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Kondo materials ( $\text{Y}=\text{Ti}, \text{V}, \text{Rh}, \text{Ir}$ ;  $\text{X}=\text{Al}, \text{Zn}$ )

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# Landau theory of multipolar orders in $\text{Pr}(\text{TM})_2\text{X}_{20}$ Kondo materials

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A series of  $\text{Pr}(\text{TM})_2\text{X}_{20}$  (with  $\text{TM}=\text{Ti}, \text{V}, \text{Rh}, \text{Ir}$  and  $\text{X}=\text{Al}, \text{Zn}$ ) Kondo materials, containing non-Kramers  $\text{Pr}^{3+} 4f^2$  moments on a diamond lattice, have been shown to exhibit intertwined orders such as quadrupolar order and superconductivity. Motivated by these experiments, we propose and study a Landau theory of multipolar order to capture the phase diagram and its field dependence. In zero magnetic field, we show that different quadrupolar states, or the coexistence of quadrupolar and octupolar orderings, may lead to ground states with multiple broken symmetries. Upon heating, such states may undergo two-step thermal transitions into the symmetric paramagnetic phase, with partial restoration of broken symmetries in the intervening phase. For nonzero magnetic field, we show the evolution of these thermal phase transitions strongly depends on the field direction, due to clock anisotropy terms in the free energy. Our findings shed substantial light on experimental results in the  $\text{Pr}(\text{TM})_2\text{Al}_{20}$  materials. We propose further experimental tests to distinguish purely quadrupolar orders from coexisting quadrupolar-octupolar orders.

## I. INTRODUCTION

Heavy fermion materials with partially filled  $4f$  or  $5f$  shells often exhibit unusual phases attributed to broken symmetries involving higher order multipolar degrees of freedom. Given the challenging task of experimentally probing such broken symmetries, they are generally dubbed “hidden orders”.<sup>1–11</sup> In order to obtain a broad understanding of such systems, it is useful to study families of materials which share similar underlying microscopics and related phenomenology. A particularly useful example is provided by the  $\text{Pr}(\text{TM})_2\text{X}_{20}$  intermetallic compounds, with  $\text{TM}=\text{Ti}, \text{V}, \text{Rh}, \text{Ir}$  and  $\text{X}=\text{Al}, \text{Zn}$ .<sup>12–24</sup> All these materials have been shown to exhibit quadrupolar orders and superconductivity at lower temperatures. The common ingredient in this family is the local moment degree of freedom provided by the Pr ion. The interplay of strong spin-orbit coupling (SOC) and weaker crystal field splitting leads to a ground state  $\Gamma^{(3)}$  non-Kramers doublet on Pr, with a significant gap to the higher order multiplets. This doublet carries no dipole moment, but has nonzero quadrupolar and octupolar moments.<sup>14</sup> A key motivation to explore such materials was the theoretical proposal that conduction electrons scattering off such doublets would lead to non-Fermi liquid behavior associated with the single ion two-channel Kondo model.<sup>25–27</sup> The low temperature fate of the Kondo *lattice system*, however, remains an important open question. An understanding of these ground states is also important for clarifying the possible quantum phase transitions of these heavy fermion materials.<sup>28–31</sup>

Recent experiments on these  $\text{Pr}(\text{TM})_2\text{X}_{20}$  materials have confirmed the existence of quadrupolar order-

ing. For instance,  $\text{PrTi}_2\text{Al}_{20}$  displays ferroquadrupolar (FQ) order below  $T_Q \sim 2\text{K}$ , while antiferroquadrupolar (AFQ) order is found in  $\text{PrV}_2\text{Al}_{20}$  ( $T_Q \sim 0.75\text{K}$ ), in  $\text{PrIr}_2\text{Zn}_{20}$  ( $T_Q \sim 0.11\text{K}$ ), and  $\text{PrRh}_2\text{Zn}_{20}$  ( $T_Q \sim 0.06\text{K}$ ).<sup>13,17–19,23,32,33</sup> Interestingly,  $\text{PrV}_2\text{Al}_{20}$  exhibits an additional phase transition at  $T^* \sim 0.65\text{K}$ , and shows non-Fermi liquid behavior above  $T_Q$  in contrast to the Fermi liquid behavior observed in  $\text{PrTi}_2\text{Al}_{20}$ .<sup>16,22,32</sup> This may be due to stronger hybridization between local moments and conduction electrons in  $\text{PrV}_2\text{Al}_{20}$ , leading to proximity to an underlying quantum critical point.<sup>22,34,35</sup> The precise nature of the antiferroquadrupolar orders and the additional transition in  $\text{PrV}_2\text{Al}_{20}$  however remain to be understood.

Further insights into the phase diagram come from experiments studying the impact of a magnetic field.<sup>22,32,33,36–39</sup> For FQ order, it is well known that the magnetic field couples at  $\mathcal{O}(\mathbf{B}^2)$  directly to the order parameter, which converts the sharp paramagnet-to-FQ thermal transition into a crossover; this has been observed in  $\text{PrTi}_2\text{Al}_{20}$ .<sup>32</sup> On the other hand, the multiple transitions in  $\text{PrV}_2\text{Al}_{20}$  at  $T_Q$  and  $T^*$  are found to survive at nonzero fields, and moreover evolve in a manner which depends strongly on the field direction.<sup>40</sup>

In this work, we investigate a symmetry-based Landau theory to gain insight into multipolar orders, their phase transitions, and the impact of the magnetic field, which are motivated by experiments on  $\text{Pr}(\text{TM})_2\text{Al}_{20}$  with  $\text{TM}=\text{Ti}, \text{V}$ . Given that a microscopic model of the Pr doublet, which hosts both quadrupolar and octupolar moments hybridized to conduction electrons, is likely to depend on details of the material-specific band structure and Kondo couplings, we believe such a symmetry-based approach should also be of broader relevance.

