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# Mean-field phase diagram for cubic-based praseodymium compounds

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Calculating the *exact* mean-field free energy from a Heisenberg-like Hamiltonian we determine the magnetic phase diagram for cubic-based praseodymium compounds with a $\Gamma_3$ doublet ground state and a $\Gamma_4$ triplet first-excited state. We find lines of first- and second-order phase transitions, separated by a tricritical point. We also calculate the temperature dependence of the magnetic-order parameter.

## I. INTRODUCTION

The increasing development of neutron-scattering techniques and the advances in chemical separation methods have honed important tools in the field of rare-earth (RE) magnetism. Particular attention has been given to the intermetallic RE systems, in which conduction electrons hybridize with incomplete *f* shells,[1,2] and among these to the cases in which the hybridization is small compared with the *f*-level energy $\epsilon_f$, measured from the Fermi level. In such cases, a RE ion maintains its atomic character, in spite of the perturbations due to the crystalline-electric field (CEF) of the neighboring ions. The total (Hund's rule) angular momentum $\mathbf{j}$ is then conserved, although the CEF break the $(2j+1)$ degeneracy of the ground state. The energy separation between the CEF levels, of the order of 1 meV, can be probed by inelastic neutron scattering.

The history of the observation of crystal-field effects in cubic praseodymium is long[3–5]. Inelastic neutron-scattering experiments show that the ground state is a nonmagnetic doublet of $\Gamma_3$ symmetry and reveal an excited $\Gamma_4$ triplet as part of the $j=4$ multiplet.[3–5] At low temperatures one might thus expect no magnetic ordering. $\mathrm{PrAl_2}$ nevertheless undergoes a transition from a paramagnetic phase to a ferromagnetic one as the temperature is reduced below 34 K,[6] a clear indication that the Hund's rule magnetic moments interact. Other cubic-symmetry Praseodymium compounds also have ferromagnetic ground states.

Both the CEF and the ion-ion magnetic interaction are, therefore, important ingredients of the low-temperature physics of such compounds. This paper analyzes a simple model giving attention to the competition between the nonmagnetic character of the $\Gamma_3$ ground state and the intersite magnetic coupling. We find a rich mean-field phase diagram displaying first- and second-order phase-transition lines, separated by a tricritical point. This feature was found in hexagonal compounds by Libero and Cox.[7] More recently, Ranke *et al.*[8] reported a tricritical point in a cubic compound. This analysis, however, is based on a Landau expansion and hence only qualitatively valid in the first-order transition. Our work, by contrast, deals with the full expression for the free energy and is uniformly accurate in the entire phase diagram. Leaving aside $\mathrm{PrMg_2}$, a compound dominated by quadrupolar intersite interactions for which the model is inappropriate, we are able to predict the order of the phase transition of experimentally studied cubic symmetry Pr systems.

The paper is structured as follows. Section II presents our model and the mean-field approximation upon which we base its analysis. Section III then determines the temperature dependence of the order parameter and the stability of the resulting solutions is analyzed. Section IV recapitulates our conclusions.

## II. MODEL

Our model combines a crystalline electric field with an intersite coupling between the Hund's rule magnetic moments. The cubic symmetry of the former defines our unperturbed Hamiltonian:[9]

$$H_{CEF}=\sum_i \{B_4^0(O_4^0+5O_4^4)+B_6^0(O_6^0-21O_6^4)\}_i, \qquad (1)$$

where $B_4^0$ and $B_6^0$ are crystal-field parameters and the $O_m^n$ are the Stevens operator equivalents[10] evaluated at the site *i*, as indicated by the index of the curly bracket.

The coupling between magnetic moments is mediated by the conduction electrons, an instance of the Ruderman-Kittel-Kasuya-Yosida mechanism,[11] and can hence be represented by a Heisenberg exchange Hamiltonian[3,12]

$$H_{ex}=-J_{ex}\sum_{\langle i,j\rangle}\vec{M}_i\cdot\vec{M}_j, \qquad (2)$$

where $\vec{M}_i$ is the magnetic moment operator at site *i*. We treat $H_{ex}$ as a perturbation that, added to the CEF term, defines our model Hamiltonian $H=H_{CEF}+H_{ex}$.

