Quasispin Glass in a Geometrically Frustrated Magnet

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The spin glass state in the spinel $ZnCr_{2(1-x)}Ga_{2x}O_4$ is studied with magnetization and specific heat for $x < 0.05$. The freezing temperature is independent of disorder, despite a two-level-like density of states that varies linearly with x. This relationship implies the energy scale for freezing is independent of disorder, in contrast to mean field theories of spin glass. We suggest that the degrees of freedom are shielded spin vacancies, quasispins, which interact via an emergent long-range force mediated by the frustrated spin background.

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In geometrically frustrated (GF) magnets, long-range antiferromagnetic (AF) order occurs not at the Néel temperature, T_N, expected from mean field theory, but at a temperature at least an order of magnitude lower [1]. When the suppression of T_N is complete, spin liquid or spin ice states appear [2]. Early studies of GF magnets showed that a spin glass (SG) phase often occurs in materials with low quenched disorder [3,4]. While Villain predicted the existence of a SG state with zero quenched disorder [5], there are to date no experimental examples of such a system—all GF SG systems have been shown to possess some amount, if extremely small, of quenched disorder. Nevertheless, the low level of disorder in GF magnets implies the existence of SG phenomena in a qualitatively different regime of disorder than in canonical SG materials, which are highly disordered either structurally or chemically [6]. Specifically for GF magnets, as we show below, a physical description is needed for the sparse degrees of freedom that undergo SG freezing in the presence of a dense background of correlated spins.

In this Letter we study the evolution of AF order and SG freezing in the *B*-site spinel $ZnCr_{2(1-x)}Ga_{2x}O_4$ [ZCGO(x)] at very low density of magnetic ion vacancy, $x < 0.05$. Specific heat $C(T)$ and dc-susceptibility $\chi(T)$ data confirm the existence of a SG state coexisting with the AF state. We find that this SG state, previously observed [7] for $x > 0.1$, persists to an order of magnitude lower defect density. Most importantly, however, below $x \sim 0.05$, the freezing temperature, T_F, is independent of disorder: $\partial T_F/\partial x = 0$ for $x < 0.05$. These results suggest that the degrees of freedom undergoing SG freezing in ZCGO(x) are not simple orphan spins [8] interacting via a short-range force but rather spin vacancies that are magnetically shielded by the surrounding spins. This result is also suggested in recent theories [9–11], but important differences between theory and phenomenology exist.

Among the many GF magnets available for a detailed study of SG behavior at low defect concentration, the *B*-site spinel ZCGO(x) has several desirable features. The $x = 0$ pure phase has a Weiss temperature of $\theta_W \cong 400$ K and an easily accessible Néel temperature of $T_N = 12$ K. The Cr^{3+} ion with $S = 3/2$ is readily substituted with nonmagnetic Ga^{3+}, whose ionic radius differs from Cr^{3+} by less than 1%, thus producing little strain in the lattice. In previous dilution studies, Fiorani *et al.* showed that for $x = 0.10$ and 0.15, a SG state exists well below T_N [7]. Most importantly, the Néel state is characterized by the formation of a 3D spin-Peierls gap of 4.5 meV [12]. Thus, unlike most other GF magnets, which have either spin-liquid or spin-ice states, ZCGO(x) has vanishing low-temperature entropy, potentially allowing a SG density-of-states signature to be discernible in specific heat measurements.

The samples used here were carefully synthesized as ceramic powders for $x = 0.00$, 0.01, 0.02, 0.03, 0.04, 0.05, as well as for several other concentrations up to $x = 0.4$. The metal oxides, ZnO_2 [Alfa Aesar (AA) 99.99%], Cr_2O_3 (AA 99.97%), and Ga_2O_3 (AA 99.99%), were mixed stoichiometrically at the 2.5 gram scale. The powders were ground in an agate mortar and then pressed into pellets using a die with a tungsten liner and anvil. The samples were fired in three intervals, 1000 °C, 1100 °C, and 1250 °C for 16 hr with each firing. The samples were reground and pellets were made between each firing. X-ray diffraction confirmed the purity of the compounds and showed a lattice parameter vs x of $a = 8.3308 + 0.01499x$ Å with a standard deviation of 0.00427 Å. Thus the variation in lattice parameter over the range of the present experiments is at the resolution limit. Susceptibility (χ) and specific heat (C) measurements were performed using Quantum Design platforms. Data in zero-field cooling (ZFC) conditions were obtained on heating after first cooling to 2 K in zero magnetic field and then applying 5000 Oe. Field-cooled (FC) data were obtained on cooling after the same field was applied. To facilitate thermal equilibration for specific heat, the powders were reground and cold sintered with fine Ag powder, whose contribution was measured separately.