We emphasize that our approach is a reasonable starting point on the ordered side of the conventional Doniach phase diagram, as we progressively come closer to the transition into the hybridized heavy Fermi liquid phase. On the heavy Fermi liquid side, where the local moments are strongly hybridized with the conduction electrons, it is no longer meaningful or legitimate to integrate out the conduction electrons, and a Landau theory for local moment ordering is inappropriate.

Our Landau theory includes uniform and staggered quadrupolar orders which are relevant to the  $FQ$  and  $AFQ$  states. For  $FQ$  order, we find that the Landau theory permits a cubic anisotropy term, which was previously pointed out within a microscopic theory and classical Monte Carlo study of a lattice model.<sup>41,42</sup> This selects an  $FQ$  ordered state which is consistent with experimental results on  $PrTi_2Al_{20}$ .<sup>37</sup> On the other hand,  $AFQ$  order is generally accompanied by a “parasitic”  $FQ$  order due to a cubic term which couples them. However, previous work found a single transition at which both orders are generated, and it thus does not explain the emergence of the two transitions observed in  $PrV_2Al_{20}$  at zero field. Moreover, the octupole moment carried by the doublet is ignored in previous studies. Our Landau theory approach, which incorporates quadrupolar as well as octupolar order parameters, and symmetry-allowed clock anisotropies in the free energy, suggests two possible ways to explain the multiple thermal transitions in  $PrV_2Al_{20}$ ,<sup>16</sup> and understand the field evolution of the phase diagrams.

(i) Within a purely quadrupolar description, we show that the interplay of  $AFQ$  and  $FQ$  orders can lead to a second (lower temperature) transition at  $T^*$  within the  $AFQ$  phase due to a competition between different clock terms in the free energy. The intermediate phase in this picture preserves an Ising  $S_{4z}$  symmetry, which is further broken for  $T < T^*$ .

(ii) Alternatively, we consider the more exotic possibility that the lower temperature transition at  $T^*$  might correspond to the ordering of octupolar degrees of freedom within the  $AFQ$  phase, which would lead to spontaneous time-reversal symmetry breaking for  $T < T^*$ .

We find that both scenarios can potentially lead to similar experimental phase diagrams and their magnetic field evolution while the way that zero and finite temperature transitions are connected may be different in the two cases. We therefore conclude with a discussion of possible further experimental tests to distinguish between these two scenarios.

## II. SYMMETRIES

$Pr(TM)_2X_{20}$  (with  $TM=Ti, V, Rh, Ir$  and  $X=Al, Zn$ ) are cage compounds with the space group  $Fd\bar{3}m$ . In particular, the  $Pr^{3+} 4f^2$  ions live on a diamond lattice, with each ion at the center of the Frank Kasper cage formed by 16 neighboring  $X$  ions with the local point group  $T_d$ .<sup>14</sup> Strong SOC leads to a total angular momentum  $J = 4$  on the  $Pr$  ion, while crystal field splitting leads to a  $\Gamma_3$  doublet ground state. (We note that  $PrRh_2Zn_{20}$  has the local point group  $T$  due to a further structural transition, and has a  $\Gamma_{23}$  doublet ground state.)<sup>14,32</sup> The  $\Gamma_3$  doublet wavefunctions are given by<sup>13,41</sup>

$$\begin{aligned} |\Gamma_3^{(1)}\rangle &= \frac{1}{2}\sqrt{\frac{7}{6}}|4\rangle - \frac{1}{2}\sqrt{\frac{5}{3}}|0\rangle + \frac{1}{2}\sqrt{\frac{7}{6}}|-4\rangle \\ |\Gamma_3^{(2)}\rangle &= \frac{1}{\sqrt{2}}|2\rangle + \frac{1}{\sqrt{2}}|-2\rangle. \end{aligned} \quad (1)$$

In these compounds, the first excited triplet  $\Gamma_4$  or  $\Gamma_5$  is separated from the ground doublet by  $\Delta \approx 30\text{-}70\text{K}$ . This allows us to study the broken symmetry phases, which typically have transition temperatures  $\lesssim 5\text{K}$ , by projecting to the  $\Gamma_3$  (or  $\Gamma_{23}$ ) doublets. Using these doublets, we define pseudospin-1/2 basis as in Ref. [43], namely,

$$|\uparrow\rangle \equiv \frac{1}{\sqrt{2}}(|\Gamma_3^{(1)}\rangle + i|\Gamma_3^{(2)}\rangle) \quad (2)$$

$$|\downarrow\rangle \equiv \frac{1}{\sqrt{2}}(i|\Gamma_3^{(1)}\rangle + |\Gamma_3^{(2)}\rangle). \quad (3)$$

We identify the corresponding pseudospin operators in terms of Stevens operators<sup>44,45</sup>  $O_{22} = \frac{\sqrt{3}}{2}(J_x^2 - J_y^2)$ ,  $O_{20} = \frac{1}{2}(3J_z^2 - J^2)$ , and  $T_{xyz} = \frac{\sqrt{15}}{6}\overline{J_x J_y J_z}$  (with the overline denoting a fully symmetrized product), as

$$\tau^x = -\frac{1}{4}O_{22}; \quad \tau^y = -\frac{1}{4}O_{20}; \quad \tau^z = \frac{1}{3\sqrt{5}}T_{xyz}. \quad (4)$$

Here, the components of the pseudospin  $\vec{\tau}$  are such that  $(\tau^x, \tau^y) \equiv \vec{\tau}^\perp$  describes a time-reversal invariant quadrupolar moment, while  $\tau^z$  describes a time-reversal odd octupolar moment.