The unperturbed Hamiltonian is easily diagonalized. The cubic symmetry of the CEF breaks the degeneracy of the $j=4$ total angular momentum manifold into four irreducible representations: the $\Gamma_1$ singlet, the $\Gamma_3$ doublet, and the $\Gamma_4$ and $\Gamma_5$ triplets. Since each representation appears only once in this list,[9,13] the eigenvectors of $H_{CEF}$ cannot depend on the coefficients $B_4^0$ or $B_6^0$. We can therefore set either one equal to zero to obtain the $\beta$th eigenvector of the $\alpha$th irreducible representation $|\Gamma_{\alpha,\beta}\rangle$:[9]

$$|\Gamma_{3,1}\rangle=-\sqrt{\frac{5}{12}}|0\rangle+\sqrt{\frac{7}{24}}(|4\rangle+|-4\rangle), \qquad (3)$$

$$|\Gamma_{3,2}\rangle=\frac{1}{\sqrt{2}}(|2\rangle+|-2\rangle),$$

$$|\Gamma_{4,1}\rangle=\frac{1}{\sqrt{8}}(|3\rangle+\sqrt{7}|-1\rangle),$$

$$|\Gamma_{4,2}\rangle=\frac{1}{\sqrt{8}}(|-3\rangle+\sqrt{7}|1\rangle),$$

$$|\Gamma_{4,3}\rangle=\frac{1}{\sqrt{2}}(|4\rangle-|-4\rangle),$$

$$|\Gamma_{1,1}\rangle=\sqrt{\frac{7}{12}}|0\rangle+\sqrt{\frac{5}{24}}(|4\rangle+|-4\rangle),$$

$$|\Gamma_{5,1}\rangle=\frac{1}{\sqrt{8}}(\sqrt{7}|3\rangle-|-1\rangle),$$

$$|\Gamma_{5,2}\rangle=\frac{1}{\sqrt{8}}(\sqrt{7}|-3\rangle-|1\rangle),$$

$$|\Gamma_{5,3}\rangle=\frac{1}{\sqrt{2}}(|2\rangle-|-2\rangle).$$

The experimental data for $\mathrm{PrAl_2}$ suggest that the $\Gamma_3$ doublet be the ground state.[3,12] At low temperatures, it suffices to keep only the first excited state, the $\Gamma_4$ triplet,[3,12] with energy $\Delta=27.4\,\mathrm{K}$. Inclusion of the next state, the $\Gamma_1$ singlet at 65.8 K, changes the order parameter at 30 K by less than 0.5%.[12] Also for $\mathrm{PrRu_2}$ and $\mathrm{PrRh_2}$ it is sufficient to keep only the ground and first-excited states.[14] In this approximation, since the eigenvectors do not depend on the crystal-field parameters $B_2^0$ and $B_6^0$, only the energy $\Delta$ distinguishes a $j=4$ compound from the other two.

### A. Mean-field Hamiltonian

Even with all states above energy $\Delta$ neglected, the exchange interaction $H_{ex}$ makes it very difficult to diagonalize the Hamiltonian $H$. Previous works[3,4,12] have shown that the mean-field approximation describes well the temperature dependence of the magnetic order parameter, specific heat, and resistivity. To implement this approximation, at the Hamiltonian level, we first rewrite the magnetizations on the right-hand side of Eq. (2) as sums of their mean values and deviations:

$$H_{ex}=-J_{ex}\sum_{\langle i,j\rangle}(\vec{\overline{M}}+\Delta\vec{M}_i)\cdot(\vec{\overline{M}}+\Delta\vec{M}_j), \tag{4}$$

where $\Delta\vec{M}_i=\vec{M}_i-\vec{\overline{M}}$.

We next neglect the second-order term $\Delta\vec{M}_i\cdot\Delta\vec{M}_j$ on the right-hand side to obtain the single-particle Hamiltonian

$$H_{ex}=-12J_{ex}\overline{M}\sum_i(2g\mu_B j_{zi}-\overline{M}). \tag{5}$$

Here, we have taken advantage of the cubic symmetry of the crystal, which imposes magnetic ordering along the principal axis $\hat{z}$.