Previous thermodynamic studies of ZCGO(x) focused on the full phase diagram for $x = 0$ and $0.05 \leq x \leq 0.6$ [7], while here we concentrate on $0 \leq x \leq 0.05$. Figure 1(a) shows $\chi^{-1}(T)$ for several different samples between $x = 0$ and 0.15. The high-temperature data sets exhibit a uniform offset from each other, but share a common slope, indicating mean field behavior of $\theta_W(\sim 400$ K) and effective moment $\mu_{\mathrm{eff}}(\sim 3.9\mu_B)$. We note that $\chi^{-1}(T)$ below 50 K exhibits a transition from an upturn for $x < 0.03$ to a sharp downturn $T \sim 8$ K for $0.04 \leq x \leq 0.10$, to a smooth downturn for $x > 0.1$, the latter of which is a common feature among GF SG materials. In the present work we focus on the first part of the transition. The smooth downturn has been discussed previously as a generic feature of GF magnets due to so-called "orphan spins," which we discuss below. The specific heat for several samples is shown in Fig. 1(b). The first-order transition at $T_N = 12.8$ K for $x = 0$ in crystals is seen as a second-order transition lambda peak for $x \geq 0.01$ with T_N shifting to lower values for increasing x. The replacement of the first-order latent heat by a second-order effect is likely to be a finite size effect of the polycrystalline grains.

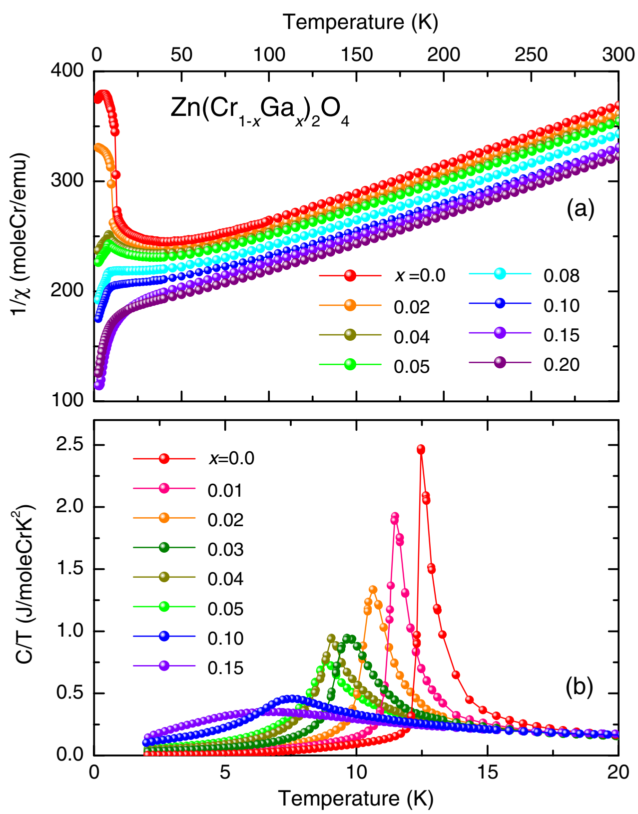

FIG. 1 (color online). (a) Susceptibility of $ZnCr_{2(1-x)}Ga_{2x}O_4$ obtained in field-cooled mode at 5000 Oe for various x values over a wide temperature range. (b) Specific heat at low temperature, showing the switch from a first-order transition at $x = 0$ (crystal) to second-order transition for finite x.