The point group symmetries of  $Pr^{3+}$  ions include  $S_{4z}$  ( $\pi/2$  rotation about  $z$  axis and inversion about a site),  $C_{31}$  ( $2\pi/3$  rotation along (111) direction),  $\sigma_{d1}$  (mirror reflection with a plane perpendicular to  $(\bar{1}10)$  direction) and  $\mathcal{I}$  (bond-centered inversion). Under these point group operations and time reversal ( $\Theta$ ), the pseudospins

transform as:

$$\Theta : \tau_{A/B}^z \rightarrow -\tau_{A/B}^z, \quad (5)$$

$$\mathcal{I} : \vec{\tau}_A \leftrightarrow \vec{\tau}_B, \quad (6)$$

$$\mathcal{S}_{4z} : \tau_{A/B}^\pm \rightarrow -\tau_{A/B}^\mp; \tau_{A/B}^z \rightarrow -\tau_{A/B}^z \quad (7)$$

$$\sigma_{d1} : \tau_{A/B}^\pm \rightarrow -\tau_{A/B}^\mp; \tau_{A/B}^z \rightarrow -\tau_{A/B}^z \quad (8)$$

$$\mathcal{C}_{31} : \tau_\mu^\pm \rightarrow e^{\pm i2\pi/3} \tau_\mu^\pm \quad (9)$$

Note that we have dropped explicit site indices, keeping in mind that these sites will transform under lattice operations. However, we have kept sublattice labels since this will be important when we construct the Landau theory in the next section. We next use these symmetries in order to construct the Landau theory.

### III. LANDAU THEORY

In this paper, we study the simplest scenarios with uniform or two-sublattice orders which do not enlarge the unit cell of the diamond lattice. Thus, we consider FerroQuadrupole (FQ), AntiFerroQuadrupole (AFQ), FerroOctupole (FO) and AntiFerroOctupole (AFO) broken symmetry states. Some of these orders could potentially coexist. Let us introduce uniform and staggered multipolar order parameters

$$\phi_{u,s} \equiv \langle \tau_A^+ \rangle \pm \langle \tau_B^+ \rangle \quad (10)$$

$$m_{u,s} \equiv \langle \tau_A^z \rangle \pm \langle \tau_B^z \rangle. \quad (11)$$

Here, the complex scalars  $\phi_{u,s}$  denote, respectively, the uniform (for FQ) and staggered parts (for AFQ) of the XY quadrupolar order, while the real scalars  $m_{u,s}$  refer to the uniform (for FO) and staggered parts (for AFO) of the Ising octupolar order. The underlying crystal and time-reversal symmetry transformations act on the order parameters  $\phi_{u,s}$  and  $m_{u,s}$  as follows:

$$\Theta : \phi_{u,s} \rightarrow \phi_{u,s}; m_{u,s} \rightarrow -m_{u,s} \quad (12)$$

$$\mathcal{I} : (\phi_u, m_u) \rightarrow (\phi_u, m_u); (\phi_s, m_s) \rightarrow -(\phi_s, m_s) \quad (13)$$

$$\mathcal{S}_{4z} : \phi_{u,s} \rightarrow -\phi_{u,s}^*; m_{u,s} \rightarrow -m_{u,s} \quad (14)$$

$$\mathcal{C}_{31} : \phi_{u,s} \rightarrow e^{i2\pi/3} \phi_{u,s}; m_{u,s} \rightarrow m_{u,s}. \quad (15)$$

For two-sublattice orders, the pseudospins transform in the same manner under  $\mathcal{S}_{4z}$  and  $\sigma_{d1}$  (since we do not have to keep track of the precise sites); thus, we drop the  $\sigma_{d1}$  symmetry in the following analysis. The symmetry-allowed terms in the Landau free energy with independent order parameters are thus:

$$\mathcal{F}_{\phi u} = r_{u\phi} |\phi_u|^2 + iv(\phi_u^3 - \phi_u^{*3}) + g_{u\phi} |\phi_u|^4 + \dots \quad (16)$$

$$\mathcal{F}_{\phi s} = r_{s\phi} |\phi_s|^2 + g_{s\phi} |\phi_s|^4 + w(\phi_s^6 + \phi_s^{*6}) + \dots \quad (17)$$

$$\mathcal{F}_{mu} = r_{um} m_u^2 + g_{um} m_u^4 + \dots \quad (18)$$

$$\mathcal{F}_{ms} = r_{sm} m_s^2 + g_{sm} m_s^4 + \dots, \quad (19)$$

where the ellipses denote dropped higher order terms. The important difference between the FQ versus AFQ free energies appears in the “clock” anisotropy terms which break XY symmetry for  $\phi_u, \phi_s$  respectively; this is cubic for FQ and sixth order for AFQ. This free energy must be supplemented by  $\mathcal{F}_{\text{int}}$  which encapsulates interactions between the different order parameters. Symmetry allows for a single cubic interaction,

$$\mathcal{F}_{\text{int}}^{(3)} = i\lambda(\phi_s^2 \phi_u - \phi_s^{*2} \phi_u^*). \quad (20)$$

This leads to “parasitic” FQ order  $\phi_u \sim \phi_s^{*2}$  in an AFQ state. Additional quartic interactions between order parameters take the form

$$\begin{aligned} \mathcal{F}_{\text{int}}^{(4)} = & c_1 |\phi_u|^2 |\phi_s|^2 + c_2 m_u^2 m_s^2 + c_3 |\phi_u|^2 m_u^2 \\ & + c_4 |\phi_s|^2 m_s^2 + c_5 |\phi_u|^2 m_s^2 + c_6 |\phi_s|^2 m_u^2. \end{aligned} \quad (21)$$

Such terms can lead to coexistence of quadrupolar and octupolar order parameters depending on the signs of the coefficients. Below, we will analyze this Landau free energy in various cases, starting from the simplest example.