On the basis of the vectors $|\Gamma_{\alpha,\beta}\rangle$, defined in Eq. (3), the diagonalization of $H$ is straightforward. The following eigenvectors $|E_n\rangle$ and eigenvalues $E_n$ (expressed in units of $\Delta$) result:

$$E_0=A+bBx,$$

$$|E_0\rangle=[|\Gamma_{3,1}\rangle+x|\Gamma_{4,3}\rangle]/\sqrt{1+x^2},$$

$$E_1=A,$$

$$|E_1\rangle=|\Gamma_{3,2}\rangle,$$

$$E_2=A+1+B/2,$$

$$|E_2\rangle=|\Gamma_{4,2}\rangle,$$

$$E_3=A+1-B/2,$$

$$|E_3\rangle=|\Gamma_{4,1}\rangle,$$

$$E_4=A-bBx,$$

$$|E_4\rangle=[x|\Gamma_{3,1}\rangle-|\Gamma_{4,3}\rangle]/\sqrt{1+x^2}, \tag{6}$$

where $b=2\sqrt{7/3}$. With the shorthands $\overline{m}\equiv\overline{M}/(g\mu_B)$ and $\eta=48b^2(g\mu_B)^2J_{ex}/\Delta$, the constants $A$, $B$, and $C$ are given by

$$A=\eta\overline{m}^2/(4b^2) \tag{7}$$

and

$$B=-\eta\overline{m}/(2b^2), \tag{8}$$

while $C=\sqrt{1+4(bB)^2}$ and the mixing coefficient $x$ is given by

$$x=(1-C)/(2bB). \tag{9}$$

At each temperature, the magnetization $\overline{M}$ must be computed self-consistently, as now described.

### B. The order parameter

The dimensionless magnetization $\overline{m}$, a convenient order parameter, can be extracted from the partition function $Z(\overline{m},t)=\mathrm{Tr}\,e^{-\beta H}$. In practice, it is easier to compute the thermal average

$$\overline{m}=\langle j_z\rangle=\mathrm{Tr}(j_z e^{-\beta H})/Z, \tag{10}$$

where $\beta\equiv\Delta/k_BT\equiv 1/t$ defines the reduced temperature $t$.

From Eq. (6) it is a simple matter to compute the traces on the right-hand side of Eq. (10). This yields

$$\overline{m}(t)=\frac{\dfrac{-4b^2B}{C}e^{\beta/2}\sinh\left(\dfrac{\beta C}{2}\right)-\sinh\left(\dfrac{\beta B}{2}\right)}{e^{\beta}+2e^{\beta/2}\cosh\left(\dfrac{\beta C}{2}\right)+2\cosh\left(\dfrac{\beta B}{2}\right)}. \tag{11}$$

At zero temperature, Eqs. (7) and (8) then imply that

$$\overline{m}_0=b\,\frac{(\eta^2-1)^{1/2}}{\eta}. \tag{12}$$

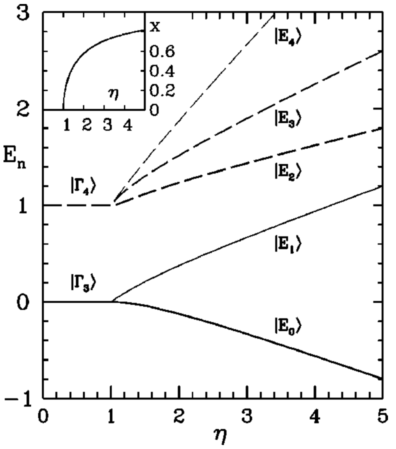

FIG. 1. Energy levels $E_n$, Eq. (6), as functions of the dimensionless coupling $\eta$, at zero temperature. For $\eta\leqslant 1$ the ground state is the $|\Gamma_3\rangle$ doublet and the excited states is the $|\Gamma_4\rangle$ triplet. For $\eta>1$ the ground state is always $|E_0\rangle$, which is a mixing of the states $|\Gamma_{3,1}\rangle$ and $|\Gamma_{4,3}\rangle$. The inset shows the dependence of the mixing coefficient $x=(1-C)/2bB$ on $\eta$ [see Eqs. (6)-(9)].

We can now substitute the zero-temperature dimensionless magnetization $\overline{m}_0$ on the right-hand side of Eq. (6) to obtain the energy levels $E_n$ at $T=0$ as functions of the coupling $\eta$. Illustrative results appear in Fig. 1. For $\eta\leqslant 1$, the order parameter $\overline{m}$ vanishes, even at zero temperature. As the inset shows, for such small values of $\eta$, the mixing coefficient $x$ also vanishes, so that the states $|\Gamma_{3,1}\rangle$ and $|\Gamma_{3,2}\rangle$ become degenerate in the ground state, as if there were no exchange.

For $t=0$ and $\eta>1$, the ground state is always $|E_0\rangle$, defined in Eq. (6). The mixing coefficient no longer vanishes, $x=\sqrt{(\eta-1)/(\eta+1)}$, and approaches unity for $\eta\to\infty$.

