Fractional Impurity Moments in Two-Dimensional Noncollinear Magnets

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We study dilute magnetic impurities and vacancies in two-dimensional frustrated magnets with noncollinear order. Taking the triangular-lattice Heisenberg model as an example, we use quasiclassical methods to determine the impurity contributions to the magnetization and susceptibility. Most importantly, each impurity moment is not quantized but receives nonuniversal screening corrections due to local relief of frustration. At finite temperatures, where bulk long-range order is absent, this implies an impurity-induced magnetic response of Curie form, with a prefactor corresponding to a fractional moment per impurity. We also discuss the behavior in an applied magnetic field, where we find a singular linear-response limit for overcompensated impurities.

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Impurities have been established as a powerful means to both probe and tune bulk properties of correlated-electron materials. In quantum magnets, nontrivial phenomena include vacancy-induced magnetism in quantum paramagnets [1] and quantum percolation [2]. Single-impurity behavior has been predicted to be exotic in quantum critical magnets, where a universal fractional Curie moment appears at low temperatures [3–5]. Isolated impurities in magnets with long-range order have been studied as well, with most works focusing on the square-lattice Heisenberg magnet [3,4,6,7].

This Letter is devoted to impurities in geometrically frustrated spin-S magnets which order noncollinearly—a topic which has received little attention [8]. As we show below, vacancies (i.e., nonmagnetic impurities) in noncollinear magnets display a behavior which is richer and qualitatively different compared to their collinear counterparts. In particular, the magnetic moment m associated with a single vacancy is not quantized, in contrast to the collinear case [3] where it is locked to $m = S$. This effect is already present at the classical level: nearby spins readjust their directions in response to the vacancy, reflecting that frustration is locally reduced. This partially screens the vacancy moment, with the screening cloud decaying algebraically due to Goldstone modes.

At zero temperature, the direction of the vacancy moment m is fixed by the bulk magnetic order. In contrast, at $T > 0$ in two dimensions (2D) there is no long-range order due to the Mermin-Wagner theorem, and the vacancy moment is free to rotate. This rotation is classical, as it is coupled to a rotation of the bulk spins surrounding the vacancy [3,4]. As a result, the linear-response susceptibility has a singular piece, $\chi_{\mathrm{imp}}(T) = m^2/(3kT)$, corresponding to the Curie response of a fractional moment for each vacancy [9]. For the triangular-lattice Heisenberg antiferromagnet (AFM) with nearest-neighbor interactions, we find in a $1/S$ expansion

$$m = -0.040S + 0.196 + \mathcal{O}(1/S), \tag{1}$$

where a negative sign reflects overcompensation; see below. In stark contrast to fractional effective moments found at bulk or boundary quantum critical points [3,5,10], the present mechanism is realized deep inside the renormalized classical regime [11] of a 2D magnet.

A magnetic field h has two effects which tend to compete: it orients the impurity moment parallel to the field and it induces a macroscopic bulk moment. This bulk-boundary competition is governed by a field-induced length scale $l_h \propto 1/h$ and limits the linear-response regime [12]. For an overcompensated impurity in the triangular lattice, we find this competition to be particularly drastic: Linear response breaks down at any finite field.

In the body of this Letter, we sketch the derivation of these results and propose tests and extensions of the nontrivial screening advocated here. Our considerations qualitatively apply to a large class of frustrated AFMs with noncollinear ground states, which are unique up to global spin rotations. For definiteness, we will present results for the spin-S triangular-lattice Heisenberg model

$$\mathcal{H} = \sum_{\langle ij\rangle}[J\vec{S}_i \cdot \vec{S}_j + K(\vec{S}_i \cdot \vec{S}_j)^2] - h\sum_i S_i^z. \tag{2}$$

The biquadratic exchange [13], with its strength parametrized by $k = K/(JS^2)$, generates a family of models and, in particular, lifts the accidental classical degeneracy of the nearest-neighbor AFM in an applied field [14]. In zero field, the ground state is given by the familiar coplanar 120° ordering at wave vector $\vec{Q} = (4\pi/3, 0)$ for $-2/9 < k < 2/9$.

