B(A)} \cdot \boldsymbol{J}\end{aligned} \tag{3}$$

where we allowed for two-sublattice (A and B) order on the bcc lattice ($z = 8$). $g = 4/5$ is the Landé factor, Q the quadrupolar and I the dipolar coupling constant. We mention that a simplified interaction, with quadrupolar coupling only, was treated in a previous communication [17]. However, the inclusion of $\mathcal{H}_{dipole}$ is important for getting a better fit to the experimental results, in particular the susceptibility.

The diagonalization of (3) in the basis (1) is straightforward. We show only the results. We have found that the (ferromagnetic) dipolar coupling $I = 106$ mK, the antiferroquadrupolar coupling $Q = -9.5$ mK, and the crystal field splitting $\Delta = 3$ K give good overall agreement with the observations (in case Q appears implausibly small, check that $\mathcal{O}_2^2$ has big matrix elements). With these parameters, the only phase transition is the onset of antiferroquadrupolar

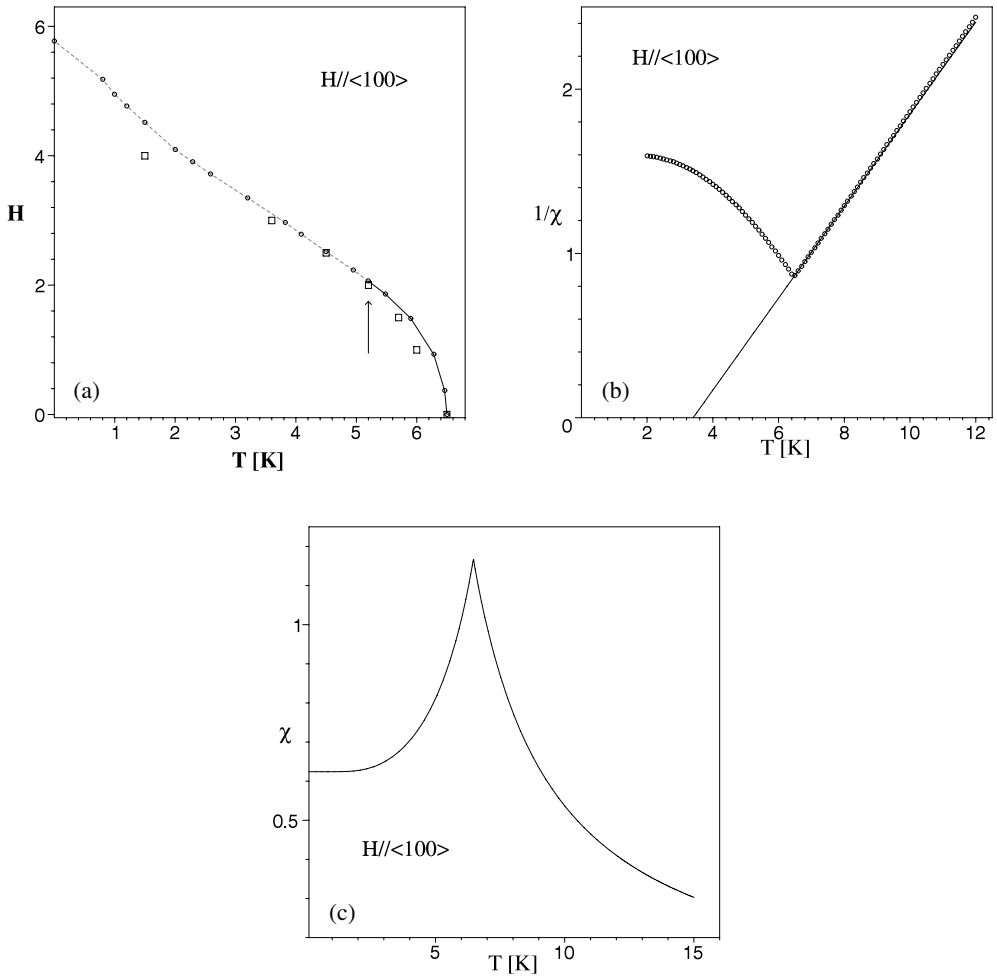

Figure 1. (a) The phase boundary in the H–T plane ($H \parallel \hat{x}$). Continuous curve: second-order, dashed curve: first-order transitions. Open circles: calculated, open rectangles: measured (after [2]). (b) and (c) the inverse susceptibility $1/\chi$, and the susceptibility χ, as a function of T. χ is in units of μ_B Tesla^{-1}/(Pr site).