The low-field dc magnetization for samples with $0 \leq x \leq 0.05$ is shown in Fig. 2. In all samples we see the characteristic $\partial^2 M/\partial T^2 = 0$ signature of an AF transition, which coincides with the values for which $\partial C/\partial T = 0$. Below T_N a spin freezing temperature, T_F, is observed, as evidenced by the sharp bifurcation between ZFC and FC data. We have verified that this bifurcation temperature is field dependent—for both $x = 0.02$ and 0.04, this temperature is reduced from 7 K in 5000 Oe to roughly 4 K in 50 000 Oe. In Fig. 3(a) we show the difference in $M(T)$ between FC and ZFC conditions, scaled by the zero-temperature extrapolated value of the frozen magnetization, M_F. Even the nominally pure material ($x = 0$) shows a frozen moment, which we interpret as evidence for a small amount of disorder, presumably removable with longer synthesis times. We note that the temperature axis has *not* been scaled and while the spin glass transition becomes broader for samples with lower defect concentrations, T_F is independent of x. This is the central result of the paper.

Schiffer and Daruka showed that $\chi(T)$ of GF magnets diluted with nonmagnetic impurities can be described as the sum of a Curie-Weiss term from the majority of spins and a Curie susceptibility from free, defect-induced orphan spins [8] as mentioned above. In the orphan-spin model, these free spins possess the moment of the constituent magnetic ion and, while the Curie constant of the orphans is found to be linearly proportional to defect density for several compound families, the ratio of orphans to defects, R_{OD}, is significantly less than unity. For example, in the kagome compound $SrCr_{9x}Ga_{12-9x}O_{19}$ [SCGO(x)], $R_{\mathrm{OD}} = 0.160 \pm 0.02$ over the range $0.11 \leq x \leq 0.61$. In the

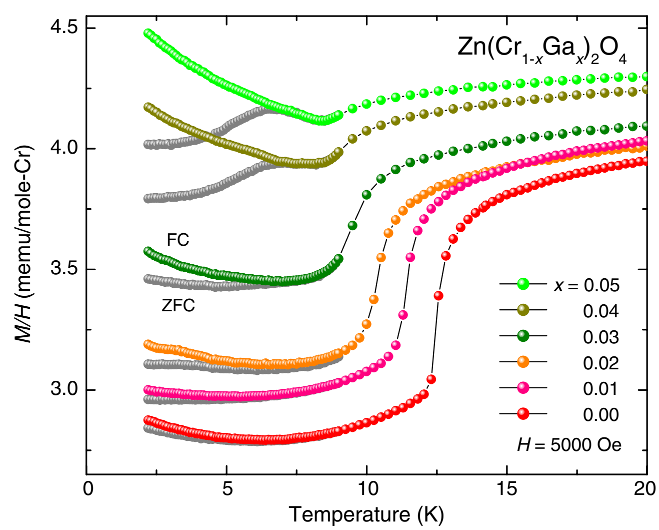

FIG. 2 (color online). dc magnetization for $Zn_{(1-x)}Ga_{2x}O_4$ for $x = 0.00$, 0.01, 0.02, 0.03, 0.04, and 0.05. Colored symbols correspond to data collected in FC conditions, while gray symbols indicate zero-field cooling. The frozen magnetization $M_F = (\mathrm{MFC\text{-}MZFC})_{T\to 0}$ increases with x, but the spin glass freezing temperature T_F, defined as the bifurcation point between FC and ZFC curves, is constant.

