

Hyperfine coupling in singlet ground state magnets

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The influence of hyperfine coupling to nuclear spins and of their quadrupolar splitting on the induced moment order in singlet ground state magnets is investigated. The latter are found among non-Kramers f electron compounds. Without coupling to the nuclear spins, these magnets have a quantum critical point (QCP) separating the paramagnetic and induced moment regimes. The hyperfine interaction suppresses the QCP and leads to a gradual crossover between induced electronic and nuclear hyperfine coupling dominated magnetic order. It is shown how the critical temperature depends on the electronic and nuclear control parameters, including the nuclear spin size and its possible nuclear quadrupole splitting. In particular, the dependence of the specific heat on the control parameters and applied field is investigated for ferro- and antiferromagnetic order. It is shown that the three-peak structure in the electronic-induced moment regime gradually changes to a two-peak structure in the hyperfine coupling dominated nuclear moment order regime or for increasing field strength. Most importantly, the possibility of a reentrance behavior of magnetic order or likewise nonmonotonic critical fields due to hyperfine coupling influence is demonstrated. Finally, the systematic evolution of the phase diagram under the influence of nuclear quadrupole coupling is clarified.

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I. INTRODUCTION

The common picture of semiclassical magnetism involves ions with a degenerate spin or pseudospin ground state which carry free magnetic moments in the paramagnetic state. They then order spontaneously due to intersite interactions at the magnetic transition temperature [1]. The size of the ordered saturation moment will be reduced from the classical value by the effect of quantum fluctuations and possibly by geometric or interaction frustration [2]. This simple picture is applicable to numerous compounds with transition elements, in particular the $4f$ -based materials. For these, the presence of the crystalline electric field (CEF) plays an essential role. For half-integer total angular momentum J of the $4f$ ions, the ground state always has Kramers degeneracy, implying the picture of semiclassical order may be used, except in the quasi-one-dimensional case. But for integer J non-Kramers ions such as Pr, Tm, and Tb, a distinct possibility arises because the CEF ground state may be a singlet $|0\rangle$ that is *nonmagnetic*, i.e., $\langle 0|\mathbf{J}|0\rangle = 0$, preventing the application of the quasiclassical theory of magnetic order. However, if there is a close-by excited state, e.g., another nonmagnetic singlet $|1\rangle$, the two states can be connected by a finite nondiagonal matrix element $m_s = \langle 0|J_z|1\rangle$ of a total angular momentum component. Then the intersite exchange of CEF states may spontaneously mix the two states and thus induce a moment in the superposition ground state of $|0\rangle, |1\rangle$ that forms below

the induced moment ordering temperature. In this mechanism, the creation and ordering of moments happens simultaneously at the transition temperature. Literally, this picture of induced moment order applies if the other CEF states happen to lie at much higher energy.

The theory of induced magnetic ordering for singlet ground state systems has been systematically presented in previous publications where more general cases, such as three-singlet models [3] or singlet-doublet models on the honeycomb lattice with nontrivial topology, were investigated [4]. Furthermore, a comparative study of models with singlet, doublet, and triplet excited states has been performed; in particular, the conditions for the existence of critical “soft-mode” magnetic excitons and their connection to induced order were deduced [5]. Finally, the theory of magneto- and barocaloric properties of the singlet-singlet induced magnets and field dependence of critical magnetic excitons was developed in [6]. We note that it is also possible that higher hidden-order (HO) multipole moments such as quadrupoles [7] or hexadecapoles [8] may appear through the induced moment mechanism. However, these previous treatments involved only f -electronic (CEF state) degrees of freedom (“e-dominated region”) and neglected the influence of coupling to nuclear spin states which may become important at very low temperatures compared to the CEF splitting, in particular for control parameters around the quantum critical point (QCP) (cooperative “e/n region”). Indeed, close to the QCP where the induced ground state moment collapses with a square-root singularity [5], the ordering is naturally very sensitive to external perturbations such as magnetic field [6] or pressure [9]. A similar sensitivity is caused by further internal interactions such as the hyperfine coupling to nuclear spins and the splitting of the latter originating from a nuclear quadrupole potential. Further below the QCP (“n-dominated region”), the hyperfine coupling

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becomes the driving force for magnetic ordering. The present work supplements the previous purely electronic CEF singlet-singlet model with the hyperfine and quadrupolar terms of nuclear spins and investigates their influence on the systematic variation of magnetic transition temperature, specific heat, magnetocaloric properties, and phase boundaries with a peculiar type of reentrant behavior. Mostly, these nuclear hyperfine effects have been investigated for $4f$ magnetic compounds with Kramers ground state ions such as Ce or Yb [10–14] or non-Kramers ions with degenerate ground states such as Pr [15] or Ho [16] cage compounds. By applying magnetic fields, the ordered phases of such compounds may be tuned to quantum critical points, which are also influenced by the presence of hyperfine coupling effects [17].

The hyperfine interaction may indeed be strong for some of the non-Kramers ions which have possible CEF singlet ground states, depending on local site symmetry and CEF potential of the $4f$ compound in which they appear. These ions and some of their essentials, including the strength of hyperfine couplings, are listed in Table I. Their importance for compounds where non-Kramers rare-earth (RE) ions have a nonmagnetic singlet ground state has, in fact, been known for some time [9,18–23] and has gained renewed attention more recently [24–26]; in particular, concerning the magnetocaloric properties and anomalous critical field dependence on temperature which may be interpreted as reentrance of multipolar or magnetic order. The latter effect has also been seen in Kramers ion Yb compounds [13] for magnetic order and was attributed to the effect of hyperfine coupling.

In this work, we investigate in detail how the hyperfine coupling and quadrupolar splitting of nuclear spins can be included in the induced moment mechanism for singlet ground state magnets. We reconsider the phase diagram as a function of electronic (CEF) and nuclear control parameters and discuss how the QCP is suppressed by the nuclear interactions and changed into a gradual crossover from CEF exchange dominated induced moment magnetism to hyperfine coupling dominated nuclear magnetism. Particular attention is given to the specific-heat anomalies (peak signatures) that have both electronic CEF and nuclear contributions. It is demonstrated that depending on the location of the control parameters, a triple-peak or double-peak structure of the specific heat is expected as a function of temperature. Furthermore, we discuss the magnetic field dependence of specific heat of singlet ground state ferro- (FM) and antiferromagnetic (AFM) cases with nuclear spins involved and identify their characteristic signatures on both sides of the QCP. Most importantly, we show that for the AFM case, the coupled system of split electronic singlets and nuclear spins leads to a reentrance of magnetic order as function of temperature for high fields. This observation and the equivalent anomalous nonmonotonic critical field dependence on temperature is a direct consequence of the hyperfine coupling. Finally, we show that the crossover between electronic and nuclear ordering regimes is quite sensitive to the sign and size of the nuclear quadrupole interaction.

II. HYPERFINE COUPLING FOR SINGLET GROUND STATE INDUCED MOMENT SYSTEMS

For investigating the effect of nuclear hyperfine coupling on induced electronic magnetic order and the resulting

signatures in the specific heat, we use the most simple and yet illustrative and experimentally relevant singlet-singlet model coupled to nuclear spins (nSSM), consisting of a transverse Ising-type electronic part and, concomitantly, an Ising-type nuclear hyperfine coupling term. It is a nuclear-spin extension of the induced moment model investigated previously [5,6] for various thermodynamic and dynamic properties. The electronic states consist of two slightly split CEF singlets $|0\rangle$ and $|1\rangle$ at energies $\pm\Delta/2$, respectively, where Δ is the splitting energy. They may originate as low-lying states for non-Kramers ions with total angular momentum $J = 4, 6$ which are split off from the group of higher-lying states by a suitable crystalline electric field. As an example, we can have such non-Kramers quasidoublet in a uniaxial CEF (e.g., D_{4h} symmetry) for total angular momentum $J = 4$. Then the SSM corresponding to a D_{4h} representation may be given in terms of free ion states $|J, M\rangle \equiv |M\rangle$ ($|M| \leq 4$) by

$$\begin{aligned} |0\rangle &= \cos\alpha|0\rangle + \sin\alpha\frac{1}{\sqrt{2}}(|+4\rangle + |-4\rangle) \quad (\Gamma_1^{(1)}), \\ |1\rangle &= \frac{1}{\sqrt{2}}(|+4\rangle - |-4\rangle) \quad (\Gamma_2). \end{aligned} \quad (1)$$

This Ising-type SSM is relevant for Pr compounds [5,9] with uniaxial symmetry and has also been applied to U compounds [27–29]. The mixing angle α is determined by the CEF parameters. The Ising moment operator $J_z = m_s S_x$ in pseudospin representation within this subspace where $m_s = \langle 0|J_z|1\rangle = 8\sin\alpha$ is then given by

$$J_z = \frac{m_s}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = m_s S_x, \quad (2)$$

where $\mathbf{J}$ operators refer to the free $|JM\rangle$ states and $\mathbf{S}$ are the pseudospin operators in the reduced subspace of CEF singlet states. We note that a singlet-singlet level scheme in a uniaxial symmetry is not able to support an xy -type SSM. An inspection of the point-group multiplication tables leads to the conclusion that this is forbidden for any symmetry [5].

The nuclear spin states $|II_z\rangle \equiv |I_z\rangle$ of the magnetic ion with spin size I form a $(2I + 1)$ -fold degenerate multiplet. It will be split in the magnetically ordered phase due to the action of a molecular field mediated by the hyperfine coupling with strength A in Table I, here assumed to be positive. Later, we also include possible single-site nuclear quadrupole terms which will also split the nuclear multiplet. We do not consider the effect of long-range nuclear dipole interactions.

The nuclear extended nSSM in pseudospin representation is then defined by the Hamiltonian

$$\begin{aligned} H &= \Delta \sum_i S_{zi} - m_s^2 I_0 \frac{1}{2} \sum_{\langle ij \rangle} S_{xi} S_{xj} \\ &\quad + A \sum_i S_{xi} I_{zi} - m_s h \sum_i S_{xi}, \end{aligned} \quad (3)$$

where the first term is the CEF splitting, the second one is the effective nearest neighbor (NN) intersite exchange of $4f$ pseudospins, and the third one is the hyperfine coupling which is also necessarily of Ising type since the $S_{x,y}$ components are absent in the two-singlet space of Eq. (1). The last term is the Zeeman energy of the electronic states in external field

TABLE I. Magnetic characteristic quantities of $4f$ shell for non-Kramers rare-earth elements with J denoting ground state total angular momentum, g_J the associated Landé factor, and $\mu_{\text{eff}} = g_J \sqrt{J(J+1)}$ the effective moment. These stable rare-earth isotopes have 100% abundance ratio with resulting unique nuclear ground state spin I and nuclear moment μ (with $\mu_n = e\hbar/2M_p c$ defining the nuclear magneton; M_p = proton mass) and hyperfine coupling constant A .