order at $T_{\rm tr} = 6.5$ K. The transition is gradually suppressed by an external magnetic field (figure 1(a)). We locate the tricritical point at $T_{\rm tri} \approx 5$ K, $H_{\rm tri} \approx 2$ T, in agreement with experiment. The same set of parameters also gives the observed Weiss temperature $\Theta = 3.6$ K from the intercept in the inverse susceptibility (figure 1(b)).

We note that our estimate of the crystal field splitting $\Delta \approx 3$ K is substantially smaller than the one quoted in [2]; considering the scale of $T_{\rm tr}$, we have a quasi-quadruplet. However, this is not necessarily unreasonable; a calculation indicates a region where the gaps become very small (see [28]).

To conclude our review of the results from the Γ_1–Γ_4 scheme[1], we show the magnetization curves for three representative temperatures (figure 2). In the region of first-order transitions

[1] We did not make a comparable study of the full range of models, so we cannot claim that the present model gives the best agreement with experiments. Rather, we wished to demonstrate that the Γ_1–Γ_4 scheme is not obviously excluded, in spite of the absence of ground state quadrupolar moments.

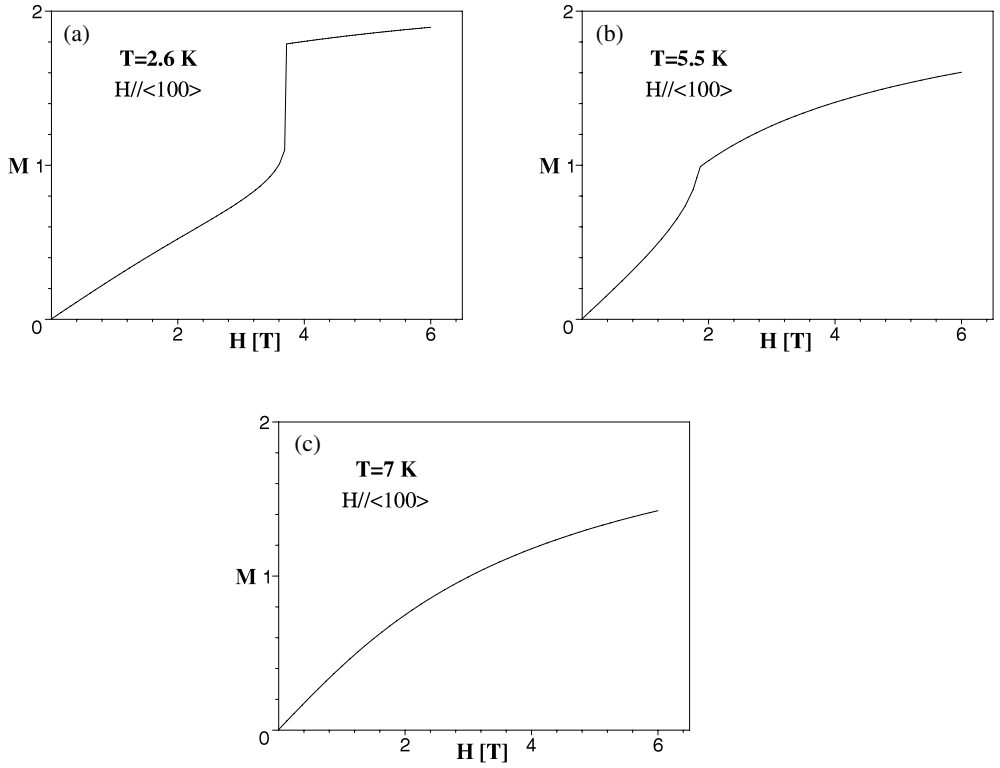

Figure 2. Magnetization curves for the Γ_1–Γ_4 model, below (a) and above (b) the tricritical temperature, and in the disordered phase (c). Parameter values are the same as in figure 1.

below the tricritical temperature, one finds a sharp metamagnetic transition which becomes smoother in the regime of continuous transitions. These results show a good overall resemblance to the measured curves [2].