At nonzero temperatures, the nonmagnetic first excited state contributes to the partition function and reduces the magnetization. This in turn reduces the mixing coefficient, so that for given $\eta$, the ground state $|E_0\rangle$ has a larger projection on $|\Gamma_{3,1}\rangle$ than at zero temperature. This qualitative picture is unfortunately insufficient to describe the relatively complex phase diagram that arises from the interplay between magnetization and level structure. In Sec. III, we therefore turn to a quantitative analysis of Eq. (11).

## III. RESULTS

Numerically, it is straightforward to solve Eq. (11) for the order parameter $\overline{m}(t)$. To study the stability of the solutions at each temperature, for each coupling $\eta$, it is convenient to measure the free-energy from the zero-magnetization free-energy. We thus define the dimensionless free energy $f(\overline{m},t)=t[\ln Z(0,t)-\ln Z(\overline{m},t)]$. To compute the partition functions $Z$, one must evaluate traces involving the energies in Eq. (6). This immediately leads to

$$f(\overline{m},t)=\frac{-1}{\beta}\ln\left[\frac{e^{\beta}+2e^{\beta/2}\cosh\left(\frac{\beta C}{2}\right)+2\cosh\left(\frac{\beta B}{2}\right)}{(3+2e^{\beta})\,e^{\beta A}}\right]. \tag{13}$$

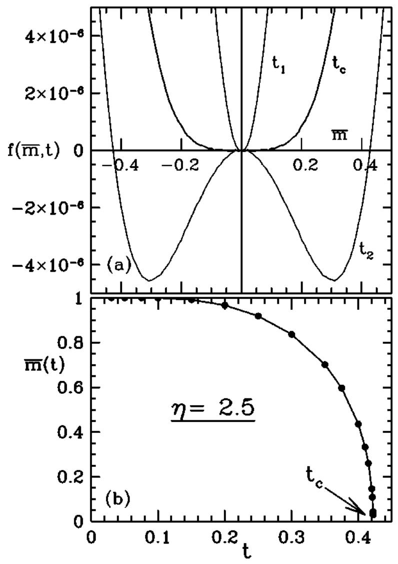

FIG. 2. (a) shows the relative free energy in units of $\Delta$, as function of the order parameter $\overline{m}=\overline{M}/(g\mu_B)$, for the dimensionless coupling $\eta=2.5$ and three values of the reduced temperature $t\equiv k_BT/\Delta$. The critical temperature, where $f(\overline{m},t)$ changes its curvature at $\overline{m}=0$, is $t_c=0.42218$. For $t>t_c$, like $t_1=0.430$, the only minimum of $f(\overline{m},t)$ is at $\overline{m}=0$. For $t<t_c$, like $t_2=0.421$, there is a stable nonzero magnetization corresponding to the minimum of $f(\overline{m},t)$. (b) shows the temperature dependence of $\overline{m}(t)$ normalized by their value at zero temperature; $\overline{m}(t)$ goes continuously to zero at the critical temperature $t_c$, characterizing a second-order phase transition.

Figure 2(a) shows this dimensionless free-energy as a function of the order parameter $\overline{m}$, for the coupling $\eta=2.5$. For the same coupling, the temperature dependence of $\overline{m}(t)$ appears in Fig. 2(b). The continuous evolution of the free-energy minimum as a function of temperature (or what is the same, the behavior of $\overline{m}$ near the critical temperature $t_c=0.422\,18$), indicates that the transition is of second order. The temperature dependence of the order parameter near $t_c$ is well described by $\overline{m}\sim(t_c-t)^{\beta_m}$, with the usual mean-field exponent $\beta_m=1/2$.

The coupling $\eta=2$ yields a free energy with richer temperature dependence. Figure 3(a) displays absolute maxima, absolute minima, and local minima, corresponding to unstable, stable, and metastable solutions for the order parameter, respectively. Two stable degenerate solutions define the critical temperature $t_c=0.2224$, one associated with $\overline{m}=0$, the other with $\overline{m}\neq 0$. Since the former evolves into the absolute minimum for $t>t_c$, while the latter becomes the minimum for $t<t_c$, this degeneracy signals a first-order phase transition. The resulting discontinuity in the magnetization at $t=t_c$ is shown by the filled circles in Fig. 3(b). Thermal hysteresis appears in the range $t_c<t<t_2\equiv 0.2280$.