RE ³⁺ ion	¹⁴¹ Pr	¹⁵⁹ Tb	¹⁶⁹ Tm
J	4	6	6
g_J	$\frac{4}{5}$	$\frac{3}{2}$	$\frac{7}{6}$
$\mu_{\text{eff}} (\mu_B)$	3.58	9.72	7.56
I	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$
$\mu (\mu_n)$	3.92	1.52	-0.20
A (mK)	52.5 [9]	71.9 [31]	-18 [32]

H with $h = g_J \mu_B H$. The direct Zeeman term of nuclear spins is not included due to the much smaller nuclear magneton, $\mu_n \ll \mu_B$. The pseudospins and nuclear spins are, for simplicity, placed on a three-dimensional (3D) simple cubic lattice; then the Fourier transform of the intersite exchange coupling (second term) is given by $I_{\mathbf{q}} = z I_0 \gamma_{\mathbf{q}}$, where $z = 6$ is the coordination number and $\gamma_{\mathbf{q}} = (2/z) \sum_i \cos q_i$ ($i = x, y, z$) is the structure factor (lattice constant $a \equiv 1$). This type of NN exchange leads either to FM [$\mathbf{q} = (0, 0, 0)$, $I_0 > 0$] or AFM [$\mathbf{q} = (\pi, \pi, \pi)$, $I_0 < 0$] order, in which cases only the effective exchange $I_e = z|I_0|$ occurs in the thermodynamic and static properties. Note that we use the convention I_0 being positive or negative for FM or AFM exchange, respectively, while $A > 0$ means the electronic and nuclear spins are oriented oppositely.

In the molecular field approximation (MFA), we then have $H_{mf} = \sum_{i\lambda} h_{mf}^\lambda(i)$ with

$$\begin{aligned} h_{mf}^\lambda(i) &= \hat{h}_{mf}^\lambda(i) + \frac{1}{2} \sigma m_s I_e \langle S_x \rangle_{\bar{\lambda}} \langle S_x \rangle_{\bar{\lambda}} - A m_s \langle S_x \rangle_{\lambda} \langle I_z \rangle_{\lambda}, \\ \hat{h}_{mf}^\lambda(i) &= \Delta S_z(i) - m_s h_e^\lambda S_x(i) + h_n^\lambda I_z(i). \end{aligned} \quad (4)$$

Here, $\lambda = A, B$ ($\bar{\lambda} = B, A$) denotes the sublattices in the case of AFM order with $\langle S_x \rangle_{\bar{\lambda}} = -\langle S_x \rangle_{\lambda}$, and likewise $\langle I_z \rangle_{\bar{\lambda}} = -\langle I_z \rangle_{\lambda}$ for zero field. The sublattice index is to be suppressed for FM order. The electronic and nuclear molecular fields (MFs) are given by

$$\begin{aligned} h_e^\lambda &= h + \sigma m_s I_e \langle S_x \rangle_{\bar{\lambda}} - A \langle I_z \rangle_{\lambda}, \\ h_n^\lambda &= m_s A \langle S_x \rangle_{\lambda}, \end{aligned} \quad (5)$$

where $\sigma = \pm 1$ for FM and AFM, respectively. We note that the nuclear Zeeman term in Eq. (3) which would give a direct contribution $g_n \mu_n H$ to h_n^λ above is neglected [30], assuming $g_n \mu_n H \ll m_s A \langle S_x \rangle_{\lambda}$ in the present context. Because the hyperfine term does not mix nuclear spin states in this Ising-type model, the Hamiltonian will factorize for each $\tau = I_z$ subspace ($|\tau| \leq I$) and then we obtain the coupled electronic-nuclear MF energy levels given by

$$E_{\lambda s}^\tau = \frac{\Delta}{2} [s(1 + \gamma_{e\lambda}^2)^{\frac{1}{2}} + 2\tau \gamma'_{n\lambda}], \quad (6)$$

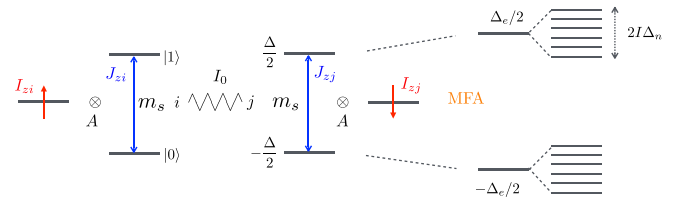


FIG. 1. Schematic presentation of the singlet-singlet electronic ($J_z = m_s S_x$) and nuclear spin (I_z) interaction model. Their on-site hyperfine interaction A and intersite electronic exchange I_0 lead to (FM or AFM) order causing the shifting and splitting of molecular field levels on the right side.

where we defined the dimensionless MFs as $\gamma'_{e\lambda} = m_s h_e^\lambda / \Delta \equiv \hat{\Delta}_{e\lambda}$ and $\gamma'_{n\lambda} = h_n^\lambda / \Delta \equiv \hat{\Delta}_{n\lambda}$. Furthermore, $s = \pm 1$ refers to the two MF shifted singlet states originating from original $|1\rangle$, $|0\rangle$ states, respectively. The second term describes the splitting of nuclear spin states by the MF. The eigenstates are still product states of electronic and nuclear states and therefore

$$\begin{aligned} |E_{\lambda+}^\tau\rangle &= \cos(\theta_\lambda) |1\tau\rangle - \sin(\theta_\lambda) |0\tau\rangle, \\ |E_{\lambda-}^\tau\rangle &= \sin(\theta_\lambda) |1\tau\rangle + \cos(\theta_\lambda) |0\tau\rangle, \end{aligned} \quad (7)$$

with the mixing angle given by $\tan 2\theta_\lambda = \gamma'_{e\lambda}$. The spectrum illustrated in Fig. 1 is highly symmetric, which facilitates further analytical treatment. In the basis of MF eigenstates, the two-singlet pseudospin is represented by

$$S'_x = \frac{1}{2} (1 + \gamma_{e\lambda}^2)^{-\frac{1}{2}} \begin{pmatrix} -\gamma'_{e\lambda} & 1 \\ 1 & \gamma'_{e\lambda} \end{pmatrix}. \quad (8)$$

Since the nuclear spin states are not mixed by the Ising-like hyperfine term, nuclear spin operator I_z is unchanged.

III. THE CRITICAL TEMPERATURE FOR INDUCED ORDER OF ELECTRONIC AND NUCLEAR MOMENTS

Before solving the MF self-consistency equations for the order parameters, we can determine the phase boundary, i.e., the critical temperature $T_m(\xi_e, \xi_n, I)$ as a function of control parameters ξ_e, ξ_n introduced below and nuclear spin size I by starting from the paramagnetic regime. It is obtained from the divergence of the static random phase approximation (RPA) susceptibility at the critical temperature for the zone center or zone boundary wave vectors of the FM or AFM structure, respectively. The static single-ion susceptibility for a multi-level system corresponding to operator $O = J_z (= m_s S_x)$, I_z is generally given by

$$\begin{aligned} \chi_O^O(T, h') &= \sum_{E_\mu \neq E_{\mu'}} |\langle \mu | O | \mu' \rangle|^2 \frac{p_\mu - p_{\mu'}}{E_{\mu'} - E_\mu} \\ &+ \frac{1}{T} \left[\sum_{E_\mu = E_{\mu'}} |\langle \mu | O | \mu' \rangle|^2 p_\mu - \langle O \rangle^2 \right], \end{aligned} \quad (9)$$

where $|\mu\rangle = |s\rangle \otimes |\tau\rangle$ are the paramagnetic states, with $s = 0, 1$ denoting the singlets, $\tau = -I \dots I$ the nuclear spin states, and E_μ, p_μ their energies and thermal populations (see Appendix A), respectively. There is no mixing or splitting of

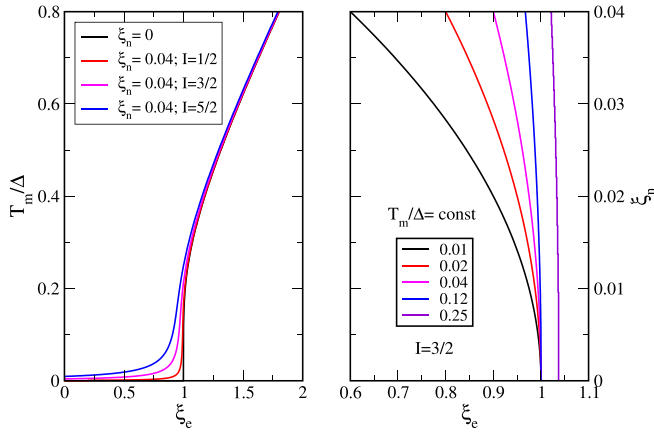


FIG. 2. Left panel: Critical temperature T_m for induced magnetic order (FM or AFM) as a function of electronic ξ_e for fixed nuclear ξ_n and three different sizes of nuclear spin I . The black line is for vanishing ξ_n when induced order appears only above the QCP at $\xi_e = 1$ [Eq. (14)]. For finite ξ_n , T_m is finite for any ξ_e , progressively suppressing the QCP with increasing I . Right panel: Complementary contour plot of $T_m/\Delta = \text{const}$ in the ξ_e - ξ_n plane.

these states in the paramagnetic regime; then the susceptibilities are simply decoupled with

$$\chi_0^J = \frac{m_s^2}{2\Delta} \tanh \frac{\Delta}{2T}, \quad \chi_0^I = \frac{\frac{1}{3}I(I+1)}{T}. \quad (10)$$

The $\mathbf{q}$ -dependent RPA susceptibility corresponding to the Hamiltonian in Eq. (3) is then obtained for both operators as

$$\chi_{\mathbf{q}}^{J,I} = \frac{\chi_0^{J,I}}{1 - \chi_0^J(I_{\mathbf{q}} + A^2\chi_0^I)}, \quad (11)$$

with $I_{\mathbf{q}}$ defined below Eq. (3). The susceptibility now includes the effect of the hyperfine coupling proportional to A . The transition temperature to the induced magnetic order is then given by the condition of vanishing denominator in Eq. (11). This leads to the implicit equation for $T_m(\xi_e, \xi_n, I)$,

$$\left[\xi_e + \frac{1}{3}I(I+1)(2\xi_n)^2 \frac{\Delta}{2T_m} \right] \tanh \left(\frac{\Delta}{2T_m} \right) = 1. \quad (12)$$

Here we introduced the dimensionless electronic and nuclear control parameters,

$$\xi_e = \frac{m_s^2 I_e}{2\Delta}, \quad \xi_n = \frac{m_s A}{2\Delta}, \quad (13)$$

which characterize intersite exchange and hyperfine coupling strength, respectively. For vanishing hyperfine coupling ($\xi_n = 0$), one obtains explicitly the purely electronic-induced moment transition temperature,

$$T_m^0(\xi_e) = \frac{\Delta}{2 \tanh^{-1}(\frac{1}{\xi_e})}. \quad (14)$$

This is shown in Fig. 2 (black line) together with the general numerical solution of Eq. (12) for nonzero hyperfine coupling and it will be further discussed in Sec. VI. Importantly, the QCP at $\xi_e = 1$ for vanishing hyperfine control parameter ξ_n is now replaced by a crossover for finite ξ_n from a high- T_m CEF-induced moment region where $T_m \approx T_m^0$ to a low

$T_m \ll \Delta$ nuclear moment dominated ordering region (see, also, Fig. 2). For $\xi_e \rightarrow 0$, we have the asymptotic form derived from Eq. (12) as $T_m \simeq (2/3)\Delta I(I+1)\xi_n^2(1-\xi_e)^{-1}$.