#### A. FQ order in PrTi<sub>2</sub>Al<sub>20</sub>

PrTi<sub>2</sub>Al<sub>20</sub> exhibits FQ order, so we can focus on the single term  $\mathcal{F}_{\phi u}$  in Eq. (16) above.<sup>13,32,33</sup> For  $r_{u\phi} > 0$ , this describes a paramagnetic (PM) phase with  $\phi_u = 0$ , while  $r_{u\phi} < 0$  leads to FQ order with  $\phi_u \neq 0$ . The phase of  $\phi_u \equiv |\phi_u| e^{i\theta_u}$  is determined by the clock term  $v$ . For  $v > 0$ , we favor  $\theta_u = \pi/6 + 2n\pi/3$  (with integer  $n$ ), while  $v < 0$  pins  $\theta_u = \pi/6 + (2n+1)\pi/3$ . In particular, either sign of  $v$  favors  $O_{20}$  order over  $O_{22}$  order, which is consistent with nuclear magnetic resonance (NMR) experiments<sup>37</sup> on PrTi<sub>2</sub>Al<sub>20</sub>. In the ‘hard-spin’ limit, the theory for the PM-to-FQ transition is a  $Z_3$  clock model which is known to exhibit a first-order transition in three dimensions (3D).<sup>46,47</sup> However, disorder effects<sup>48</sup> may modify this expectation, leading to a continuous transition as appears to be observed in experiments; this needs further theoretical investigation.

#### B. AFQ with ‘parasitic’ FQ order

Let us ignore the octupolar orders  $m_u, m_s$ , and focus on the free energy  $\mathcal{F}_{\phi u} + \mathcal{F}_{\phi s} + \mathcal{F}_{\text{int}}^{(3)} + c_1 |\phi_u|^2 |\phi_s|^2$ . For an AFQ transition driven by  $r_{s\phi} < 0$ , we get  $\phi_s \neq 0$ . This AFQ transition will happen within mean field theory at  $T_Q$  if we set  $r_{s\phi} = \alpha_s(T - T_Q)$ , with  $\alpha_s > 0$ . In this case, even if  $r_{u\phi} > 0$ , the cubic interaction  $\lambda \neq 0$  in  $\mathcal{F}_{\text{int}}^{(3)}$  leads to  $\phi_u \neq 0$ . It is useful to begin our analysis

of the interplay of AFQ and FQ orders by considering the regime where  $r_{u\phi}$  is large. The resulting FQ order is then parasitic, and it will be slaved to the AFQ order. Let us simplify the problem by setting  $(v, g_{u\phi}) \rightarrow 0$  to leading order, and minimizing the free energy with respect to  $\phi_u$  which leads to

$$\phi_u = \frac{i\lambda}{r_{u\phi}} \phi_s^{*2}. \quad (22)$$

Substituting back, the full free energy is given by

$$\mathcal{F}_{\phi s}^{\text{eff}} = r_{s\phi} |\phi_s|^2 + g_{s\phi}^{\text{eff}} |\phi_s|^4 + w^{\text{eff}} (\phi_s^6 + \phi_s^{*6}) + \dots, \quad (23)$$

where

$$g_{s\phi}^{\text{eff}} = g_{s\phi} - \frac{\lambda^2}{r_{u\phi}} \quad (24)$$

$$w^{\text{eff}} = w + v \frac{\lambda^3}{r_{u\phi}^3}. \quad (25)$$

With  $\phi_s = |\phi_s|e^{i\theta_s}$ , we find that the clock term with  $w^{\text{eff}} > 0$  favors  $\theta_s = (2n+1)\pi/6$ , while  $w^{\text{eff}} < 0$  would favor  $\theta_s = 2n\pi/6$ . Now, even if  $r_{u\phi} > 0$ , it may have a temperature dependence as  $r_{u\phi} = r_{u\phi}(0) + \alpha_u T$  with  $r_{u\phi}(0) > 0, \alpha_u > 0$ . Such a (benign) temperature dependence of  $r_{u\phi}$  could, nevertheless, lead to a change of sign of  $g_{s\phi}^{\text{eff}}$  which could lead to first-order transitions, or a sign change of  $w^{\text{eff}}$  (if the product  $wv\lambda < 0$ ) which may modify the competition between the different clock terms. This, admittedly crude, argument suggests that the interplay of AFQ and FQ orders could lead to a rich phase diagram with new phases and phase transitions.

In order to examine this scenario, we numerically minimize the Landau free energy  $\mathcal{F}_{\phi s} + \mathcal{F}_{\phi u} + \mathcal{F}_{\text{int}}^{(3)}$ , as a function of  $r_{u\phi}$  and  $r_{s\phi}$ , while keeping  $r_{u\phi} > 0$ . For illustrative purposes, we fix  $g_{u\phi} = 1$  and  $g_{s\phi} = 1/2$ , and consider the choice for the coefficients of the clock terms  $(w, v, \lambda) \equiv (1/4, -1/4, 1/4)$ . The resulting phase diagram is shown in Fig. 1(a), and exhibits five different phases: a paramagnet (PM), a FQ state driven by the cubic term  $v$ , and three types of AFQ phases (with coexisting FQ order) which result from competition between the different clock terms in the free energy. Solid and dashed lines indicate the second order and the first order phase transitions respectively. Fig. 1(c) shows the nature of the different AFQ phases, which are distinguished by the behavior of the quadrupole moment on the two sublattices.