Vacancy in the ground state of a classical noncollinear magnet.—Consider a bulk AFM with geometric frustration, where not all energetic constraints (e.g., all neighboring spins pairwise antiparallel) can be satisfied. Removing a single spin locally reduces frustration due to the elimination of constraints. For a noncollinear magnet, this seeds a readjustment of spin directions.

For the triangular lattice, this readjustment is illustrated in Fig. 1(a), which shows the ground state of a finite system of size L^2 with $L = 51$, where a single spin has been removed. The spins remain coplanar and rotate by angles $\delta\Theta$ relative to the original 120° configuration, such that the spins near the vacancy tend to be more antiparallel. $\delta\Theta(\vec{r}_i)$ shows a sixfold (f-wave) angular symmetry and is consistent with a spatial decay of $\delta\Theta(r) \propto 1/r^3$, Fig. 1(b) [8].

This result is rationalized as follows: The rotation pattern can be understood as the response of the system to a field $\tilde{h}$ which couples to the six neighbors of the vacancy such that these spins are rotated towards an antiparallel configuration. Hence, the field $\tilde{h}$ acting on these six sites is locally transverse and alternating, in a rotated frame compactly written as $\tilde{h}\sum_{j=1}^{6}\beta_j S_j^x$, with $\beta_j = (-1)^j$. The long-distance rotation is determined by a transverse susceptibility, which is dominated by the modes near the ordering wave vector with linear dispersion ω_q. Formally, this susceptibility is the Fourier transformation of a spin-wave propagator supplemented by matrix elements, which eventually gives $\delta\Theta(r) \propto \int d^d q e^{i\vec{q}\cdot\vec{r}}\beta_q/\omega_q^2 \propto 1/r^{d+1}$, where $\beta_q \propto q^3$ and one factor ω_q arises from spin-wave coherence factors.

The state with a single vacancy has a finite magnetization m. While this would simply be $m = S$ without readjusted angles (i.e., in the collinear case), the readjustment tends to screen this moment. For the triangular lattice, the numerical result, obtained from integration over the screening cloud, is $m/S = -0.0396(3)$, i.e., the missing spin is overcompensated such that the total moment points in the direction of the removed spin. The value of m is nonuniversal, i.e., depends on details of the Hamiltonian:

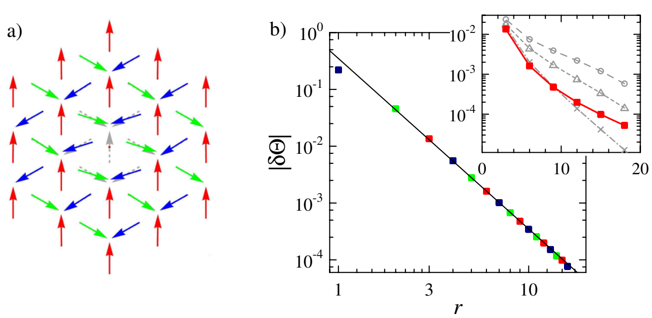

FIG. 1 (color online). (a) Classical ground-state spin configuration of the triangular AFM with vacancy, showing the spin readjustment near the vacancy; the dashed arrows indicate the original 120° order. (b) Rotation angle $|\delta\Theta|(r)$ along a high-symmetry line for $k = 0$ and $L = 51$, together with the asymptotic power law $\delta\Theta \propto 1/r^3$. The inset shows the same data (solid line), together with $|\delta\Theta(r)|$ at finite field $h/J = 0.5$ (dashed line), 1.0 (short dashed line), 1.5 (dash-dotted line), all for $k = -0.05$, for one sublattice in a log-linear plot. The exponential (instead of power-law) decay for $h > 0$ is obvious.

Fig. 2(a) shows m/S as a function of the biquadratic exchange coupling K in Eq. (2).

Vacancy: 1/S corrections.—Quantum corrections to the classical $T = 0$ results can be obtained using spin-wave theory. Holstein-Primakoff bosons a are introduced to capture deviations from the classical state in the presence of a vacancy, Fig. 1(a). Upon expressing the Heisenberg model in terms of the a bosons, terms linear in a vanish as required. Linear spin-wave theory amounts to a diagonalization of the quadratic-in-a piece of the Hamiltonian, which has to be done numerically for finite lattices [15] due to the inhomogeneous reference state. From the spectrum we can calculate $1/S$ corrections to thermodynamic observables as well as response functions.