From the derivations in Sec. II, we can now obtain the self-consistent MF equations for electronic and nuclear moments as

$$\begin{aligned} \langle S_x \rangle_\lambda &= \frac{1}{2} \frac{1}{\Delta_e} [m_s h' + 2(\sigma \xi_e \langle S_x \rangle_{\bar{\lambda}} - \xi_n \langle I_z \rangle_\lambda)] \hat{P}_{e\lambda}(T), \\ \langle I_z \rangle_\lambda &= -\frac{1}{2} \hat{P}_{n\lambda}(T; \langle S_x \rangle_\lambda), \end{aligned} \quad (15)$$

with the thermal occupation functions $\hat{P}_{(e,n)\lambda}$ defined by Eq. (A3) in Appendix A. Using Eq. (5), the corresponding molecular fields, normalized to Δ , may be expressed as

$$\begin{aligned} \gamma'_{e\lambda} &= m_s h' + 2(\sigma \xi_e \langle S_x \rangle_{\bar{\lambda}} - \xi_n \langle I_z \rangle_\lambda), \\ \gamma'_{n\lambda} &= 2\xi_n \langle S_x \rangle_\lambda, \end{aligned} \quad (16)$$

where $h' = h/\Delta$ is the dimensionless field strength. With these expressions, the MF singlet splitting and nuclear spin splittings are given by

$$\hat{\Delta}_{e\lambda} = (1 + \gamma_{e\lambda}^{\prime 2})^{\frac{1}{2}}, \quad \hat{\Delta}_{n\lambda} = 2\xi_n \langle S_x \rangle_\lambda = \gamma'_{n\lambda}, \quad (17)$$

respectively, which are again normalized according to $\hat{\Delta}_{e\lambda} = \Delta_{e\lambda}/\Delta$ and $\hat{\Delta}_{n\lambda} = \Delta_{n\lambda}/\Delta$. The former is always positive, while the latter, which is caused by the hyperfine coupling to the induced moment, may have both signs, depending on the sublattice. This allows us to also present the $2 \times (2I+1)$ split energy levels at each sublattice $\lambda = A, B$ in the compact form

$$E_{\lambda s}^\tau = \frac{\Delta}{2} (s \hat{\Delta}_{e\lambda} + 2\tau \hat{\Delta}_{n\lambda}), \quad (18)$$

where the electronic two-singlet and the nuclear indices are $s = \pm$, $\tau = -I \dots I$, respectively.

The coupled MF equations (15) for $\langle S_x \rangle$ and $\langle I_z \rangle$ have to be solved numerically for each nuclear spin size I as a function of control parameters ξ_e and ξ_n characterizing the intersite electronic exchange and the on-site hyperfine coupling.

Examples for the temperature and field evolution of electronic and nuclear order parameters are shown in Figs. 3 and 10. For the FM case, the phase transition turns into a continuous crossover at T_m , while in the AFM case, it persists up to a critical field. The critical field curve $h_{cr}(T)$ is implicitly defined by the vanishing of the staggered moment $M_s = \frac{1}{2}(\langle S_x \rangle_A - \langle S_x \rangle_B)$ via the equation $M_s(h_{cr}, T) = 0$ and likewise this determines the field dependence of $T_m(h)$. The phase boundary is strongly influenced by the action of the hyperfine coupling, as shown in Fig. 9, and its resulting anomalous characteristics will be discussed further in Sec. VI.

At this point, one should reflect to which degree the MFA-RPA treatment of the model gives reasonable and reliable results, assuming we are dealing with a 3D lattice structure (which, as mentioned before, does not appear explicitly). Corrections beyond the MFA would involve the quantum and thermal fluctuations governed by the excitation spectrum of the model. According to the structure of the Hamiltonian in Eq. (3), only the electronic pseudospins have dynamics which lead to magnetic exciton bands that may be considered as dispersive singlet-singlet CEF excitations. Their dispersion, temperature, and field dependence for the various singlet

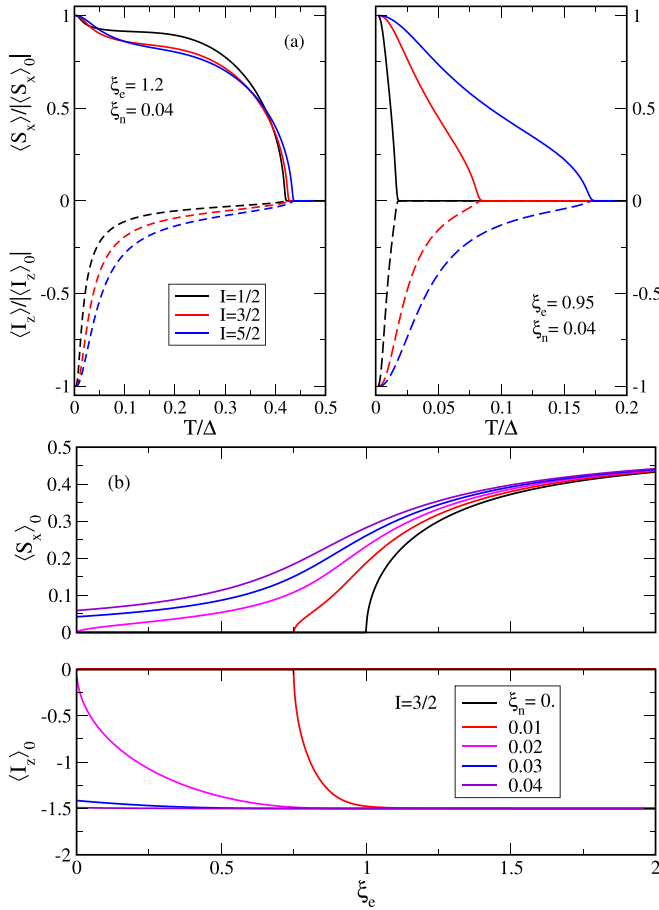


FIG. 3. (a) Dependence of (normalized) electronic and nuclear order parameters on temperature for hyperfine coupling $\xi_n = 0.04$. Left panel: For ξ_e above the QCP $\xi_e^c = 1$ and various I . Differences in T_m for the three cases correspond to Fig. 2 above the QCP. Right panel: For ξ_e below the QCP when order is due to finite ξ_n . Here, $\langle S_x \rangle$, $\langle I_z \rangle$ exhibit similar T dependence in contrast to (a), but T_m now depends strongly on I . (b) Electronic and nuclear saturation moments ($T/\Delta = 0.001$) as a function of control parameters. When $T < T_m(\xi_e, \xi_n)$ (Fig. 2), $\langle S_x \rangle_0$ is finite and $\langle I_z \rangle \simeq -I$. Otherwise, both drop to zero.

ground state models were investigated in detail in [3–6]. It was found that under most circumstances for the AFM case with $\mathbf{Q} = (\pi, \pi, \pi)$ at $T_m(h')$, the spectrum has a finite gap given for both $\lambda = A, B$ by [5]

$$\omega(\mathbf{Q}, T_m(h')) = \omega_0 (\hat{\Delta}_{eT_m}^2 - 1)^{\frac{1}{2}} (1 - \xi_e^{-2} \hat{\Delta}_{eT_m}^2)^{\frac{1}{2}}, \quad (19)$$

with $\omega_0 = \Delta[(\xi_e \Delta)/(2T_m)]^{\frac{1}{2}}$, which is nonvanishing except for the zero field where $\hat{\Delta}_e(T_m) = 0$ and at the critical field when $T_m(h'_c) = 0$, and then $\hat{\Delta}_e(T_m) = \xi_e$. Then the phase boundaries in Fig. 9 might only be affected at the endpoints by fluctuation contributions beyond MFA. One has to keep in mind that on these two points, the soft mode occurs only at the ordering wave vector $\mathbf{Q}$, and then, for the 3D lattice, the momentum region for fluctuation contributions is small and, in particular, will not lead to diverging corrections. However, at zero field, the soft mode occurring at T_m may modify the specific-heat temperature dependence around the transition

temperature. Furthermore, when the excited state is not a singlet but a triplet, the excitations always stay gapped. The same is true for the singlet-singlet model when the contribution of higher-lying states is included in the ordering temperature [5]. Therefore, in any realistic situation, the critical magnetic exciton “soft modes” at the ordering wave vector that give fluctuation corrections to order parameters, phase boundaries, and specific heat will be arrested at a finite frequency gap. In fact, in all of the singlet ground state induced magnets that have been investigated by inelastic neutron scattering, a true soft mode has not been found. In such case, the fluctuations will not qualitatively invalidate the molecular field picture used here, but only lead to quantitative modifications. An actual computation of these modifications would, however, require a different approach beyond the scope of this work by using the Bogoliubov technique to calculate the magnetic exciton dispersion and their interactions [3] to be able to treat their bosonic statistics at low temperatures properly.

Susceptibility in the ordered regime

The electronic and nuclear single-site zero-field ($h=0$) susceptibilities in the ordered phase may also be derived using the transformed pseudospin operator of Eq. (8) and the expression in Eq. (9). We obtain, for the electronic part $\chi_0^J(T) = (\frac{m_e^2}{2\Delta}) \hat{\chi}_0^J(T)$ with [cf. Eq. (17)],

$$\hat{\chi}_0^J(T) = \frac{1}{\hat{\Delta}_e^3} \tanh \frac{\Delta_e}{2T} + \left(1 - \frac{1}{\hat{\Delta}_e^2}\right) \left(\frac{\Delta}{2T}\right) \cosh^{-2} \frac{\Delta_e}{2T}, \quad (20)$$

which now contains a modified van Vleck and a pseudo-Curie term. Note that the latter vanishes for small temperature despite the $(1/T)$ factor due to the other exponential population factor. In the paramagnetic phase, $\Delta_e = \Delta$ and then the expression in Eq. (10) is recovered. The nuclear spin susceptibility is now modified due to the splitting of nuclear spin states and leads to another pseudo-Curie expression $\chi_0^I(T) = (\frac{m_n^2}{\Delta}) \hat{\chi}_0^I(T)$ with

$$\hat{\chi}_0^I(T) = \left(\frac{\Delta}{2T}\right) [\hat{P}_n^C(T) - \langle I_z \rangle^2], \quad (21)$$

where an additional nuclear level population function is defined by

$$\hat{P}_n^C(T) = 2Z_n^{-1} \sum_{\tau=\frac{1}{2}}^I \tau^2 \cosh \left[\left(\frac{\Delta}{2T}\right) 2\tau \hat{\Delta}_n \right]. \quad (22)$$

On approaching $T = 0$, the two terms in Eq. (21) approach I^2 and compensate, leading to exponential suppression of the Curie prefactor $(1/T)$. In the paramagnetic state with $\langle I_z \rangle = 0$ and $\hat{P}_n^C = \frac{1}{3}I(I+1)$, this reduces to Eq. (10).