2.2. The role of quadrupolar coupling in $PrBa_2Cu_3O_6$

All the (RE)$Ba_2Cu_3O_7$ systems, with the exception of RE = Pr, are $T_C \approx 90$ K superconductors. Whenever the RE^{3+} ion has a magnetic moment, they also undergo RE antiferromagnetic ordering at $T_N = 1$–2 K. Analogous results hold for the parent Mott insulators (RE)$Ba_2Cu_3O_6$, where most T_N follow de Gennes scaling [27], the peak belonging to RE = Gd with $T_N \approx 2.2$ K [23]. This is well understood on the basis of the $I_{Gd-Gd} = 156$ mK measured by ESR [23]. We would expect that for RE = Pr,

$$T_N(\mathrm{Pr})|_{\mathrm{de\,Gennes}} = \frac{\{(g-1)^2 J(J+1)\}_{\mathrm{Pr}}}{\{(g-1)^2 J(J+1)\}_{\mathrm{Gd}}} T_{\mathrm{tr}}(\mathrm{Gd}) \approx 0.1 \text{ K}.$$

Instead, magnetic ordering and, at the same time, tetragonal-to-orthorhombic distortion, is observed at $T_N \approx 17$ K for $PrBa_2Cu_3O_7$, and $T_N \approx 11$ K for $PrBa_2Cu_3O_6$ [20], exceeding the de Gennes estimate by two orders of magnitude. There must be a mechanism for producing substantially stronger exchange, or a different kind of ordering, or both.

ESR on Gd:$PrBa_2Cu_3O_6$ gives the intersite exchange $I_{Pr-Gd} = -140$ mK [26]. De Gennes scaling would lead us to expect this sign, but also an absolute value of about a factor of