In AFQ-I, the staggered quadrupolar order points along  $\tau_x$  ( $O_{22}$ ) while the parasitic uniform component points along  $\tau_y$  ( $O_{20}$ ). This phase minimizes the clock anisotropy terms  $v$  and  $\lambda$ . The AFQ-I state depicted in Fig. 1(c) preserves  $S_{4z}$  and  $\Theta$  symmetries.

In AFQ-III, both the staggered and uniform components favor  $O_{20}$  order, so the overall magnitude of the

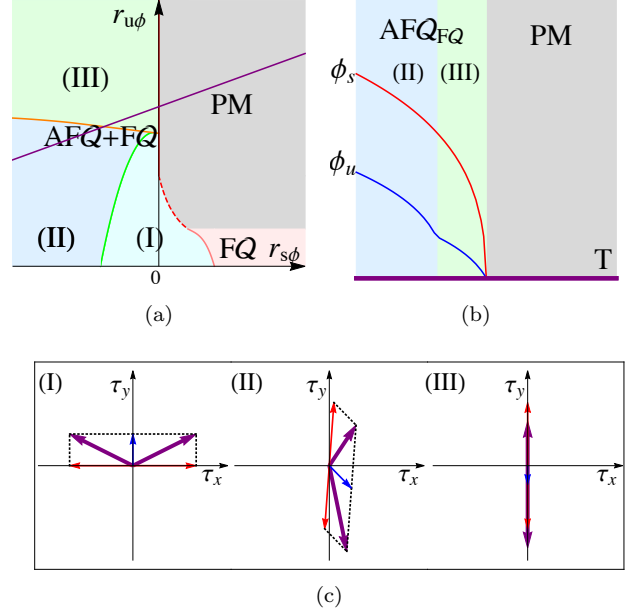


FIG. 1. [Color online] (a) Phase diagram of the Landau theory described by  $\mathcal{F}_{\phi u} + \mathcal{F}_{\phi s} + \mathcal{F}_{\text{int}}^{(3)}$  with AFQ and FQ order parameters as functions of  $r_{s\phi}$  and  $r_{u\phi}$ . Solid (dashed) lines indicate the second (first) order phase transitions. Here, we take  $wv\lambda < 0$ . The various phases are paramagnet (PM), FQ and three distinct phases (I),(II) and (III) for AFQ with parasitic FQ (AFQ<sub>FQ</sub>). See main text for details. (b) Plot of the order parameters as a function of temperature T, a cut through the trajectory (purple line) in panel (a). Red and blue lines represent the magnitude of order parameters  $\phi_s$  and  $\phi_u$ . (c) Common origin plots of distinct AFQ<sub>FQ</sub> phases (I),(II) and (III). Red and Blue arrows exhibit AFQ and FQ respectively and purple arrow is the direction of quadrupolar order resulting from combination of both AFQ and FQ. All these spin configurations have three-fold degeneracies with  $2\pi/3$  rotation in  $\tau_x$ - $\tau_y$  plane.

ordered quadrupole moment is different on the two sublattices. This phase minimizes the clock terms  $w$  and  $\lambda$ . Again, the AFQ-III state depicted in Fig. 1(c) preserves  $S_{4z}$  and  $\Theta$  symmetries.

Finally, AFQ-II is a ‘frustrated’ phase, where the competition of the different clock terms  $(w, v, \lambda)$  results in none of them being fully minimized. This phase exhibits a generically complex superposition of  $O_{20}$  and  $O_{22}$  orders, with unequal magnitude of the ordered moment on the two sublattices, and only preserves  $\Theta$ . We thus expect the AFQ-II state, which breaks the residual  $S_{4z}$  symmetry, and thus has lower symmetry than AFQ-I or AFQ-III, to arise from either one of them upon cooling.

We find that different choices for these clock coefficients, keeping the product  $wv\lambda < 0$  yield phase dia-



grams with the same phases and a roughly similar topology. For instance, when we decrease  $\lambda = 1/16$ , we find the following differences: (i) the AFQ-I phase shrinks, (ii) the AFQ-II to AFQ-III phase transition becomes first order, and (iii) there is no direct transition from PM into AFQ-I.

To see how this  $(r_{s\phi}, r_{u\phi})$  phase diagram might translate into a phase diagram as a function of temperature, consider a cut through Fig. 1(a) at large  $r_{u\phi}$ . Such a cut will yield a PM to AFQ-III transition, i.e., a *single* transition into a phase with coexisting AFQ order and parasitic FQ order. This scenario is consistent with what has been previously explored by Hattori and Tsunetsugu.<sup>41,42</sup>

However, for smaller  $r_{u\phi}$ , along the cut shown in Fig. 1(a), we find that the transition splits into two transitions, a PM to AFQ-III transition, and a subsequent AFQ-III to AFQ-II transition. Such phase transition originates from a competition between different clock terms of AFQ and FQ orders, thus can be captured by cubic and higher orders of spin-spin interactions. Fig. 1(b) shows the evolution of the order parameters with “temperature”, where going along the cut from PM to AFQ-III to AFQ-II is viewed as corresponding to decreasing temperature. The two thermal transitions in this scenario might potentially explain the two observed zero field thermal transitions in  $\text{PrV}_2\text{Al}_{20}$ .<sup>16,22</sup> We note that while there are many possible cuts we could take which would lead to multiple thermal transitions, the one we have chosen seems most promising from the point of view of understanding the magnetic field evolution as discussed in Section IV.