Using the above results and $I_{\mathbf{q}=\mathbf{Q}} = -I_e$ for the AFM case, the homogeneous electronic RPA susceptibility for the paramagnetic and ordered regime may then be expressed according to Eq. (11) as

$$\chi^J(\mathbf{q}=0) = \frac{(\frac{m_e^2}{2\Delta}) \hat{\chi}_0^J(T)}{1 + [\xi_e - (2\xi_n)^2 \hat{\chi}_0^I(T)] \hat{\chi}_0^J(T)}. \quad (23)$$

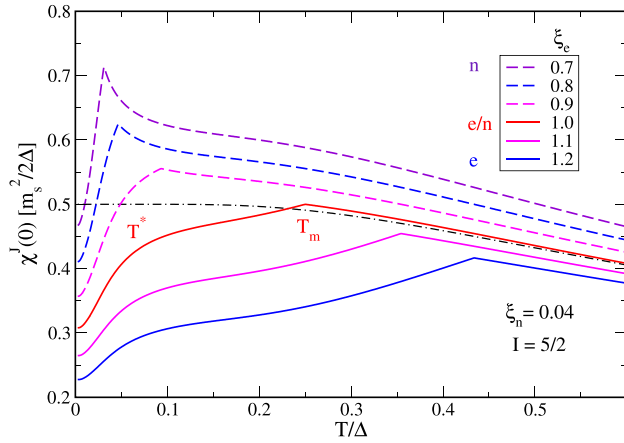


FIG. 4. Homogeneous electronic RPA susceptibility $\chi^J(\mathbf{q} = 0)$ [Eq. (23)] for AFM state for ξ_e below (< 1) and above (> 1) critical value in the n- and e-dominated regimes, respectively. For the latter, T_m (cusp) and $T^* \simeq \xi_n \Delta$ (hump) are separate energy scales that merge below the critical value of ξ_e . The cusp position for ξ_e is tracing the $T_m(\xi_e)$ curve in Fig. 2. Black dashed line is the reference of the paramagnetic ($\xi_e = 1, \xi_n = 0$) state.

The physical electronic susceptibility then has to be multiplied by $(g_J \mu_B)^2$. A similar nuclear RPA susceptibility is obtained by replacing the numerator in the above equation with $(2/\Delta) \hat{\chi}_0^I$. The latter has a physical prefactor $(g_n \mu_n)^2$. Since the nuclear magneton $\mu_n \ll \mu_B$, it gives negligible contribution to the susceptibility. The temperature dependence of the homogeneous susceptibility in Eq. (23) is shown in Fig. 4 and discussed in Sec. VI.

IV. ELECTRONIC AND NUCLEAR PARTS OF THE SPECIFIC HEAT, ENTROPY AND INTERNAL ENERGY

Of major interest is the signature of the electronic and nuclear contributions to the specific heat since caloric experiments are most common in the low-temperature regime in question. We approach this problem by first calculating the thermodynamic potentials such as entropy $S(T)$ and internal energy $U(T)$. The entropy per sublattice site is given in terms of level occupation probabilities $p_{\lambda,s}^\tau(T)$ (Appendix A) as

$$S_\lambda(T) = - \sum_{s\tau} p_{\lambda,s}^\tau \ln p_{\lambda,s}^\tau, \quad (24)$$

which may be separated into electronic and nuclear parts, $S_\lambda = S_{e\lambda} + S_{n\lambda}$ (for noninteger I), according to

$$\begin{aligned} S_{e\lambda} &= -\frac{\Delta}{2T} \hat{\Delta}_{e\lambda} \hat{P}_{e\lambda}(T) + \ln \left\{ 2 \cosh \left[\left(\frac{\Delta}{2T} \right) \hat{\Delta}_{e\lambda} \right] \right\}, \\ S_{n\lambda} &= -\frac{\Delta}{2T} \hat{\Delta}_{n\lambda} \hat{P}_{n\lambda}(T) + \ln \left\{ 2 \sum_{\tau=\frac{1}{2}}^I \cosh \left[\left(\frac{\Delta}{2T} \right) 2\tau \hat{\Delta}_{n\lambda} \right] \right\}. \end{aligned} \quad (25)$$

Note that this expression is invariant against a constant shift of the combined level scheme. The internal energy which is

related by $U_\lambda(T) = TS_\lambda(T) - T \ln Z_\lambda$ is obtained as

$$U_\lambda(T) = -\frac{\Delta}{2} \hat{\Delta}_{e\lambda} \hat{P}_{e\lambda}(T) + \Delta \sigma \xi_e \langle S_x \rangle_\lambda \langle S_x \rangle_{\bar{\lambda}}. \quad (26)$$

Formally, the nuclear part has a similar structure. But, in this case, the first term due to the nuclear spin splitting is exactly compensated by the second constant MF term describing the hyperfine interaction with the electronic moment. However, the nuclear degrees are implicitly incorporated in the electronic splitting, $\hat{\Delta}_{e\lambda}(T)$ and $\langle S_x \rangle_\lambda$. The total entropies and internal energies (per lattice site) are then obtained by averaging over the sublattices A and B in the AFM ($\sigma = -1$) case, while the sublattice index λ may be ignored in the FM case ($\sigma = 1$). Then the specific heat is obtained from the thermodynamical potentials via

$$C_V(T) = \left(\frac{\partial U}{\partial T} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V, \quad (27)$$

by numerical differentiation, which has been checked to lead to identical results for both expressions. In the case of zero hyperfine coupling $\xi_n = 0$, only the electronic singlet degrees contribute and then the specific heat may be derived in closed form from the above equations as [5]

$$\begin{aligned} C_V(T) &= \left(\frac{\Delta_T}{2T} \right)^2 \left(\cosh^2 \frac{\Delta_T}{2T} - \frac{\Delta_0}{2T} \right)^{-1}, \quad T \leq T_m \\ C_V^0(T) &= \left(\frac{\Delta}{2T} \right)^2 \cosh^{-2} \frac{\Delta}{2T}, \quad T > T_m, \end{aligned} \quad (28)$$

for magnetic and paramagnetic phases, respectively, where we used the abbreviations $\Delta_T = \Delta \hat{\Delta}_e(T)$ and $\Delta_0 = \xi_e \Delta$. $C_V^0(T)$ is the paramagnetic background Schottky anomaly which peaks around $T_{\max} = 0.42\Delta$ for the two-singlet system. It is shown as a reference by the dashed line in Fig. 5(a). $C_V(T)$ exhibits the jump at the induced moment transition temperature T_m^0 . Expressions of the jump size at T_m^0 as a function of control parameter ξ_e are given in Ref. [5]. It tends to zero when approaching the QCP from above, i.e., $\xi_e \rightarrow 1 + \delta$; $\delta \ll 1$. The field and temperature dependence of the specific heat in the above general expressions for finite ξ_n in Eqs. (26) and (27) is contained in the excitation energies $\Delta_{e,n}^\lambda$ and the order parameters $\langle S_x \rangle_\lambda, \langle I_z \rangle_\lambda$ obtained from the self-consistent solution of MF equations (15). The (magneto-)caloric properties of the model are presented in Figs. 5, 6, and 8 and are discussed in Sec. VI.

V. INFLUENCE OF NUCLEAR ELECTRIC QUADRUPOLE SPLITTING

In the previous analysis, we have assumed that the nuclear spin states are $(2I + 1)$ -fold degenerate. However, for $I \geq \frac{3}{2}$, an electric field gradient (EFG) at the nuclear site originating from the occupied electronic states and resulting in a quadrupolar potential will lift the degeneracy into pairs of time-reversed states with $I_z = \pm \tau$. It is then to be expected to significantly influence the magnetic transition temperature, in particular around and below the QCP at $\xi_e = 1$ where the hyperfine interaction plays an important role. The change in transition temperature due to the nuclear quadrupole splitting will now be investigated.

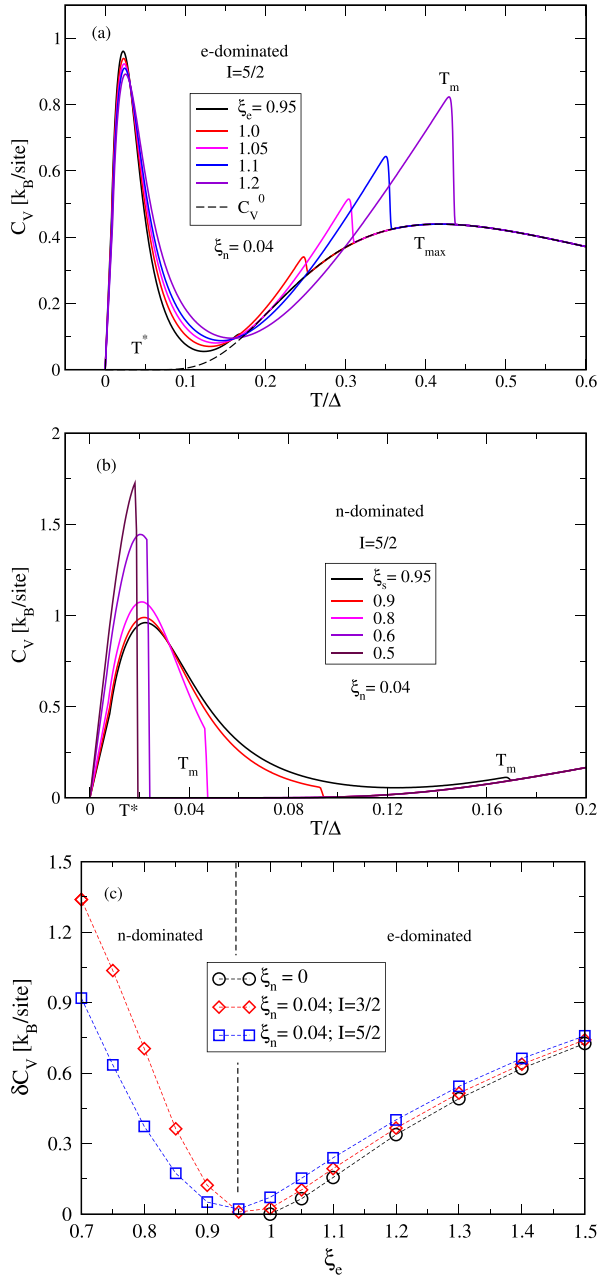


FIG. 5. (a) Specific heat for various sub- and above-critical electronic control parameters ξ_e and $I = \frac{3}{2}$. A three-peak appearance is displayed: (i) broad underlying CEF Schottky peak (dashed line) at $T_{\max}$ due to the CEF splitting, (ii) for $\xi_e > 1$, a superposed induced ordering peak at T_m , and (iii) a low-temperature nuclear specific-heat peak with maximum at $T^* \simeq \xi_n \Delta$ corresponding to nuclear spin splitting appearing below T_m . (b) For subcritical ξ_e but finite ξ_n , the ordering at T_m shows crossover into the region dominated by the hyperfine coupling around T^* (see Fig. 2). (c) Evolution of specific-heat jump $\delta C_V(T_m)$ with nonmonotonic change from e-dominated $\xi_e > 1$ [corresponding to (a)] to nuclear hyperfine n-dominated regime $\xi_e < 1$ [associated with (b)].