The local magnetization correction $\delta m(\vec{r}_i) = \langle a_i^\dagger a_i \rangle$ decays to the known bulk value of $\delta m_b = 0.26$ [16] at long distances, corresponding to a staggered magnetization of $m_b = S - 0.26$. The impurity contribution, $\delta m(\vec{r}_i) - \delta m_b$, indicates enhanced quantum corrections near the impurity which fall off as $1/r^3$, consistent with the Goldstone-mode expectation. The $1/S$ correction to the uniform moment associated with the vacancy is obtained from integration, $\delta m = \sum_i \delta m(\vec{r}_i)\cos\Theta(\vec{r}_i)$, which evaluates to $\delta m = 0.196$, Eq. (1). Further corrections at higher orders in $1/S$ will not qualitatively modify the result of a nonuniversal fractional value of m, but apparently both overcompensation and undercompensation may occur, depending on S and microscopic details. We note that local impurity-induced magnetization corrections obeying $\delta m(\vec{r}_i) - \delta m_b \propto 1/r^3$ also occur in the collinear square-lattice case, but here spin conservation demands that the integral δm vanishes; hence m remains locked to S [4,6].

Finite temperatures: Fractional Curie response.—For $T > 0$ in two space dimensions, long-range bulk magnetic order is destroyed by thermal fluctuations, with the correlation length ξ being exponentially large at low temperatures, $T \ll J$. Consequently, the direction of the

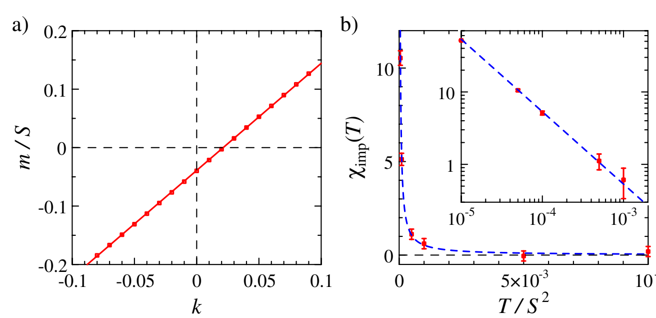

FIG. 2 (color online). (a) Effective vacancy moment m/S for the classical triangular Heisenberg AFM as function of the biquadratic exchange k in Eq. (2). (b) Monte Carlo results for $\chi_{\rm imp}$ as function of T/S^2, calculated with $JS^2 = 1$ and $k = 0$. The dashed line shows the predicted Curie law $m^2/(3kT)$ (3) with $|m/S| = 0.04$. The inset shows the low-T data in a log-log plot. The data in (a) [(b)] have been obtained for systems of size $L = 51$ [$L = 9, 12$]; finite-size effects are negligible.

impurity moment is no longer fixed but is free to rotate with the local orientation of the bulk magnetic domain surrounding the impurity. It has been shown both analytically [3,4] and numerically [7] that this rotation is classical and leads to a linear response of the Curie form:

$$\chi_{\mathrm{imp}}(T) = \frac{m^2}{3kT} + \mathcal{O}(T^0), \tag{3}$$

where the subleading term receives a multiplicative logarithmic correction in 2D [4,7,17].

In the noncollinear case, the partial screening of the vacancy moment, established above for $T = 0$, will remain intact at small $T > 0$ because of the large correlation length. This implies a Curie response (3) corresponding to a fractional moment per vacancy. This central result is fully borne out by numerics: we have performed classical Monte Carlo simulations of triangular-lattice Heisenberg magnets, using the standard Metropolis algorithm. In Fig. 2(b) we show the result for the impurity susceptibility χ_{imp}, obtained from subtracting the linear response χ of a system with vacancy from that of a system without vacancy. While the high-temperature part is difficult to analyze given the error bars, the low-temperature data clearly show a Curie divergence, with a prefactor consistent with $|m/S| = 0.04$ within error bars. For $S < \infty$, we expect a subleading $\log T$ contribution to $\chi_{\mathrm{imp}}(T)$ arising from Goldstone modes similar to the collinear case; a detailed analysis will appear elsewhere.