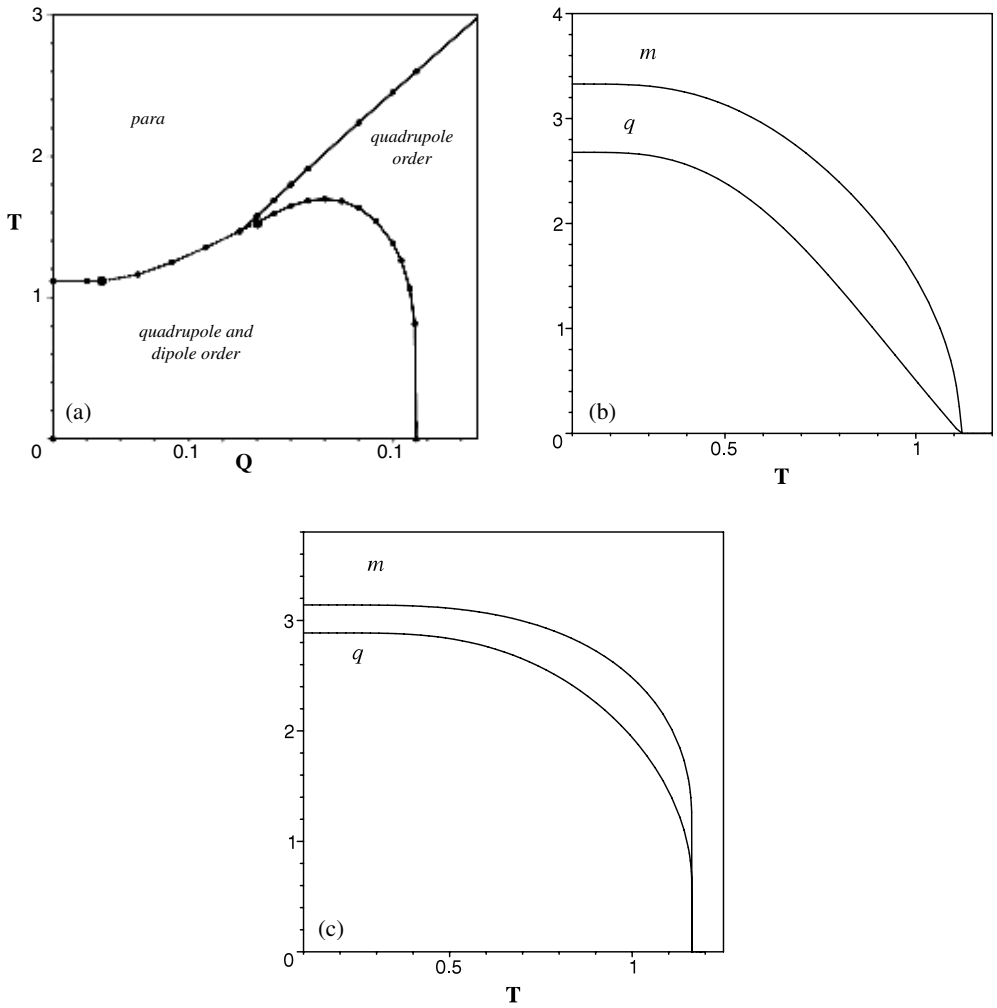

Figure 3. (a) Transition temperatures as a function of the quadrupolar coupling $Q(K)$, for $I = 0.2$ K and $\Delta = 2$ K. Circles: calculated points; the dashed (first order) and continuous (second order) curves are drawn for convenience. Filled circles: tricritical points. (b) and (c) magnetic (m) and quadrupolar (q) order parameters for $Q = 0$ and 0.05, respectively

four smaller. The greater spatial extent of Pr 4f orbitals is likely to explain the enhancement of I; correspondingly, we would expect that $I_{\mathrm{Pr-Pr}}$ is even more enhanced, but would probably still fall short of accounting for the observed T_{N}. Here we suggest that the presence of quadrupolar interactions may explain several features of the magnetic behaviour of $PrBa_2Cu_3O_6$, and also an additional enhancement of T_{N}.

All previous works agree that in the level scheme of Pr^{3+} ions, a low-lying quasi-triplet consisting of the tetragonal doublet

$$\Gamma_t^{\pm} = \alpha|\pm 3\rangle - \beta|\mp 1\rangle \tag{4}$$

and the singlet

$$\Gamma_t^0 = \sqrt{1/2}(|2\rangle - |-2\rangle) \tag{5}$$

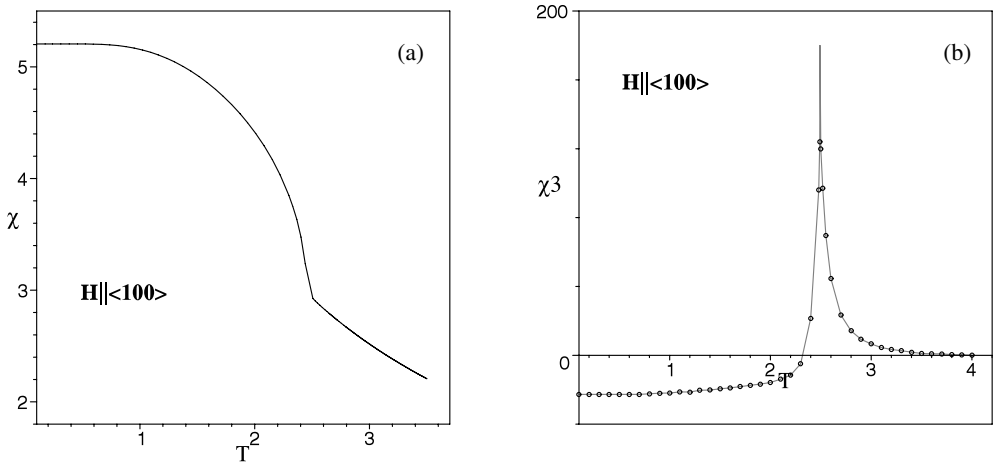

Figure 4. The T-dependence of linear (a) and nonlinear susceptibility (b) for purely ferroquadrupolar ordering. χ_3 diverges at the onset of quadrupolar order.

is well separated from the remaining six $J = 4$ states, and therefore suffices for modelling (as far as the Pr sites are concerned) all low-T phenomena [19, 20]. With $\alpha = \sqrt{7/8} \approx 0.9354$, (4) and (5) would constitute the cubic Γ_5 triplet, but our fits yield $\alpha \approx 0.943$, indicating a slight admixture from the doublet derived from Γ_4. Let us observe that the doublet carries both J^z dipole, and $\mathcal{O}_2^2$ (or alternatively $\mathcal{O}_{xy}$) type quadrupolar moment. If the doublet is the crystal field ground state, the degeneracy can be resolved either by magnetic, or by quadrupolar, ordering.