The computation of the critical temperature $t_c$ for various couplings $\eta$ leads to the phase diagram in Fig. 4. Ferromagnetic ordering appears only for $\eta>1$. The lines of first-order transitions (●) and of second-order ones (○) are separated by a tricritical point at $\eta_{tp}=2.225\pm0.005$, and $t_{tp}=0.322\pm0.002$. The continous line through the open circles is the

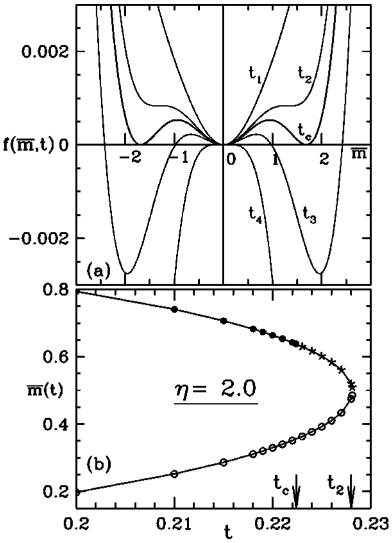

FIG. 3. Same quantities as in Fig. 2, but now with $\eta=2.0$. At high temperature, like $t_1=0.250$, the only minimum of $f(\overline{m},t)$, which is therefore necessarily stable, is at $\overline{m}=0$. Below $t_2=0.228\,13$, a metastable minimum and an unstable maximum appear; $\overline{m}=0$ remains the only stable solution. At the critical temperature $t_c=0.2224$, that metastable solution degenerates with the stable $\overline{m}=0$ and also becomes stable. Below $t_c$, as $t_3=0.21$, we still have the unstable maximum, the stable nonzero magnetization, but now, $\overline{m}=0$ is an unstable minimum. At very low $t$, like $t_4$, $f(\overline{m},t)$ changes its curvature at $\overline{m}=0$, which becomes an unstable maximum; the metastable solution disappears and we have a stable nonzero magnetization (not in the scale). All that signals a first-order transition at $t_c$. (b) shows the temperature dependence of $\overline{m}(t)$, for the stable (●), metastable (★), and unstable (○) solutions. This last vanishes continuously at very low temperature.

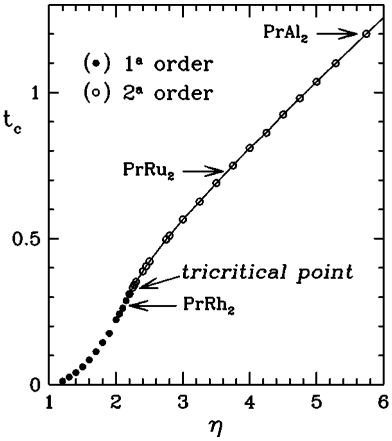

FIG. 4. Phase diagram showing the dependence of the critical temperature $t_c$ on the dimensionless coupling $\eta$. The points are the stable numerical-solutions of Eq. (11). The line of first-order transitions (●) is separated from the one of second-order transitions (○) by the tricritical point at coordinates ($\eta_{tp}=2.225\pm0.005$,$t_{tp}=0.322\pm0.002$). The value $\eta=1$ is the minimum coupling to obtain ferromagnetic ordering. The continuous line is the function given by Eq. (14). The horizontal arrows indicate the position in the critical lines of some cubic Pr compounds with $|\Gamma_3\rangle$-$|\Gamma_4\rangle$ level structure, according to their experimental value of $t_c$ (see Table I).

TABLE I. Dimensionless coupling $\eta$ and Landé factors $g$ calculated from the experimental values of the zero-temperature magnetization $M/\mu_B$ and critical temperature $t_c$.

| Compound | $M/\mu_B$ | $t_c$ | $\eta$ | $g$ |
|---|---|---|---|---|
| $PrAl_2$ | 2.88 | 1.20 | 5.7 | 0.96 |
| $PrRu_2$ | 1.73 | 0.73 | 3.6 | 0.59 |
| $PrRh_2$ | 1.15 | 0.27 | 2.12 | 0.43 |

analytical solution of Eq. (11) in the limit $\overline{m}(t\rightarrow t_c)\rightarrow0$, which defines a second-order transition at $t_c$:[15]

$$\eta=\frac{4\cosh(\beta_c/2)+\exp(-\beta_c/2)}{2\sinh(\beta_c/2)+\beta_c/(4b^2)\exp(-\beta_c/2)}. \tag{14}$$