Vacancy versus extra spin.—Thus far, we have considered the special case of a vacancy, experimentally obtained by replacing a magnetic by a nonmagnetic ion. A different type of impurity is an extra spin of size S', coupled to a single site of the bulk with a Heisenberg coupling J'. For antiferromagnetic $J' \gg J$ and $S = S'$, the impurity spin and its bulk partner lock into a singlet, and we recover the vacancy case. On the other hand, for $J' \ll J$ the readjustment of the spin directions due to the impurity will be parametrically small in J'/J, and we expect for the impurity moment $m \to S$ as $J' \to 0$. Hence, varying J'/J leads to a continuous change of m.

Finite magnetic field.—For the square-lattice AFM, it has been shown that a vacancy in an applied field generates spin textures in its vicinity, which result from the competition between aligning the vacancy moment and inducing a bulk moment [12]. Here we investigate the noncollinear case on the triangular lattice. As the nearest-neighbor Heisenberg model has an accidental degeneracy of classical ground states at finite fields, which is lifted in favor of coplanar states [Fig. 3(a)] both by quantum and thermal fluctuations [18,19], we choose to investigate the classical model with biquadratic exchange, Eq. (2) with $-2/9 < k < 0$, which leads to the same coplanar finite-field phases as the ones selected by fluctuation effects. (Noncoplanar states are favored for $0 < k < 2/9$.)

Qualitatively, the vacancy physics strongly differs between the undercompensated and overcompensated cases. For undercompensation, Fig. 3(b), a small field will orient the system such that the vacancy sublattice points antiparallel to the field. This is compatible with the field-induced bulk state; hence, a strong competition between bulk and boundary effects is absent, and the zero-field limit will be smooth.

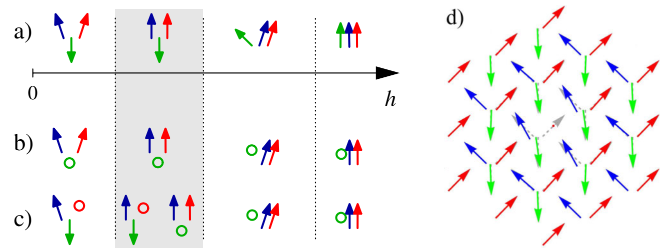

FIG. 3 (color online). (a) Schematic evolution of the three-sublattice coplanar bulk spin configurations as function of applied field for the triangular AFM, with the 1/3 magnetization plateau shaded. These states are selected out of the classical $k = 0$ ground-state manifold of $\mathcal{H}$ (2) by both thermal and quantum fluctuations as well as negative small k. A single vacancy chooses one of the sublattices: (b) undercompensated and (c) overcompensated case. In (c), an impurity-induced quantum phase transition occurs inside the plateau phase. [Note that undercompensation does not occur in our family of classical models with $k < 0$ but is expected for $S < \infty$ from Eq. (1).] (d) Spin configuration with (overcompensated) vacancy, calculated for $h/J = 1.0$, $k = -0.05$, and $L = 51$.

This is different in the overcompensated case, where orienting the vacancy moment in field direction is incompatible with the bulk state. Our numerics shows that the system chooses a compromise such that the vacancy sits in one of the sublattices directed approximately parallel to the field, with a significant distortion near the vacancy, Figs. 3(c) and 3(d). This distortion falls off exponentially (there is no coupling to the remaining Goldstone mode), with a length scale $l_h \propto 1/h$ [12], Fig. 4(b). Most importantly, the zero-field limit is singular in this case; i.e., the distortion pattern for $h \to 0$ does not recover its zero-field structure. This is seen in the insets of Figs. 1(b) and 4(a). The latter shows $m_{\mathrm{imp}}(h)$, defined as the difference of the total magnetizations with and without vacancy. By construction, $m_{\mathrm{imp}}(h = 0) = |m|$ and $m_{\mathrm{imp}}(h \to \infty) = -S$. Figure 4(a) demonstrates that $m_{\mathrm{imp}}(h \to 0)$ again represents a fractional impurity moment which is different from $|m|$ in the overcompensated case.