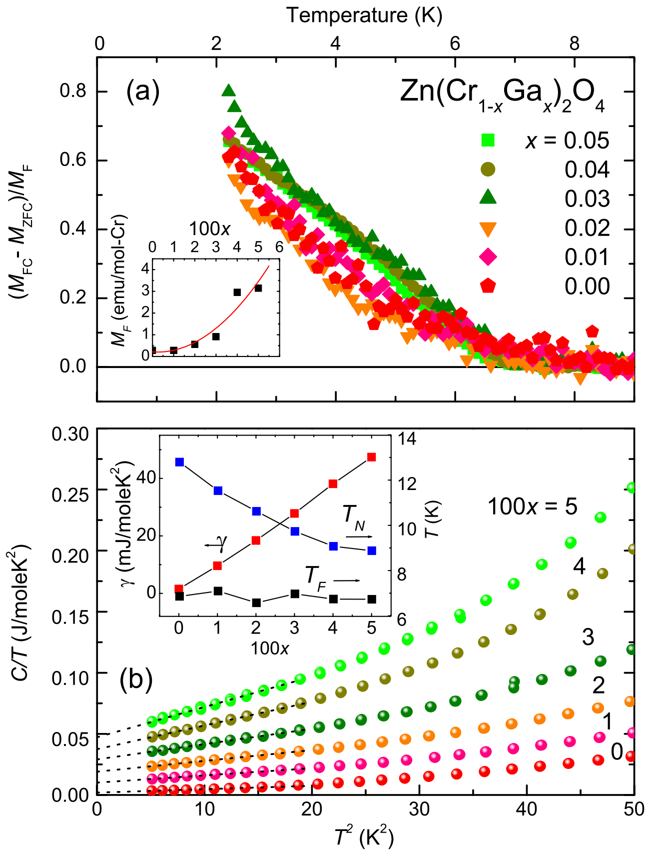

FIG. 3 (color online). (a) Difference in magnetization measured in FC and ZFC conditions, scaled by the zero-temperature extrapolated value M_F. Deviation from the line $y = 0$ indicates spin glass behavior. Note that the horizontal axis displays temperature and has not been scaled. The spin glass transition is broader for samples with low defect concentrations, but the freezing temperature is independent of x. (b) Specific heat divided by temperature versus temperature squared of $ZnCr_{2(1-x)}Ga_{2x}O_4$ for $0.0 \leq x \leq 0.05$. The dashed lines are linear fits to the data for T^2 between 5 and 20 K^2. The linear-in-T coefficient at $T = 0$ is extracted from these fits. (Inset) Néel temperature (T_N), freezing temperature (T_F), and specific heat γ coefficient of $ZnCr_{2(1-x)}Ga_{2x}O_4$ for $0 \leq x \leq 0.05$.

present case of ZCGO(x), for the sample with an unambiguous downturn in $\chi(T)^{-1}$ ($x = 0.2$), $R_{\mathrm{OD}} = 0.01$. The orphan model clearly demonstrates the existence of two independent spin populations, but it does not explain $R_{\mathrm{OD}} \neq 1$. In addition, there is no obvious structural reason why, in SCGO(x), one orphan might be produced for every six defects. A possible solution is suggested by Sen, Damle, and Moessner, who show how a frustrated background can magnetically screen a spin defect [13] and who find for SCGO(x) an effective halving of the spin associated with a vacancy. In this picture, instead of multiple defects producing one orphan with a full $s = 3/2$ moment, each defect produces a reduced or shielded moment, a "quasispin." The quasispin is formed by the response of the frustrated spins surrounding the vacancy, so the precise amount of shielding will differ among GF compounds. Indeed, for SCGO(x), using $S/2$ instead of S recovers only half of the shortfall between inferred quasispin density and x, the difference arising perhaps due to simplifications of both crystal structure and range of superexchange interactions in the theory. The near constancy of spin shielding in SCGO(x) as a function of x argues that the quasispin moment has a well-defined form factor and that interactions among quasispins are systematically related to the vacancy density. The chemical similarity of SCGO(x) and ZCGO(x) suggests that this picture can be used to understand interactions at very low defect density in the latter compound.