### C. Coexisting AFQ and octupolar orders

Finally, let us turn to the most interesting possibility, that the two thermal transitions in  $\text{PrV}_2\text{Al}_{20}$  correspond, respectively, to the onset of AFQ and of octupolar order which spontaneously breaks time-reversal symmetry. In previous work, we have considered this possibility within a particular (phenomenological) microscopic Hamiltonian with competing two-spin and four-spin interactions which we studied using classical Monte Carlo simulations.<sup>43</sup> Here, we revisit this scenario using Landau theory which goes beyond a specific microscopic model. We note the precise type of octupolar order, either ferrooctupolar or antiferrooctupolar, does not change our Landau theory analysis performed below; without loss of generality, we thus consider the case with ferro-octupolar order. This distinction will of course be important when we turn in the end to a discussion of experimental consequences.

To illustrate this interplay of AFQ and octupolar or-

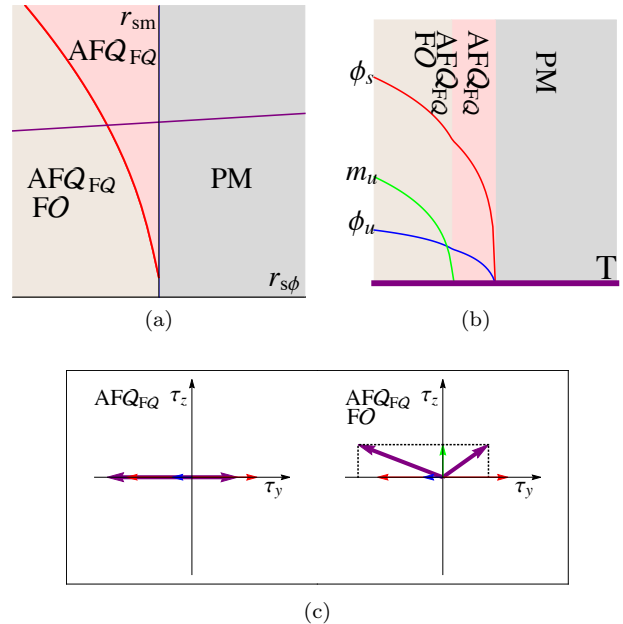


FIG. 2. [Color online] (a) Phase diagram of the Landau theory described by  $\mathcal{F}_{\phi u} + \mathcal{F}_{\phi s} + \mathcal{F}_{m u} + \mathcal{F}_{\text{int}}^{(3)} + \mathcal{F}_{\text{int}}^{(4)}$  with AFQ, FQ and FO order parameters as functions of  $r_{s\phi}$  and  $r_{sm}$ . Here, we set  $wv\lambda > 0$  distinct with the case depicted in Fig. 1. Thus, the second phase transition only arises from developing additional octupolar order. In this case, three phases exist described by continuous phase transitions; paramagnet (PM), AFQ with parasitic FQ (AFQ<sub>FQ</sub>) and coexisting AFQ and FO with parasitic FQ order (AFQ<sub>FQ</sub>FO). See main text for details. (b) Plot of the order parameters along shown trajectory (purple line) in panel (a). Red, blue and green lines represent the magnitude of order parameters  $\phi_s$  and  $\phi_u$  and  $m_u$ . (c) Common origin plots of each phase. Red, blue and green arrows exhibit magnitudes of AFQ, FQ and FO phases respectively and purple arrow is the combination of them, determining the direction of pseudospin  $\tau$ . All these spin configurations have three-fold degeneracies with  $2\pi/3$  rotation in  $\tau_x$ - $\tau_y$  plane. (Here we chose the quadrupole order configuration having only  $\tau_y$  component.)

ders, Fig. 2(a) shows a phase diagram obtained using the Landau free energy  $\mathcal{F}_{\phi s}^{\text{eff}} + \mathcal{F}_{m u} + \mathcal{F}_{\text{int}}^{(4)}$ , where we consider having integrated out  $\phi_u$  and assumed large  $r_{u\phi}$  so any multiple thermal transitions must arise from additional octupolar order. We pick  $c_6 \neq 0$  in  $\mathcal{F}_{\text{int}}^{(4)}$  in Eq. (21); specifically, we chose  $c_6 < 0$  to allow for a coexistence phase. As we vary  $r_{s\phi}, r_{um}$ , there exist four distinct phases: a paramagnet (PM) ( $\phi_s = \phi_u = m_s = 0$ ), an AFQ phase with parasitic FQ order ( $\phi_s \neq 0, \phi_u \neq 0, m_u = 0$ ), an FO phase ( $\phi_s = \phi_u = 0, m_u \neq 0$ ), and finally a phase with coexisting AFQ and FO orders with parasitic FQ order ( $\phi_s \neq 0, \phi_u \neq 0, m_u \neq 0$ ). Fig. 2(b) shows

the temperature dependence of the order parameters as we “cool” from the PM into the phase with coexisting AFQ and FQ orders; for simplicity, we consider going along the trajectory indicated in Fig. 2(a), i.e., keeping  $r_{sm}$  fixed and varying  $r_{s\phi}$ . This clearly shows the double transition, with the upper transition  $T_Q$  being associated with AFQ order (with parasitic FQ) and the lower transition at  $T^*$  arising from the octupolar order. Fig. 2(c) shows the common origin plots of pseudospin  $\tau$  for AFQ and AFQ-FQ respectively (both with parasitic FQ).