Using (4), (5), and following the procedure of [24], we fitted the high-T magnetization curves, and found that the dipole–dipole coupling has a strong planar anisotropy, and there is also a substantial ferroquadrupolar coupling of the $\mathcal{O}_2^2$ moments [26]. The latter finding may lead us to ask whether the observed transition is perhaps purely of quadrupolar nature; however, neutron scattering shows that T_N is indeed a Néel temperature, with the $T < T_N$ ordered moments strongly tilted out of the tetragonal c-direction [25]. Within the crystal field model, it is rather mysterious why the system does not take advantage of the permanent c-axis moments of the doublet (4), and chooses instead ab-plane moments which have to be interaction-induced.

The mean-field Hamiltonian acting on the quasi-triplet is similar to (3)

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_{CF} + \mathcal{H}_{Zeeman} + \mathcal{H}_{quad} + \mathcal{H}_{dipole} \\ &= \Delta|\Gamma_t^0\rangle\langle\Gamma_t^0| - g\mu_B \boldsymbol{H}\boldsymbol{J} - zQ\langle\mathcal{O}_2^2\rangle\mathcal{O}_2^2 - zI\langle J_x\rangle_{B(A)}J_x \end{aligned} \tag{6}$$

where we allow for two-sublattice antiferromagnetism, but assume ferroquadrupolar coupling. In view of the bilayer structure of $PrBa_2Cu_3O_6$, we take $z = 4$. From our susceptibility fits, we estimate $\Delta \approx 20$ K.

We note that a closely related three-state problem was considered by Líbero and Cox [21]. They assume hexagonal symmetry, so their choice of the singlet and the doublet is quite different from ours, but nevertheless, when worked out fully, the results of their mean-field theory should basically correspond to what we find. However, we calculate different quantities (such as the susceptibilities), and emphasize different aspects.

Figure 3(a) shows a representative phase diagram. At $Q = 0$, the system gains energy from antiferromagnetic ordering, with the moments lying in the $\pm x$-direction. However, it is