The quadrupolar Hamiltonian for nuclear spins reads [33]

$$H_Q^n = \frac{\zeta}{4I(I-1)} \sum_i [3I_z^2(i) - I(I+1)], \quad (29)$$

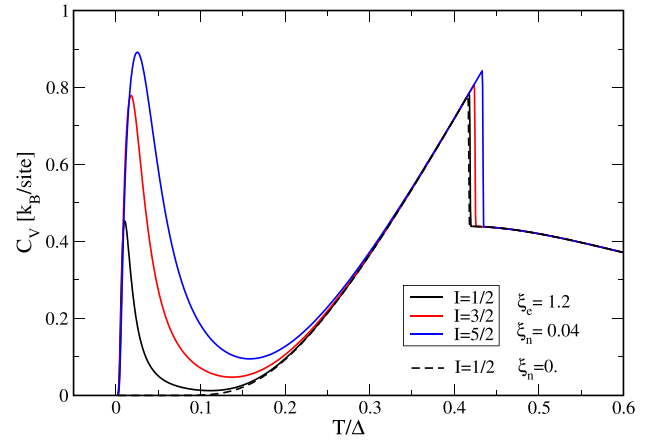


FIG. 6. Specific-heat curves for fixed control parameters ξ_e, ξ_n and various nuclear spin size I which strongly influences the peak height due to the entropy $\sim \ln(2I+1)$ contained in it. The dashed line corresponds to the CEF specific heat for $\xi_n = 0$ [Eq. (28)].

with the quadrupolar coupling constant $\zeta = \frac{e^2 q Q}{h}$, where Q is the nuclear quadrupole moment and $eq = V_{zz}$ is the uniaxial EFG. This already causes a splitting of nuclear spin states in the paramagnetic phase, which is added to the splitting caused by the molecular field in the induced moment phase. Together this leads to multiplet energy levels given by an extension of Eq. (6) as

$$E_{\lambda s}^{\tau} = \frac{\Delta}{2} (s \hat{\Delta}_{e\lambda} + 2\tau \hat{\Delta}_{n\lambda} + \tau^2 \hat{\Delta}_Q), \quad (30)$$

where the last term describes the paramagnetic quadrupolar splitting with $\hat{\Delta}_Q = \Delta_Q/\Delta = 3\zeta/[2I(I-1)\Delta]$ which can have both signs depending on the signs of the EFG, the nuclear quadrupole moment, and I . A constant shift which has no influence on the thermodynamics has been omitted. The splitting will modify the nuclear spin susceptibility. For this purpose, we need to obtain the population factors of the split nuclear levels. They are now given by

$$p_{\lambda}^{\tau} = Z_n^{-1} \exp \left[-\frac{\Delta}{2T} (2\tau \lambda \hat{\Delta}_n + \tau^2 \hat{\Delta}_Q) \right],$$

$$Z_n = 2 \sum_{\tau=1/2}^I \exp \left(-\frac{\Delta}{2T} \tau^2 \hat{\Delta}_Q \right) \cosh \frac{\Delta}{2T} 2\tau \hat{\Delta}_n. \quad (31)$$

The electronic level occupations and partition functions, and therefore the susceptibility $\chi_0^I(T)$, are unchanged because the eigenstates are not modified by the Hamiltonian of Eq. (29). With the above results, we can then obtain the quadrupolar modified nuclear spin susceptibility as

$$\chi_0^I = \frac{\hat{P}_n^Q(T)}{T},$$

$$\hat{P}_n^Q(T) = 2Z_n^{-1} \sum_{\tau=1/2}^I \tau^2 \exp \left(-\frac{\Delta}{2T} \tau^2 \hat{\Delta}_Q \right). \quad (32)$$

It is still of the Curie type due to splitting into nuclear spin doublets; however, the numerator is no longer a Curie constant as in Eq. (10), but a temperature-dependent occupation

function. It is interesting to consider three limiting cases valid for any $I \geq \frac{3}{2}$: (i) For $T \gg |\Delta_Q|$, we have $\hat{P}_n^Q(T) \rightarrow \frac{1}{3}I(I+1)$; (ii) for $T \ll |\Delta_Q|$ and $\Delta_Q > 0$, we obtain $I_{\text{eff}} := \frac{1}{2}\hat{P}_n^Q(T) \rightarrow \frac{1}{3}I_{\text{eff}}(I_{\text{eff}}+1) = \frac{1}{4} < \frac{1}{3}I(I+1)$; and (iii) finally, for $T \ll |\Delta_Q|$ and $\Delta_Q < 0$, we get $\hat{P}_n^Q(T) \rightarrow I^2 > \frac{1}{3}I(I+1)$. This means that depending on the sign of the quadrupolar splitting and its size as compared to the transition temperature, the effective Curie numerator may be smaller or larger than the numerator $\frac{1}{3}I(I+1)$ for the degenerate nuclear spin states. Therefore, a finite Δ_Q may lead to a decrease or increase in the nuclear ordering temperature for a positive or negative sign, respectively.

Inserting χ_0^I from Eq. (32) and the previous, unchanged χ_0^J from Eq. (10) into the paramagnetic RPA susceptibility of Eq. (11), the condition for the divergence of the latter now leads to a generalized implicit equation for the transition temperature $T_m(\xi_e, \xi_n, \hat{\Delta}_Q, I)$ that contains the effect of the quadrupolar splitting. It is given by

$$\left[\xi_e + \hat{P}_n^Q(T_m)(2\xi_n)^2 \frac{\Delta}{2T_m} \right] \tanh\left(\frac{\Delta}{2T_m}\right) = 1, \quad (33)$$

which may be obtained from the previous degenerate nuclear case given in Eq. (12) simply by replacing the Curie constant $\frac{1}{3}I(I+1)$ by the effective temperature-dependent Curie numerator in Eq. (32). From this, it is clear that the quadrupolar interaction dependence of $T_m(\hat{\Delta}_Q)$ is limited by the curves for actual nuclear spin size I and quadrupolar ground state doublet with $\tau = \pm\frac{1}{2}$ or $\tau = \pm I$. This is shown in Fig. 12 and discussed in Sec. VI.

VI. DISCUSSION OF NUMERICAL RESULTS

The main focus of the previous analysis is, first, the dependence of the transition temperature or phase diagram of induced moment magnetism on the electronic and nuclear control parameters, in particular the removal of the induced moment QCP by the hyperfine coupling. Second, it is the interplay and competition of various mechanisms on the entropy release witnessed by the specific-heat anomalies, namely, CEF level depopulation, exchange dominated induced moment order, and hyperfine dominated nuclear ordering. And third, it is the hyperfine coupling that leads to anomalous nonmonotonic critical field dependence on temperature or, equivalently, a reentrance signature of magnetic order for large fields. The numerical results of these important effects of coupled CEF and nuclear degrees of freedom will now be discussed in detail for typical cases.

First we have to remark on the relevant size of the dimensionless control parameters ξ_e, ξ_n involved. These are combinations of microscopic energies and matrix elements [Eq. (13)] and therefore are not known *a priori*. In the case of e-dominated induced order with ξ_e considerably above the QCP, as shown in Fig. 2, the transition temperature T_m will be virtually independent of ξ_n and may be obtained from inverting Eq. (14) to $\xi_e = 1/\tanh(\frac{\Delta}{2T_m})$, with T_m and Δ the experimental transition temperature and singlet splitting, respectively. The latter may possibly be obtained from inelastic neutron scattering or a global fit of the CEF level scheme to the high-temperature susceptibility. When ξ_e is around the

QCP or smaller, the nuclear control parameter becomes essential for T_m and, knowing the experimental value of the latter, Eq. (12) provides only a constraint for the two parameters, which is visualized in the contour plot $T_m/\Delta = \text{const}$ of Fig. 2 (right panel) where the possible values of (ξ_e, ξ_n) form a 1D manifold. Our results suggest that in this (sub)critical region, the relative size of ξ_e and ξ_n could then be further constrained by analysis of the specific-heat peak structure in Figs. 5(a)–5(c) and the low-temperature susceptibility (Fig. 4) discussed below. Alternatively, knowing A and Δ from experimental results and a calculated m_s from a CEF model for the singlet states, one can obtain ξ_n and, via Eq. (12) and/or Fig. 2, one can deduce ξ_e in the subcritical regime. An example for a Pr material is discussed in Appendix C.

For the numerical model calculations, the electronic control parameter ξ_e will be considered in the region of true induced moment order above the QCP $\xi_e = 1$, but not too large and, in particular, for subcritical region $\xi_e < 1$ where the hyperfine interaction plays an important role. The nuclear control parameter $\xi_n = m_s A / 2\Delta$ sets the hyperfine coupling in relation to the two-singlet CEF splitting. The hyperfine coupling A itself can be determined by nuclear resonance spectroscopy [33]. As mentioned, however, from the experimental T_m/Δ alone, the nuclear control parameter ξ_n can only be constrained in relation to ξ_e , but an estimate of its typical size can be given here. We take the CEF model in Eq. (1) with equal admixture coefficients corresponding to $\alpha = \pi/2$, which leads to the total angular momentum matrix element $m_s = 8$. We assume a rather small singlet splitting of $\Delta = 5$ K in order to present the electronic and nuclear specific-heat anomalies in graphs with linear rather than a distorted logarithmic temperature scale. This is not a restrictive assumption from the theory, but just convenient for the presentation. In fact, there are examples of singlet ground state systems with even smaller CEF splitting (Sec. VII). Using the typical size of $A \approx 50$ mK given in Table I for the potential singlet ground state candidate ions, the nuclear control parameter is of the order of $\xi_n \approx 0.04 \ll 1$. The sign of A or ξ_n has no influence because the spectra in Eqs. (18) and (30) are invariant under $\xi_n, \tau \rightarrow -\xi_n, -\tau$. We therefore choose the positive sign. For the nuclear spin size, we will only consider the noninteger cases $I = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ relevant from Table I. The possible nuclear quadrupolar splitting energy Δ_Q strongly depends on the nuclear environment (via the size of the EFG) and the f -electron element (via the nuclear quadrupole moment) and is again obtained from nuclear spin spectroscopy. While it is commonly smaller or comparable to the hyperfine coupling A for $4f$ nuclei, it may be considerably larger for the $5f$ case, i.e., for U -based singlet ground state magnets. Here we assume a range for the dimensionless $|\hat{\Delta}_Q| = |\Delta_Q/\Delta|$ from zero to a maximum that is considerably smaller than the hyperfine parameter ξ_n , and possibly of both signs.

With the range of parameters constrained, we first show the dramatic influence of hyperfine coupling on the ordering temperature, which is presented by the phase boundary diagram in the (ξ_e, T) plane in Fig. 2. For vanishing hyperfine coupling, there is a QCP for the intersite exchange-induced moment order at $\xi_e = 1$, and $T_m(\xi_e)$ collapses with a logarithmic singularity [5] at this point, leading to a paramagnetic state for $\xi_e < 1$. Turning on a finite hyperfine coupling to the nuclear

spins removes the QCP and the ordering temperature stays finite, though small, for all $\xi_e < 1$ with a smooth crossover between the two regions. Naturally, an increasing nuclear spin size leads to an increased T_m for fixed ξ_n . This is also true when keeping spin size fixed and increasing ξ_n . For $\xi_e \rightarrow 0$, the ordering is dominated by the hyperfine coupling and the limiting value of T_m is given below Eq. (14). Considerably above the QCP, the hyperfine coupling has little influence on $T_m(\xi_e)$, which is intersite-exchange dominated in this regime.