#### IV. IMPACT OF A MAGNETIC FIELD

We next consider the impact of an applied magnetic field  $\mathbf{B}$  on the Landau free energy, and its phases and phase transitions. The leading term is a quadratic-in-field coupling to the quadrupolar order; microscopically, this arises via second order perturbation theory in  $\mathbf{B} \cdot \mathbf{J}$ , where  $\mathbf{J}$  is the  $J = 4$  angular momentum operator. Projecting to the  $\Gamma_3$  doublet, we arrive at the form<sup>41</sup>

$$H_{\text{field}} = \gamma B^2 (b_1 \tau^x + b_2 \tau^y) \quad (26)$$

where  $b_1 \equiv \frac{\sqrt{3}}{2}(\hat{b}_x^2 - \hat{b}_y^2)$ ,  $b_2 \equiv \frac{1}{2}(3\hat{b}_z^2 - 1)$ , and  $(\hat{b}_x, \hat{b}_y, \hat{b}_z)$  describes the unit vector pointing along  $\mathbf{B}$ . The coupling constant

$$\gamma \propto \left( -\frac{14}{3\Delta(\Gamma_4)} + \frac{2}{\Delta(\Gamma_5)} \right), \quad (27)$$

with  $\Delta(\cdot)$  being the energy of the indicated higher energy crystal field multiplets.<sup>43</sup>

Note that a magnetic field along the (111) direction does not directly couple to the quadrupolar moment, but even along this direction  $B^2$  could couple to the energy density via  $|\phi_s|^2$  or  $|\phi_u|^2$ , with the coupling to  $|\phi_u|^2$  being less important if the FQ order is parasitic and small. Moreover, along this special (111) direction, the magnetic field can couple to the octupolar moment at cubic order in the field as  $\sim |B|^3 \hat{b}_x \hat{b}_y \hat{b}_z \tau_z$ ; however, given that this last term is expected to be much weaker for typical fields, we omit it in the analysis below.

To proceed, it is useful to define a complex scalar  $\psi_B \equiv b_1 + ib_2$  representing the external magnetic field, which transforms identical to the FQ order parameter  $\phi_u$ , and thus couples to it linearly. This leads to terms in the Landau free energy

$$\mathcal{F}_B = \gamma B^2 (\psi_B^* \phi_u + \phi_u^* \psi_B) + B^2 (\tilde{r}_{sB} |\phi_s|^2 + \tilde{r}_{uB} |\phi_u|^2), \quad (28)$$

where we have included extra, symmetry allowed, couplings  $\tilde{r}_{sB}, \tilde{r}_{uB}$  to the energy density as discussed above. Along key high symmetry directions,  $\psi_B(111) = 0$ ,  $\psi_B(100) = e^{i\pi/2 + i2n\pi/3}$ ,  $\psi_B(110) = \frac{1}{2}e^{-i\pi/2 + i2n\pi/3}$ .

#### A. FQ order in PrTi<sub>2</sub>Al<sub>20</sub>

As seen from the coupling in  $\mathcal{F}_B$  above, the direction of the magnetic field pins the quadrupolar moment direction, thus explicitly breaking the  $Z_3$  symmetry associated with the choice of phase of  $\phi_u$ . This converts the PM-FQ transition into a smooth crossover for both (001) and (110) field directions, as has also been predicted based on microscopic model studies and confirmed by specific heat measurements on PrTi<sub>2</sub>Al<sub>20</sub>.

#### B. AFQ with parasitic FQ order

For this case, we proceed by considering the Landau free energy  $\mathcal{F}_{\phi s} + \mathcal{F}_{\phi u} + \mathcal{F}_{\text{int}}^{(3)}$  supplemented by the field term  $\mathcal{F}_B$ . For simplicity, we set  $\tilde{r}_{sB} = 0$  and  $\tilde{r}_{uB} = 0$ , and only consider the impact of the coupling  $\gamma$ . Minimizing this full free energy along the cut shown in Fig. 1(a), we find the strongly direction-dependent field evolution displayed in Fig. 3 for fields along (001) and (110) directions. In both cases, the field couples linearly to  $\phi_u$ , and thus pins its phase as soon as  $\mathbf{B} \neq 0$ . We refer to the resulting phase as ‘FQ’ to denote that it is not a symmetry broken FQ state, but rather a field induced FQ state which is thus qualitatively similar to a PM. Along the (001) direction, the entire region of AFQ-III and AFQ-II gets replaced by the AFQ-II phase as  $\phi_u$  cants away from pure O<sub>20</sub> order, while phase AFQ-I emerges only for nonzero  $B$  from the PM-to-AFQ-III transition point. Along the (110) direction however, all three phases present at zero field and the corresponding two thermal phase transitions survive even for  $B \neq 0$ .

#### C. Coexisting AFQ and octupolar orders

Finally, let us turn to the field evolution in the case where we assume  $r_{u\phi}$  is large and positive and integrated out  $\phi_u$ , but study the interplay of  $\phi_s$  and  $m_u$  as we have done at  $B = 0$ . We thus minimize the free energy  $\mathcal{F}_{\phi s}^{\text{eff}} + \mathcal{F}_{mu} + \mathcal{F}_{\text{int}}^{(4)}$ , and supplement this with

$$\mathcal{F}_B^{\text{eff}} = iB^2 \gamma_{\text{eff}} (\psi_B \phi_s^2 - \psi_B^* \phi_s^{*2}) + B^2 \tilde{r}_{sB} |\phi_s|^2, \quad (29)$$

where the term  $\gamma_{\text{eff}}$  arises from the coupling  $\gamma$  in Eq. 28 upon integrating out  $\phi_u$ . Fig. 4 shows the direction dependent field evolution of multiple transitions for coexisting AFQ and octupolar orders. When a magnetic field is applied, the transition temperature (blue lines in Fig. 4(a) and (b)) between paramagnet (PM) and AFQ with parasitic FQ phase (AFQ<sub>FQ</sub>) increases due to field coupling term  $\tilde{r}_{sB}$  which is quadratic in  $\phi_s$ , and since the