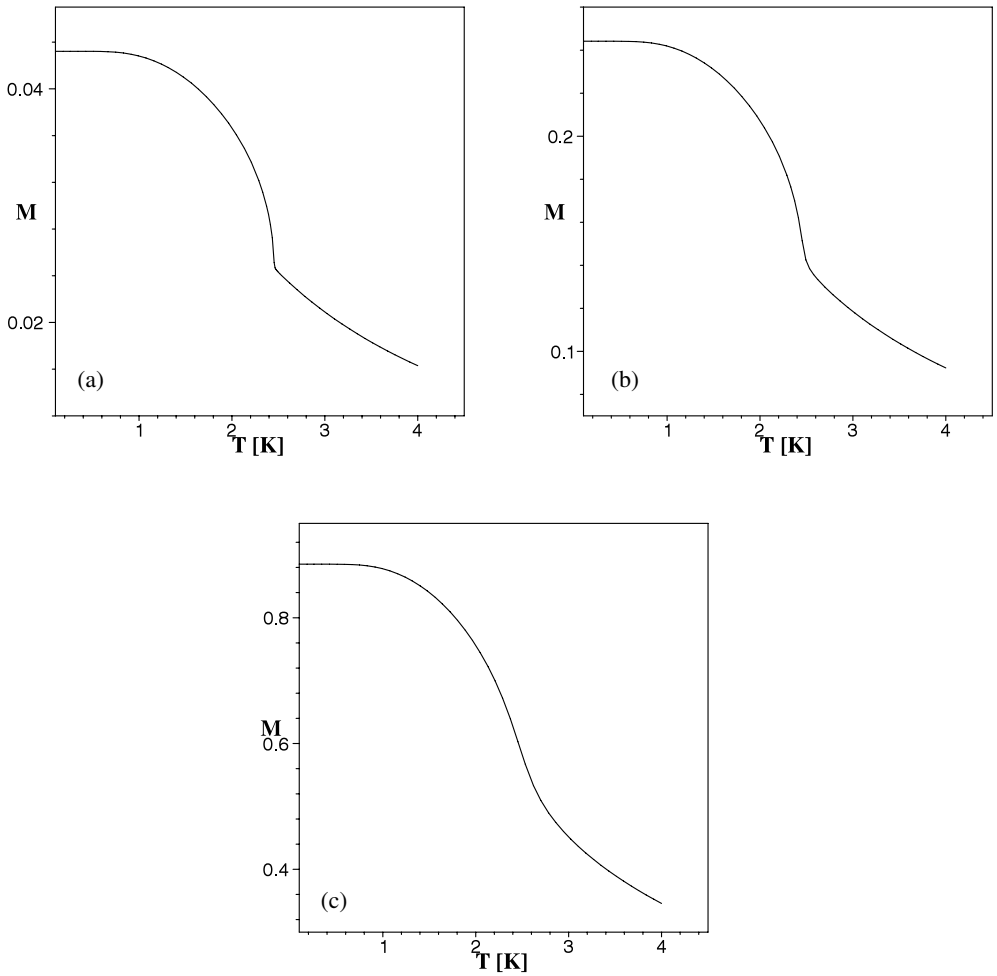

Figure 5. Magnetization (μ_B/Pr) versus temperature for the $H \parallel (1, 0, 0)$ magnetic fields 0.01 T (a), 0.1 T (b) and 0.4 T (c).

easy to convince ourselves that, at the same time, the system develops quadrupolar order: J^x connects Γ_t^0 to $\Gamma_t^+ - \Gamma_t^-$ (which is one of the quadrupolar eigenstates), but not to $\Gamma_t^+ + \Gamma_t^-$ (which would be the other). Thus, for zero or weak Q, the primary order parameter is $\langle J_x \rangle$, while $\langle \mathcal{O}_2^2 \rangle$ is a secondary order parameter (figure 3(b)). At sufficiently strong Q, both interactions are important, and the two orders appear at a first-order transition (figure 3(c)). The regime of first-order transitions is bounded by a lower, and an upper, tricritical point (big black dots in figure 3(a)). Above a Δ-dependent threshold value of Q/I, pure quadrupolar order sets in at a higher critical temperature. From this point on, the quadrupolar splitting is added to the crystal field splitting, eventually suppressing magnetism. Note, however, that for a wide range of Q/I, *magnetism is assisted by quadrupolar interactions*, in the sense that the magnetic transition temperature increases with Q/I. This also holds for part of the regime where the two transitions are distinct.

A remarkable aspect of Pr ordering is its sensitivity to magnetic field, particularly for $H \perp (001)$ [22, 26]. Quadrupolar interactions are known to have a strong signature in non-

linear magnetic response [24]. We show in figure 4 the results for $I = 0$, $Q = 0.2$, $\Delta = 2$, for the field in the ab plane. The upward curvature of χ, and the divergence of χ_3 at the transition are reminiscent of the observed behaviour. Figure 5 shows the T-dependence of the magnetization for several fields $H \parallel (100)$. It is apparent that the sharp $H = 0$ anomaly is quickly smeared out in higher fields, similar to the observed behaviour of $PrBa_2Cu_3O_6$.

To conclude, we have examined models where the local Hilbert space is spanned by the states from the lowest two crystal field levels. The near-degeneracy of two levels has interesting consequences when the splitting is comparable to both intersite interactions, and laboratory magnetic fields. We found that the induced quadrupolar moment scenario gives a good understanding of the static properties of $PrFe_4P_{12}$, and that the inclusion of quadrupolar interaction is helpful in understanding the non-linear magnetic behaviour of $PrBa_2Cu_3O_6$.

Acknowledgments

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