The temperature dependence of the two (normalized) order parameters below the transition temperature are shown in Fig. 3 for two typical control parameters, (a) above and (b) below the QCP. In the former case, the transition at T_m is CEF exchange dominated and $\langle S_x \rangle$ already saturates before the nuclear moment (I_z) becomes sizable only below a temperature $T^* \approx \xi_n \Delta$ comparable to the nuclear spin splitting induced by the saturated $\langle S_x \rangle$. Therefore, the temperature dependence of both order parameters in Fig. 3(a) has a rather asymmetric appearance. This is in contrast to Fig. 3(b) for below-critical ξ_e , where the ordering at much lower temperature (Fig. 2) is dominated by the hyperfine coupling. In this case, the nuclear and electronic moments evolve simultaneously below T_m .

The phase diagram in the ξ_e - T plane of Fig. 2 has been obtained from the singularity of the paramagnetic RPA susceptibility in Eq. (11). It is also instructive to follow the evolution of the latter in the ordered regime. We consider the noncritical *homogeneous* susceptibility for the AFM state according to Eq. (23). In the electronic-induced moment, the regime for ξ_e in the e-dominated case exhibits the typical AFM cusp at T_m and a lower separated hump and subsequent depression at $T^* \approx \xi_n \Delta$. Below the critical value in the n-dominated regime, the two energy scales merge to form a single cusp at T_m . The cusp as a function of ξ_e traces the $T_m(\xi_e)$ curve in Fig. 2. The size of the cusp and hump and, in particular, their distance on the T axis are a good indication of whether one is in the e- or n-dominated regime of (ξ_e, ξ_n) of the contours in Fig. 2 (right panel) for an experimentally known ratio T_m/Δ . For $\xi_e \geq 1$ and absent hyperfine coupling, $\xi_n = 0$ saturation [5] at a finite low-temperature value $[\xi_e(\xi_e^2 + 1)]^{-1}$ occurs, unlike the longitudinal susceptibility in a Kramers degenerate ground state (i.e., $\xi_e \gg 1$) magnet, which tends to zero there.

The zero-field specific heat of the model (Sec. IV) is shown in Fig. 5(a) for $I = \frac{5}{2}$. It exhibits three superposed anomalies: (i) the broad Schottky anomaly around $T_{\max}$ due to the two-singlet splitting, (ii) the jump at the induced ordering temperature T_m for $\xi_e > 1$ above the QCP value, and (iii) the nuclear specific-heat peak at the temperature scale T^* . As the electronic control parameter is decreased through the QCP, T_m shifts to lower temperatures (cf. Fig. 2) and the specific-heat jump is diminished. Finally, for $\xi_e < 1$, the ordering appears at a much lower temperature, $T_m \approx T^*$, dominated by the hyperfine coupling and the jump at the ordering temperature appears inside the nuclear specific-heat peak increasing again for lowering ξ_e [in Fig. 5(b)]. This intricate crossover appearance of the zero-field specific heat of Figs. 5(a) and 5(b) is also reflected in Fig. 5(c), which explicitly demonstrates the nonmonotonic evolution of the specific-heat jump across the QCP region. Furthermore, the dependence of specific-heat anomalies on the nuclear spin I is shown in Fig. 6 for $\xi_e > 1$.

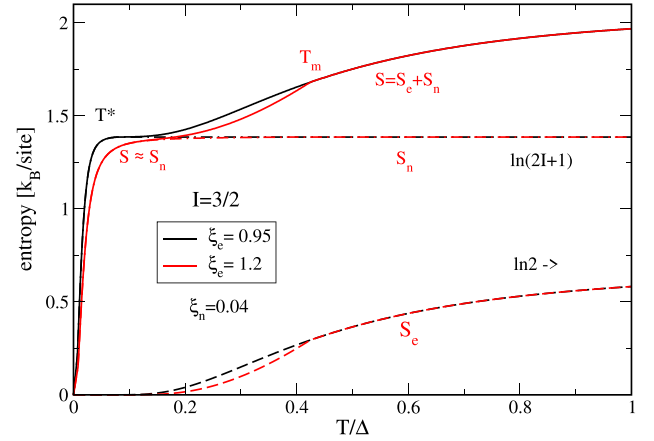


FIG. 7. Electronic (S_e), nuclear (S_n), and total entropy S as function of temperature for two above- (red) and below- (black) critical control parameters. The entropy release for S_e is mostly due to the depopulation of singlets, but is also due to induced ordering at T_m . The nuclear entropy is released due to the $(2I + 1)$ nuclear level splitting caused by the appearance of $\langle S_x \rangle$ at T_m . For subcritical $\xi_n = 0.95$, the nuclear entropy is directly released by the nuclear dominated order around $T_m \approx T^*$ [cf. Figs. 2 and 5(b)].

The jump at T_m is only weakly affected, while the nuclear part at T^* is strongly reduced by the smaller entropy release for decreasing I .

The associated entropy dependence on temperature is shown in Fig. 7 on the two sides of the QCP. As mentioned before, for $\xi_e > 1$, part of the entropy release at high temperature happens through the excited singlet depopulation as well as through the induced order at T_m , and at low temperature, the nuclear entropy is released via the nuclear spin splitting caused by the induced order parameter. For subcritical $\xi_e < 1$, there is no more entropy release at T_m and a clear plateau appears after the nuclear entropy has reached saturation, $S_n = \ln(2I + 1)$, above the now hyperfine dominated ordering around $T_m \approx T^*$. A further interesting aspect of the interplay of the three types of specific-heat anomalies is their evolution with applied field. In the model calculation, only the Zeeman term for CEF singlets has been included due to $\mu_n \ll \mu_B$, but the nuclear spins are indirectly influenced via the hyperfine coupling to the electronic order parameters $\langle S_x \rangle_\lambda$ that depend on the field. The results for the field dependence for FM and AFM exchange coupling and below- and above-critical ξ_e are shown in the four panels of Fig. 8. In the subcritical regime [Figs. 8(a) and 8(c)], the broad Schottky anomaly shifts to higher temperature for the FM case, while it is mostly unaffected for the AFM case. The nuclear peak around the temperature T^* broadens in the FM case, while it narrows in the AFM case. This behavior is caused by the quite different dependence of order parameters $\langle S_x \rangle_\lambda$ and $\langle I_z \rangle$ on field strength and is also observed in the above-critical region of ξ_e [Figs. 8(b) and 8(d)]. The higher-temperature electronic part of the specific heat is much different in the FM and AFM cases [6]. The jump at T_m is quickly broadened and shifted to higher temperature for the FM case. On the other hand, for the AFM case, the induced ordering and the associated specific-heat jump prevail in the finite field, but are

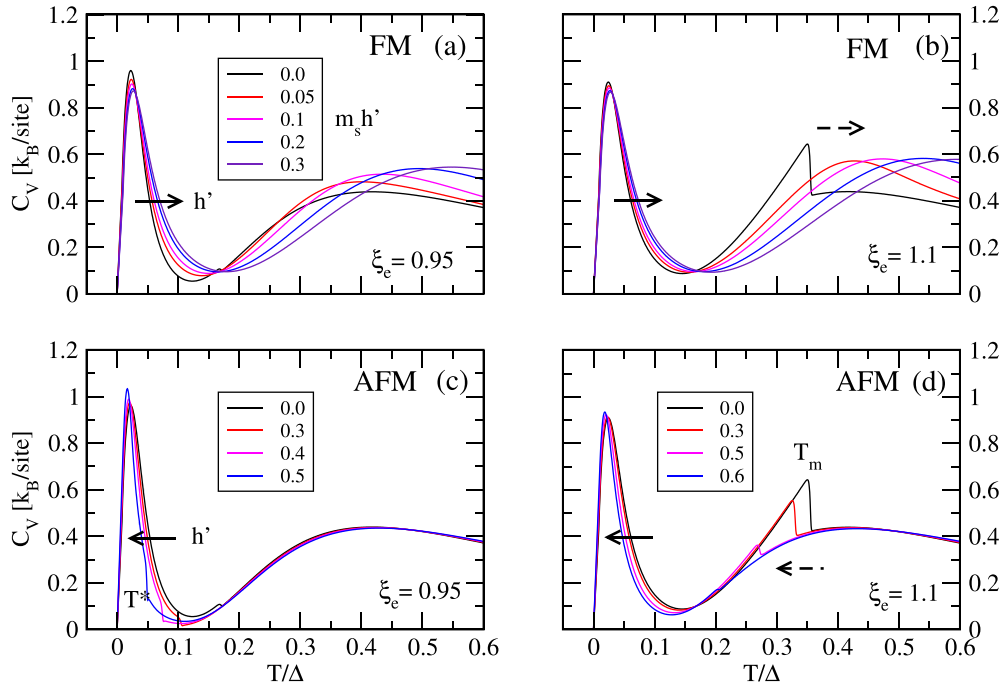


FIG. 8. Nuclear ($I = \frac{5}{2}$) and electronic specific-heat evolution in external field for (a),(b) FM and (c),(d) AFM cases for sub- and above-critical control parameter ξ_e and $\xi_n = 0.04$ throughout. Dimensionless field strength $m_s h'$ is given in the boxes [equivalent for (a),(b)]. Evolution of anomalies with *increasing* h' is indicated by arrows. In the FM case, larger fields lead to a broadening of the nuclear peak (a),(b) at $T^*/\Delta \simeq \xi_n$ (a),(b) and a rapid suppression, broadening, and shift to higher temperature of the zero field jump at T_m (b). In contrast, for the AFM case, the nuclear peak narrows with increasing field (c),(d), while the AFM transition jump at T_m (d) prevails but is reduced.

progressively suppressed in higher fields up to the critical field [6], thus approaching the subcritical appearance of the specific heat in Fig. 8(c).

The specific heat demonstrates that the FM transition changes to a gradual crossover in a finite field because there is no more symmetry breaking involved. On the other hand, the AFM transition persists up to a critical field. The corresponding H - T phase diagram as defined by the field dependence of the critical temperature is shown in the upper panels of Fig. 9. As mentioned before, it is obtained by identifying the field strength where the staggered order parameter $M_s(T, h)$ vanishes. Figure 9 demonstrates a reentrance behavior of the AFM magnetic transition temperature, most pronounced above the critical ξ_e . This corresponds to a nonmonotonic dependence of the critical field (the phase boundary) on temperature. It is caused by the rapid change of the electronic and nuclear order parameters and their coupling close to the critical field. This is demonstrated in the two panels of Fig. 10, both referring to the right panel of Fig. 9, which directly show the nonmonotonic shifting of the critical field with temperature. Equivalently the temperature dependence at fixed large field $h' = 0.85$ in this region, as shown in Fig. 11, clearly demonstrates the reentrance signature of magnetic order as witnessed in particular by the staggered order parameter $M_s(T)$ (red dashed) and its nuclear equivalent (right panel) in this figure. For the model example given in the beginning of this section (and using $g_I = \frac{4}{5}$ for Pr^{3+}), we also give the absolute temperature and field scale for the critical field curves in Fig. 9. There, $T_m/\Delta = 0.35$ corresponds to $T_m = 1.75$ K and $m_s h' = 0.9$ to $H = 1.05$ T. These rather low scales are due to the low singlet splitting $\Delta = 5$ K in this model.