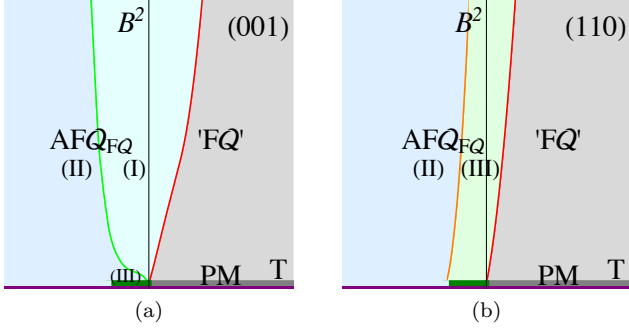


FIG. 3. (a) Phase diagram of quadrupolar order as functions of magnetic field  $\mathbf{B}//(001)$  and temperature  $T$  taking the shown trajectory along the purple line in Fig. 1 (a). In the presence of field  $\mathbf{B}//(001)$ , the type (I) phase of  $\text{AFQ}_{\text{FQ}}$  is stabilized at intermediate temperature, whereas the type (III) phase is no longer stable with fields along (001) direction. See the main text for details. (b) Phase diagram of quadrupolar order with  $\mathbf{B}//(110)$ . With fields, the type (III) phase is stable favored by both cubic anisotropy and field coupling of  $\text{FQ}$ .

phase is directly locked to the field direction. On the other hand, the lower transition temperature strongly depends on field direction; it decreases with  $\mathbf{B}//(001)$  (red line in Fig. 4(a)) and increases with  $\mathbf{B}//(110)$  (red line in Fig. 4(b)). The decrease of transition temperature with field (001) originates from the competition between the sixth order anisotropy term and field coupling terms for finite magnitudes of  $\phi_s$ . Thus, an anisotropic evolution of the phase diagram in a magnetic field can be also present due to  $\text{AFQ}$  and octupolar orders.

## V. DISCUSSION

In this paper, we have formulated and studied the Landau theory of multipolar orderings in the  $\text{Pr}(\text{TM})_2\text{Al}_{20}$  systems, including quadrupolar and octupolar orders. In the absence of any octupolar order, the phases of the Landau theory preserve time-reversal symmetry. In this case, examining the different quadrupolar orders, we find that while a single thermal transition is expected in the case of  $\text{FQ}$  order, there may be multiple thermal transitions for the case of  $\text{AFQ}$  orders. Such a scenario involves a higher temperature transition from a paramagnetic phase into an  $\text{AFQ}$  order which breaks all point group symmetries except  $S_{4z}$ , followed by a lower temperature transition into a phase where this residual Ising symmetry is broken. The residual  $S_{4z}$  symmetry in the intermediate phase has implications for  $^{27}\text{Al}$  NMR experiments which probe the induced dipole order for a ‘probe’ magnetic field applied

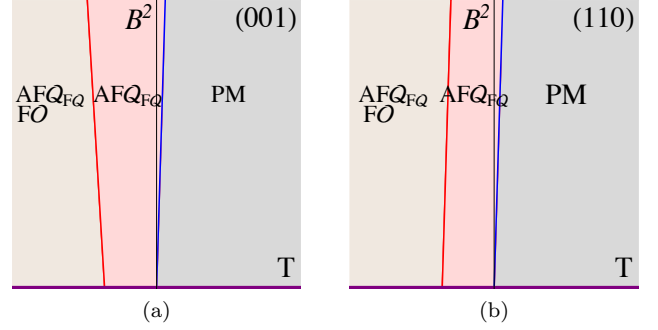


FIG. 4. (a) Phase diagram of quadrupole-octupole order as functions of magnetic field  $\mathbf{B}//(001)$  and temperature  $T$  taking the shown trajectory along the purple line in Fig. 2(a). With fields along (001) direction, the phase transition temperature between  $\text{AFQ}_{\text{FQ}}$  and  $\text{AFQ}_{\text{FQ}}\text{-FO}$  decreases, whereas increases for between  $\text{AFQ}_{\text{FQ}}$  and paramagnet. (b) Phase diagram of coexisting quadrupole-octupolar order as functions of magnetic field  $\mathbf{B}//(110)$ . In this case, magnetic fields induce the increase of phase transition temperature for both cases. See the main text for details.

along the (111) direction. For a (111) field, there are a set of ‘3c’ Al sites on the Frank-Kasper cage which are symmetry equivalent in the paramagnetic phase, and yield a single NMR line.<sup>37</sup> Based on symmetry, an  $\text{AFQ}$ -III state with  $S_{4z}$  symmetry is expected to split this into four NMR lines, with a 1:2 intensity ratio (i.e., two weak and two strong). However, the lower temperature  $\text{AFQ}$ -II state with broken  $S_{4z}$  should exhibit six NMR lines with equal intensity. Thus, upon cooling from the  $\text{AFQ}$ -III state, which preserves  $S_{4z}$  symmetry, into the low temperature  $\text{AFQ}$ -II state with broken  $S_{4z}$  symmetry, each of the two original high intensity lines should split into two peaks. Alternatively, the lower temperature transition may be from an intermediate  $\text{AFQ}$ -III state which preserves  $S_{4z}$  and time reversal into a state where time-reversal is broken by the octupolar order. In this case, the NMR should show four lines with a 1:2 intensity ratio in both broken symmetry phases assuming that the octupolar order is only weakly affected by field, but the time reversal breaking or distinctions between  $\text{FO}$  and  $\text{AFQ}$  could be possibly detectable by  $\mu\text{SR}$ .<sup>24</sup> Further work is needed to understand the role of domains and nature of domain walls in systems with such multipolar orders due to possible spin-lattice couplings. Clarifying the nature of these multipolar orders in the  $\text{Pr}(\text{TM})_2\text{Al}_{20}$  systems would be a significant step in understanding the phase diagram and quantum critical points of such multipolar Kondo materials.



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