The three horizontal arrows in the diagram indicate the points along the line corresponding to the critical temperatures of $PrAl_2$, $PrRu_2$, and $PrRh_2$, respectively.[14] From this construction, one expects the first two to undergo second-order transitions and the third to undergo a first-order transition; this agrees with experiment. One might be tempted to add a fourth extensively studied cubic compound, $PrMg_2$, to the diagram. In this case, however, our model is inadequate, since quadrupolar pair interactions are important.[16,17]

It has been shown that doping of $PrAl_2$ with La or Y can bring the critical temperature down by a factor larger than two.[18] If further reduction can be achieved, our diagram would predict a first-order transition below $t_c=0.322$. For $PrRh_2$, which is a lot closer to the tricritical point, any disturbance, such as stoichiometrical changes, can drive the transition through the tricritical point. Experimental work with these two compounds would therefore be able to test the accuracy of our findings.

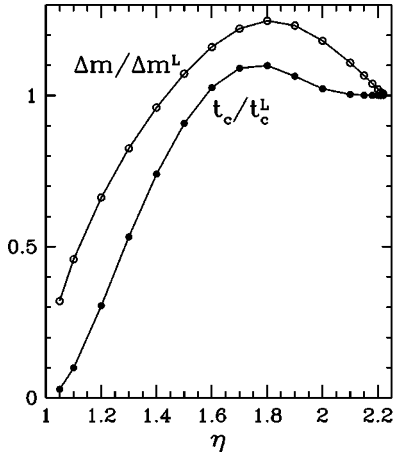

FIG. 5. Critical temperature $t_c$, and magnetization discontinuity $\Delta m$ at $t_c$, obtained from our exact-mean-field calculation divided respectively by $t_c^L$, and the corresponding $\Delta m^L$, obtained from the Landau expansion of the free-energy in powers of the order parameter $\overline{m}$. The ratios show nonuniform and substantial deviations from unity for coupling $\eta$ in the interval $1<\eta<\eta_{tp}=0.2225$, which correspond to first-order transitions in our phase diagram.

The construction in Fig. 4 also determines the Landé factors, $g$, for the three praseodymium compounds. For each compound, given the critical temperature,[14] we read the intersite coupling $\eta$ off the abscissa in the figure. We then plug $\eta$ in Eq. (12) to calculate $\overline{m}_0 \equiv M/g\mu_B$, where $M$ is the zero-temperature magnetization, which has been determined experimentally.[14] The resulting Landé factors, listed in Table I, are considerably lower than the Hund's rule value of 1.25. For $PrAl_2$ and $PrRu_2$, this procedure yields results in agreement with those found by Ranke *et al.*[19] For $PrRh_2$, however, our result, extracted from an analysis attentive to the order of the transition, seems more reliable than the one in Ref. 19.

Finally, we turn to a comparison between our analysis and an alternative procedure, often adopted in the literature,[8,20] which consists of expanding the free energy in powers of the order parameter and retaining only the three leading terms in the expansion. This Landau expansion is convenient, for it leads to simple expressions relating the critical temperature and the magnetization discontinuity at the critical temperature to the expansion coefficients. As Fig. 5 shows, however, in the first-order region of the phase diagram ($\eta < \eta_{tp} = 2.225$), it leads to substantial deviations between the approximate critical temperature and magnetization discontinuity ($t_c^L$ and $\Delta m^L$, respectively) and our exact–mean-field values ($\Delta m$ and $t_c$).

## IV. SUMMARY

In agreement with Ranke *et al.*,[8] we have found a tricritical point in the phase diagram of Praseodymium compounds. The essential features of the model are found in a number of such compounds: a Heisenberg Hamiltonian with cubic symmetry, a nonmagnetic $\Gamma_3$-doublet ionic ground state followed by a $\Gamma_4$-triplet excited state and low temperatures. Our mean-field treatment is expected to be valid but in the vicinity of the critical temperature and in contrast to that found in a recent publication,[8] involves no other approximation. Although additional theoretical investigations are necessary to encompass other systems, such as those significantly affected by quadrupolar interactions ($PrMg_2$,[7,14,17,21–23] for instance), and to study the (admittedly remote) possibility that the magnetic Pr instability be related to the supression of superconductivity in Pr-BaCuO materials,[24,25] our results call for renewed experimental work to locate the tricritical point.

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