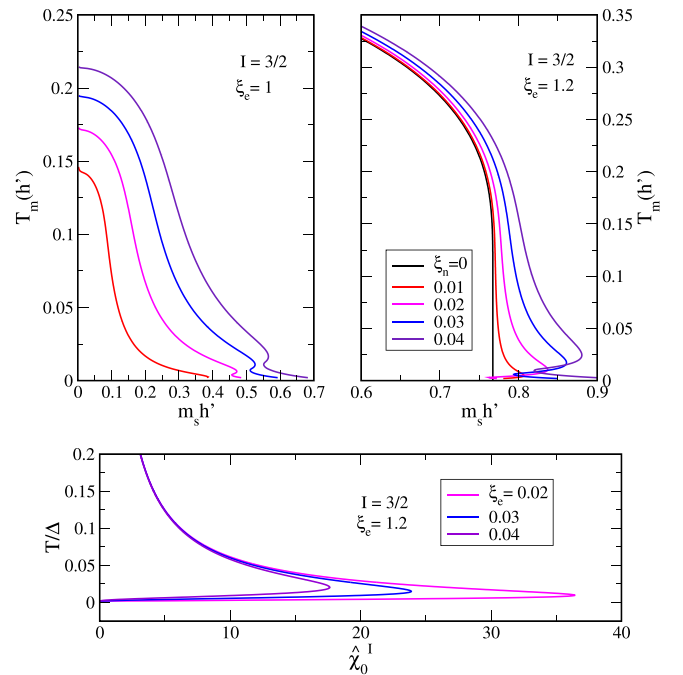


FIG. 9. Field dependence of the AFM transition temperature in the QCP regime (left) and the exchange dominated regime (right) for various ξ_n . In the left panel, T_m increases rapidly with ξ_n and develops reentrant behavior for large critical fields [low $T_m(h')$]. This becomes more pronounced in the right panel ($\xi_e > 1$); cf. Figs. 10 and 11. Bottom panel shows concomitant T dependence of single-site nuclear susceptibility [Eq. (21)] for field $m_s h' = 0.95$ slightly above the critical value.

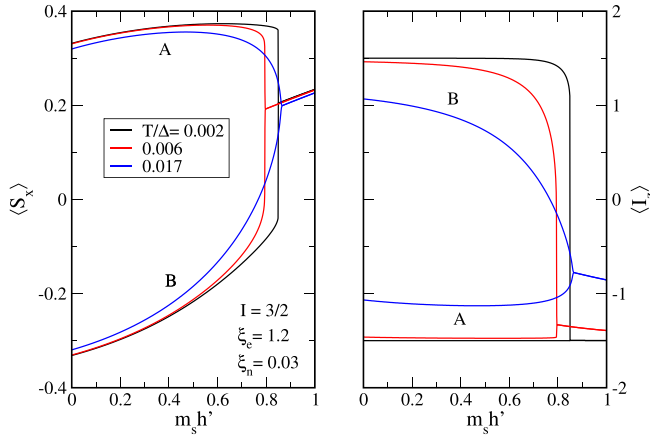


FIG. 10. Field dependence of electronic ($\langle S_x \rangle$) and nuclear ($\langle I_z \rangle$) order parameters on the A and B sublattices (left and right panels) in the low- T reentrant regime of the right panel in Fig. 10. At the lowest T , the transition appears first-order type, while it changes to second-order type when moving from the sharp minimum of the critical field to its maximum in Fig. 9. The critical field $h'_c(T)$ varies nonmonotonically with T .

The reentrance behavior appears at the temperature scale $T^* \simeq \xi_n \Delta$ corresponding to the nuclear spin splitting given by Eq. (17) around the critical field. In this region, the homogeneous on-site nuclear susceptibility given by the pseudo-Curie expression in Eq. (21) exhibits a pronounced maximum (lower panel of Fig. 9) which destabilizes the staggered AFM order and leads to the minimum in the critical field curve around T^* and the concomitant reentrance as a function of temperature. This reentrance is stable and not subject to fine tuning since the peaked structure of the nuclear susceptibility given by Eq. (21) caused by population/depopulation of nuclear levels is universal. We note that this kind of reentrance caused by hyperfine coupling is seen experimentally in a singlet ground

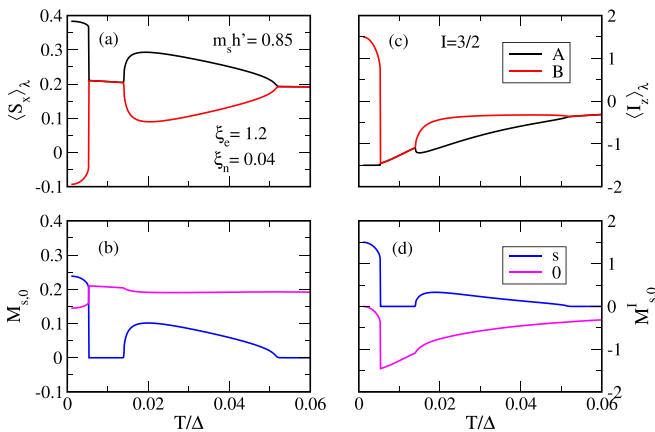


FIG. 11. Complementary reentrant magnetic order as a function of temperature for large $m_s h' = 0.85$ close to the maximum critical field in Fig. 9(b). (a) Electronic and (c) nuclear order parameters on sublattices A and B. (b) The staggered AFM electronic order parameter is $M_s = \frac{1}{2}(\langle S_x \rangle_A - \langle S_x \rangle_B)$ and the homogeneous moment is $M_0 = \frac{1}{2}(\langle S_x \rangle_A + \langle S_x \rangle_B)$. Likewise for the nuclear case, $M_{s,0}^I$ (with $A \leftrightarrow B$). In an intermediate-temperature regime, the staggered order parameters reemerge.

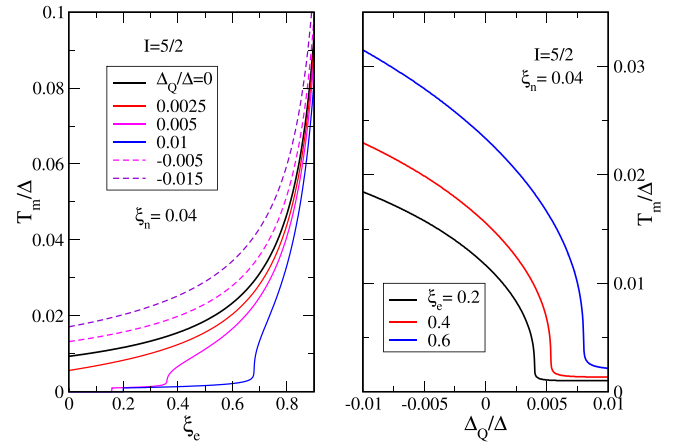


FIG. 12. Left panel: Ordering temperature as a function of ξ_e for various positive and negative nuclear quadrupole coupling constants $\hat{\Delta}_Q = \Delta_Q/\Delta$ in the nuclear dominated regime with subcritical $\xi_e < 1$. Right panel: Complementary dependence of ordering temperature T_m on the nuclear quadrupole coupling constant for subcritical ξ_e .

state Pr-skutterudite compound [25]. The details of the ordering are different for this compound because its low-lying CEF states are of singlet-triplet type, rather than two singlets, and the ordered phase is the field-induced quadrupolar type. In fact, it has also been observed in the Yb compound with Kramers doublet ground state [13], where it has been attributed to the influence of hyperfine coupling.

Finally, we discuss the effect of possible quadrupole splitting of nuclear spin states on the (zero-field) magnetic phase transition and how the phase boundary changes with the size of the quadrupolar nuclear coupling constant. The latter we constrain to the regime $|\hat{\Delta}_Q| \ll \xi_n$, which is appropriate for 4f elements. We expect it to be relevant only deep in the n-dominated regime with ξ_e considerably below the QCP. This is shown in Fig. 12 (left panel) with the critical temperature curves obtained from solving Eq. (33). The full red curve gives the reference for zero quadrupolar potential $\hat{\Delta}_Q$ under the presence of finite hyperfine coupling $\xi_n = 0.04$. An increasing (positive) $\hat{\Delta}_Q$ leads to a rapid characteristic suppression of subcritical $T_m(\xi_e)$, but never quite to zero. For above-critical ξ_e , its influence is negligible. The overall shape of the critical temperature curve for the large- $\hat{\Delta}_Q$ (blue line) value approaches the behavior for zero hyperfine coupling. In contrast, for negative quadrupolar coupling constants, T_m increases and the shape of the (red) reference curve is preserved. This distinctive influence of nuclear quadrupole splitting is also seen in the complementary right panel of Fig. 12, which plots directly the $\hat{\Delta}_Q$ dependence for two subcritical ξ_e and two nuclear spin sizes. The reason for the opposite dependence for different signs of $\hat{\Delta}_Q$ was attributed in Sec. V to the different modification of the nuclear Curie-type susceptibility in the two cases.

VII. REMARKS ON CANDIDATE SINGLET GROUND STATE f -ELECTRON MATERIALS

This work is primarily intended as a model investigation to clarify the cooperation of electronic exchange and

TABLE II. Collection of data for CEF singlet ground state compounds (the first excited CEF state may not be a singlet) with induced order where FM, AFM denote the ferro-/antiferromagnetic case, IC incommensurate magnetic order, and HO hidden multipolar order. Here T_m is the ordering temperature, Δ the splitting of lowest two CEF levels, and ξ_e the electronic control parameter. The electronic dominated, intermediate, and nuclear dominated regimes of induced order are denoted by e, e/n, and n, respectively.

Regime	Compound	State	T_m	Δ (K)	ξ_e	Ref.
e	PrNi	FM	21 K	26	1.8	[34]
	TbSb	AFM	15 K	12	2.7	[35]
	UGa ₂	FM	125 K	38	6.6	[36]
	URu ₂ Si ₂	HO	17.5 K	35	1.3	[8]
e/n	Pr ₃ Tl	FM	11.6 K	60	1.011	[37–39]
	UPd ₂ Al ₃	AFM	14.3 K	66	1.015	[28]
	Tb ₃ Ga ₅ O ₁₂	AFM	0.25 K	2.55	$\simeq 1$	[40,41]
n	PrCu ₂	FM	54 mK	2.9	< 1	[42]
	dhcp Pr	IC	50 mK	41	< 1	[22]
	PrNi ₅	FM	0.4 mK	47	< 1	[20,43]
	PrCu ₆	FM	2.45 mK	20	< 1	[23,44]

nuclear hyperfine coupling in the induced moment mechanism without focusing on a specific compound. Nevertheless, we give a brief overview of f -electron compounds that qualify as induced moment systems in the three possible regimes: above (e), around (e/n), and below (n) the QCP of Fig. 2(a). The empirical criterion of this classification is given by the experimentally determined ratio of T_m/Δ , as obtained from inspection of this figure. We apply this to some known singlet ground state compounds (sometimes with degenerate first excited state) by giving the values of T_m , Δ and, wherever possible, ξ_e in Table II. They can be roughly assigned to three groups:

(e) For $T_m/\Delta > 0.3$, one enters the e-dominated regime where the effect of hyperfine coupling is negligible.