It is likely that all known GF materials with clearly identified quasispins eventually exhibit a SG transition at low enough temperature. The most fundamental aspects of this transition, namely the dependence of frozen moment and T_F on defect concentration, are not understood in these systems however. An example was found by Martinez *et al.*, who showed in SCGO(x) that T_F is *inversely* related to x despite a frozen moment that grows with x. Given that x is proportional to the quasispin density, this behavior is in contrast to that of conventional spin glass, such as $Eu_xSr_{1-x}S$ [14], AuFe [15], CuMn [16], and others [17] where T_F varies in proportion to the spin density. It is possible to argue that, instead of x, one should consider the spin density—not the quasispin density—as the degree of freedom subject to a random potential and thus controlling T_F. This would fail to explain, however, the behavior of the frozen moment with x. Thus, greater consistency among the observations is obtained in a picture of quasispins as the source of SG freezing in GF systems. The remaining puzzle is then the finite value of T_F near zero quasispin density and, in ZCGO(x), the constancy of T_F for small x.

To support the claim of a SG state with an anomalous relationship between T_F and quasispin density, one needs to know, in addition to the magnetic response, the density of states of the low-energy magnetic spectrum. Anderson, Halperin, and Varma argued that the low-energy spectrum causing the linear $C(T)$ in SG systems is due to two-level systems resulting from spin orientation states in a random potential [18]. Thus, a test of the existence of a random potential related to SG response would be the observation of a linear term in $C(T)$ and its relationship to a controlled level of quenched disorder. For most GF systems, a small linear term is not observable due to the dominance of the spectral weight from the fluctuating spin majority. Because of its spin-Peierls gap, however, ZCGO(x) provides an exception. In Fig. 3(b) we present low-temperature $C/T(T)$ versus T^2 data for $0 \leq x \leq 0.05$. We see that the activated specific heat is replaced by a $C \propto T^3$ AF magnon term, reflecting the appearance of the lambda anomaly. The T^3 term grows with x, as expected for T_N decreasing with x. Although a magnon term appears with x, it remains small enough to allow the clear observation of a linear term, $C = \gamma T$, given by the $T = 0$ intercept. The γ coefficient is plotted in the inset to Fig. 3, along with T_N and T_F, as a function of x. A linear term has no simple explanation in a weakly diluted system where the low-energy spectrum will still be defined by its Goldstone modes. Instead, given the observed SG freezing and the putative increase of quasispin density with x, we postulate that the linear term is due to two-level systems associated with SG freezing. We note that it is not uncommon in SG for the linear term to be well developed above T_F [19].

The observation of a linear term in $C(T)$ in ZCGO(x) reinforces the notion of a defect-induced "quasispin glass" state. As x increases from zero, the linear term from $C(T)$ grows linearly with x, while the dependence of frozen moment on x seems to follow a quadratic dependence, possibly the result of an effective microscopic moment with a many-body origin. The concept of quasispins is well motivated—they are essentially the response of a many-body spin singlet to the introduction of spin vacancies, similar in spirit to the behavior of uncompensated spins at the boundary of an antiferromagnet. It is natural, also, that these defects not possess the free moment of the missing spin, since the moment is formed by polarization of the surrounding spins. What is unusual here is the interaction between quasispins, which is revealed by their SG freezing transition, and its x independence. One consequence of this independence is that of a magnetic system at near-zero disorder that is critically unstable to SG freezing. At our lowest value of $x = 0.01$, defects are separated by $x^{-1/3} \sim 5$ lattice constants, a distance over which the superexchange interaction between spins should decrease dramatically [20], yet there is little change in the many-body energy scale, $\propto T_f$. Recent theoretical work predicts that quasispins in a background of a classical spin liquid, more applicable to SCGO(x), interact with a strength that decays exponentially beyond a thermal correlation length [21]. The present results suggest that defects separated by macroscopic distances can interact substantially, and it would be of interest to explore whether the stiffness of the background AF state can mediate such a long-range interaction. In particular, this effect might be related to the Dirac strings that link monopoles in spin ice, connecting defects through entropic sampling [22–24]. Interactions such as the type identified here might provide a basis for information processing via spin interactions without the need for charge motion.

In conclusion, we have observed SG freezing in both $M(T)$ and $C(T)$ measurements of ZCGO(x) at low x. The freezing temperature, T_F, is independent of quasispin density, a result that implies an interaction range beyond that describable by mean field theories of SG systems. Clearly more experimental work is needed to explain the interaction between sparse defects in GF magnets.

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