The evolution of $m_{\mathrm{imp}}(h)$ through the bulk magnetization plateau is also very different in the undercompensated and overcompensated cases, Figs. 3(b) and 3(c). While it is smooth for undercompensation, a jump occurs at $h = 3J$ in the overcompensated case, Fig. 4(a). This signals a transition where the vacancy site "switches" the sublattice: As the vacancy is immobile, this implies that its presence induces a first-order bulk phase transition, which, however, is only accompanied by nonextensive changes in thermodynamic observables, due to the Z_3 symmetry underlying the bulk plateau phase.

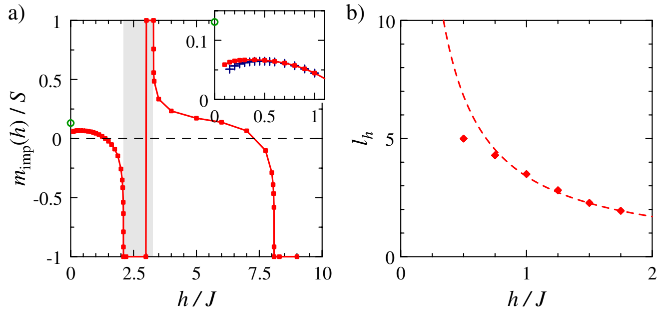

FIG. 4 (color online). (a) Impurity contribution to the magnetization, $m_{imp}(h)/S$, as function of applied field h, for the classical triangular AFM (2) with $k = -0.05$. The shaded region corresponds to the bulk $1/3$ magnetization plateau. The inset shows a zoom onto the small-field region; squares (crosses) are data for $L = 51$ ($L = 21$). The circle at $h = 0$ represents the linear-response value $|m/S|$, demonstrating the breakdown of linear response for this overcompensated case. (b) Field-induced length scale $l_h(h)$ obtained from an exponential fit to $\delta\Theta(r)$ for $L = 51$, together with the anticipated $l_h \propto 1/h$ behavior (dashed line). Finite-size effects are important for small $h > 0$ where $l_h \ll L$ is violated.

Finite impurity concentration.—We finally discuss the measurable consequences of our findings in the realistic case of a finite impurity concentration n_{imp}. Assuming that the impurities are distributed equally over all sublattices, their moments tend to average out at $T = 0$ and $h = 0$. This behavior persists at finite T, provided that $\xi \gg l_{imp}$ where $l_{imp} = n_{imp}^{1/d}$ is the mean impurity distance. In the opposite limit, $\xi \ll l_{imp}$, the impurity moments fluctuate independently, and their response simply adds up. Hence, observing fractional Curie response of independent impurity moments is possible at elevated T and small n_{imp} [9]. Note that elevated fields which induce $l_h \ll l_{imp}$ also lead to an effective decoupling of multiple impurity moments, which, however, are polarized in this limit. The spin rearrangement predicted to occur inside the plateau phase for overcompensated impurities is detectable by local probes like NMR, and also via an order-n_{imp} jump in the bulk magnetization.

Conclusions.—For impurities in noncollinear magnets, our main result is a partial screening of the impurity magnetic moment, leading to a fractional Curie response at low temperatures in the 2D case. We have evaluated the vacancy moment for the spin-S triangular-lattice AFM in a $1/S$ expansion, but we expect our qualitative results to be valid for any frustrated AFM with a noncollinear ground state (which is unique up to global spin rotations).

Our predictions could in principle be verified by large-scale numerical studies in analogy to Refs. [5,7]; however, quantum Monte Carlo approaches are plagued by the sign problem which is serious for most frustrated AFMs.

On the experimental side, one can expect the physics described here to be generically realized, as Curie tails in $\chi(T)$ due to impurities are routinely observed in magnets. A quantitative analysis of these tails in samples with a known concentration of impurities would allow one to extract the fractional moment size m (in a regime where interactions between the impurity moments are small); our prediction is $m \ll S$ in contrast to the behavior in collinear magnets.

An interesting open question is how the fractional moment advocated here evolves upon approaching a quantum critical point of the bulk magnet, where at criticality a universal fractional response is expected. Our results also call for investigations of vacancies in frustrated collinear magnets where vacancies may induce noncollinear spin textures in order to reduce frustration.

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