(e/n) For $T_m/\Delta < 0.3$ but still sizable, one is close to the QCP with $\xi_e \simeq 1^+$ (Fig. 2) and hyperfine coupling is becoming important in this regime.

(n) For $T_m/\Delta \ll 0.3$, one is in the n-dominated regime with $\xi_e < 1$ and mainly hyperfine coupling responsible for induced ordering.

One has to keep in mind that the experimental determinations of the singlet ground state–excited state splittings commonly have a considerable margin, depending on the method used, and therefore these classifications are not unambiguous. The above listings, however, indicate that the nuclear dominated induced ordering is primarily observed among the Pr compounds, as indeed has been realized before [18]. Of these material examples, PrCu₂ in the n-dominated regime is considered in more detail in Appendix C.

VIII. SUMMARY AND CONCLUSION

In this work, we investigated the influence of the hyperfine coupling with nuclear spins on the properties of CEF singlet-singlet induced moment magnets in the context of a highly symmetric Ising-type model that allows a mostly analytical treatment. Furthermore, we include the effects of an external

field and the influence of nuclear quadrupole potential leading to a splitting of nuclear spin states.

We have shown that the QCP existing in the purely electronic model is suppressed by the hyperfine coupling and replaced by a crossover from electronic exchange CEF induced moment order with large critical temperature T_m to a subcritical regime below the QCP where the order at a much lower T_m is dominated by the hyperfine coupling and comes to lie within the temperature regime of nuclear spin splitting energy.

Furthermore, the temperature and field dependence of both electronic and nuclear order parameters in both ordered regimes were calculated, showing characteristic differences in their appearance. In particular, the specific heat, its temperature, and field and control parameter dependence were investigated. It was found that it is determined by the interplay of three anomalies, which is also reflected in the entropy release. They correspond to Schottky-type anomaly due to upper singlet depopulation, specific-heat jump at the induced moment ordering for above-critical electronic control parameter, and large and narrow nuclear peak due to the lifting of nuclear spin degeneracy. The specific-heat jump exhibits a pronounced nonmonotonic evolution when crossing the QCP region. The field dependence shows characteristic differences for these anomalies for FM/AFM models and below-/above-critical control parameter. In particular, the nuclear specific-heat peak is broadening for the FM case and, in contrast, shows narrowing in the AFM case, reflecting the distinct field dependence of the order parameters and associated excitation gaps in the two cases. Importantly, the resulting H - T phase diagram was found to exhibit a peculiar reentrance signature connected with nonmonotonic critical field dependence on temperature, which becomes more pronounced with increasing hyperfine coupling. In addition, we studied in detail the effect of a possible nuclear quadrupole coupling which lifts the nuclear spin degeneracy. It was found that a positive quadrupolar potential suppresses the transition temperature curve, while the negative quadrupole coupling enhances the ordering temperature preserving the shape of the phase boundary. This distinction may be traced back to the properties of the pseudo-Curie nuclear spin susceptibility in the two cases.

Finally, we may summarize the main achievements of this investigation: We have given a treatment of electronic nuclear coupling and its influence on induced order for general nuclear spin size and a calculation of the systematic evolution of two- and three-peak appearance of the total specific heat as a function of electronic and nuclear control parameters and nuclear spin size. Furthermore, the systematic evolution of the electronic/nuclear specific-heat peak structure in a magnetic field for FM as well AFM order was clarified and, most importantly, we identified a reentrance behavior of the critical field curves and the associated behavior of electronic order parameter and nuclear spin ordering. It is the consequence of competition between hyperfine coupling to induced order and homogeneous nuclear polarization. In addition, the qualitative influence of the quadrupolar nuclear potential on the induced moment transition temperature was demonstrated.

The present work provides a solid theoretical framework for the discussion of the influence of nuclear spins with

hyperfine coupling on singlet-singlet induced moment magnetism, which may occur in compounds with non-Kramers f -electron ions with sufficiently low site symmetry of the crystalline electric field.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: PARTITION FUNCTIONS AND THERMAL OCCUPATION FUNCTIONS

For the calculation of order parameters, susceptibilities, and thermodynamic potentials, we need the thermal occupations of the split electronic/nuclear level scheme under the presence of (sublattice) order parameters and an external field. In this appendix, we define them for the case without quadrupolar splitting. The latter is included in Sec. V.

The thermal occupations of individual levels are given by

$$p_{\lambda s}^{\tau} = Z_{\lambda}^{-1} \exp(-E_{\lambda s}^{\tau}), \quad (\text{A1})$$

where Z_{λ} is the partition function for sublattice $\lambda = A, B$, and $E_{\lambda s}^{\tau}$ are the MF energy levels given by Eq. (18). Because the Ising-type hyperfine interaction does not mix the products of electronic and nuclear states, the partition function factorizes according to $Z_{\lambda} = Z_{e\lambda} \cdot Z_{n\lambda}$, respectively,

$$Z_{e\lambda} = 2 \cosh \left[\left(\frac{\Delta}{2T} \right) \hat{\Delta}_{e\lambda} \right],$$

$$Z_{n\lambda} = \begin{cases} 1 + 2 \sum_{\tau=1}^I \cosh \left[\left(\frac{\Delta}{2T} \right) 2\tau \hat{\Delta}_n \right], & I \text{ integer} \\ 2 \sum_{\tau=\frac{1}{2}}^I \cosh \left[\left(\frac{\Delta}{2T} \right) 2\tau \hat{\Delta}_{n\lambda} \right], & I \text{ noninteger.} \end{cases} \quad (\text{A2})$$

The form of $Z_{n\lambda}$ for *noninteger* nuclear spin $I = \frac{1}{2}, \frac{3}{2}, \dots$ is the relevant one for the isotopes of $4f$ elements, which we have in mind here (Table I). Then the differences of thermal populations appearing in the MF equations [Eq. (15)] for the order parameters may be derived as

$$\hat{P}_{e\lambda}(T) = \tanh \frac{\Delta}{2T} \hat{\Delta}_{e\lambda},$$

$$\hat{P}_{n\lambda}(T) = 4Z_{n\lambda}^{-1} \sum_{\tau=\frac{1}{2}}^I \tau \sinh \left[\left(\frac{\Delta}{2T} \right) 2\tau \hat{\Delta}_{n\lambda} \right]. \quad (\text{A3})$$

These population functions depend implicitly on the induced moments $\langle S_x \rangle_{\lambda}$ and $\langle I_z \rangle_{\lambda}$ for each sublattice via the excitation energies $\hat{\Delta}_{e\lambda}$, $\hat{\Delta}_{n\lambda}$, which have a sublattice λ -dependent size for finite field h . In the zero field, the sublattice dependence reduces to just a sign difference given by $P_{n\lambda}(T) = \text{sign}(\lambda)P_n(T)$, with $\text{sign}(\lambda) = \pm 1$ for $\lambda = A, B$.

APPENDIX B: SPECIAL CASE WITH $I = \frac{1}{2}$

For the special case with nuclear spin $I = \frac{1}{2}$, the self-consistency equations for the electronic and nuclear order parameters in Eq. (15) assume a more transparent and explicit

form, which is given by

$$\langle S_x \rangle_{\lambda} = \frac{1}{2} \frac{1}{\hat{\Delta}_{e\lambda}} \left\{ m_s h' - 2\xi_e \langle S_x \rangle_{\bar{\lambda}} + \xi_n \tanh \left[\left(\frac{\Delta}{2T} \right) (2\xi_n \langle S_x \rangle_{\lambda}) \right] \right\} \tanh \left[\left(\frac{\Delta}{2T} \right) \hat{\Delta}_{e\lambda} \right],$$

$$\hat{\Delta}_{e\lambda} = \left\{ 1 + \left(m_s h' - 2\xi_e \langle S_x \rangle_{\bar{\lambda}} + \xi_n \tanh \left[\left(\frac{\Delta}{2T} \right) (2\xi_n \langle S_x \rangle_{\lambda}) \right] \right)^2 \right\}^{\frac{1}{2}},$$

$$\langle I_z \rangle_{\lambda} = -\frac{1}{2} \tanh \left[\left(\frac{\Delta}{2T} \right) (2\xi_n \langle S_x \rangle_{\lambda}) \right]. \quad (\text{B1})$$

APPENDIX C: CONTROL PARAMETERS FOR PrCu₂ SINGLET STATE MAGNET

In the beginning of Sec. VI, we introduced the parameters for a hypothetical tetragonal ($J = 4$) CEF singlet-singlet system defined in Eq. (1). It was chosen to have the maximum magnetic matrix element $m_s = 8$ between the two singlets. Then, for the small CEF splitting Δ assumed, the nuclear control parameter using the hyperfine coupling A of Pr (Table I) is obtained as $\xi_n = 0.04$.

For real compounds, the singlet-singlet model is mostly realized for low symmetry such as orthorhombic D_{2h} (where only singlet CEF states can occur). Then the difficulty of estimating ξ_n stems from the fact that m_s is hard to know since it critically depends on numerous D_{2h} CEF potential parameters that determine the composition of the two singlet wave functions. Nevertheless, we attempt this for the material example of PrCu₂ which belongs to the n -dominated class described in Sec. VII with very low $T_m = 54$ mK (AFM). Its CEF potential and singlet state wave functions were proposed in [45]. For the two lowest singlets, they are approximately given by combinations of $|M\rangle = |JM\rangle$ free ion states as

$$|0\rangle = a|0\rangle + b(|+4\rangle + |-4\rangle),$$

$$|1\rangle = c(|1\rangle + |-1\rangle) + d(|3\rangle + |-3\rangle), \quad (\text{C1})$$

with the coefficients $a = 0.8433$, $b = 3797$, $c = 0.3296$, $d = -0.6720$. [Here we applied a gauge change by a factor (-1) to the $|1\rangle$ singlet.] Then the matrix element for the $\mathbf{J}$ operators may be computed and it is largest for the x direction (easy axis of AFM order). Defining now the pseudospin via $J_x = m_s S_x$, it is given by $m_s = 4(\sqrt{5}ac + \sqrt{2}bd)$ from which we obtain $m_s = 1.14$. Using the experimental singlet splitting [42] $\Delta = 2.9$ K and A of Table I, we get $\xi_n = m_s A / (2\Delta) = 0.01$, which corresponds to the low value used in most previous figures. This is due to the relatively small value of m_s for these two singlets. As explained in Sec. II for CEF uniaxial symmetry with an easy z -axis matrix, elements up to $m_s = 8$ may be achieved which leads to correspondingly higher ξ_n values provided the splitting of singlets stays sufficiently small. With the knowledge of $\xi_n = 0.01$ and using the numerical solution of Eq. (12) (Fig. 2) for the experimental ratio $T_m/\Delta = 0.019$ of PrCu₂, we obtain the $\xi_e = 0.97$ subcritical value for this compound.

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