We consider doping of non-magnetic impurities in the spin-1/2, 1/5-depleted square lattice. This structure, whose undoped phase diagram offers both magnetically ordered and spin-liquid ground states, is realized physically in CaV$_4$O$_9$. Doping into the ordered phase results in a progressive loss of order, which becomes complete at the percolation threshold. By contrast, non-magnetic impurities introduced in the spin liquids create a phase of weak but long-ranged antiferromagnetic order coexisting with the gapped state. The latter may be viewed as a true order-by-disorder phenomenon. We study the phase diagram of the doped system by computing the static susceptibility and staggered magnetization using a stochastic series-expansion quantum Monte Carlo technique.

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Doping of low-dimensional quantum spin liquids leads to a variety of phenomena, including unconventional superconductivity when localized spins are replaced by mobile holes, and effective random spin systems, whose low-temperature properties are dominated by large effective spin degrees of freedom, in the presence of static impurities. Such low-temperature phases have been observed recently in quasi-one-dimensional (1d) spin systems. In the two-leg ladder compound Ca$_{14-x}$Sr$_x$Cu$_{24}$O$_{41}$, a superconducting transition has been measured at high pressure. Zn-doping of the quasi-1d ladder material SrCu$_2$O$_3$, and of the dimerized chain CuGeO$_3$, yields low-temperature phases with weak antiferromagnetic (AF) order, arising from effective couplings of random strength and sign between unpaired spins.

The question naturally arises of whether similar phenomena can be expected in quasi-2d systems. There are several prominent examples of 2d spin liquids, including (i) structurally frustrated materials, such as SrCu$_2$(BO$_3$)$_2$, containing AF coupled spin-1/2 triangles, (ii) interaction-frustrated systems, such as the J$_1$-J$_2$ Heisenberg model on a square lattice in the gapped regime around J$_2$/J$_1 = 0.5$, and (iii) structurally decoupled materials, such as the 1/5-depleted AF square lattice formed by the spin-1/2 vanadium ions of CaV$_4$O$_9$ (Fig. 1). These systems have resonant-valence-bond (RVB) ground states with a finite spin gap. Their AF correlation length is finite, decreasing with increasing gap size, and the low-temperature uniform susceptibility is exponentially activated. We find that non-magnetic impurities in such systems act to induce a long-ranged AF order, which exists on the subsystem of uncombined spins, and coexists with the dominant, gapped phase of the spin liquid. This order arising from disorder is the central result of our analysis. As in the quasi-1d case, its origin lies in the unfrustrated nature of the exponentially weak interactions between unpaired spins introduced when impurities break the RVB singlet units in a bipartite lattice: these are ferromagnetic when the free spins lie on the same sublattice, and AF for opposite sublattices.

FIG. 1. The 1/5-depleted square lattice. Intra-plaquette couplings $J$ are indicated by solid lines, and inter-plaquette couplings $J'$ by dashed lines.

In this work we consider the effects of non-magnetic impurities in the 1/5-depleted square lattice geometry (Fig. 1), motivated by the structure of CaV$_4$O$_9$, and by the possibility of doping this particular material with Ti. The set of superexchange parameters required to model CaV$_4$O$_9$ has been found to be dominated by the frustrating, next-neighbor AF interaction, which to a reasonable approximation allows the real system to be considered as an ensemble of weakly coupled metaplaquettes (a square of side $\sqrt{2}$ larger than the nearest-neighbor spacing) of 4 $V^{4+}$ spins. We present first a theoretical analysis for the unfrustrated system, which contains all the qualitative features we wish to address, and return thereafter to the experimental situation.

The effective magnetic Hamiltonian,

$$H = J \sum_{\square} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{\square-\square} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

is a spin-1/2 AF Heisenberg model with $J$ is the intra-
plaquette and \( J' \) the inter-plaquette exchange coupling constant, in which the sums marked by \( \square \) and \( \square - \square \) run over nearest neighbors within and between the plaquettes. We will explore the full parameter range \( J'/J \geq 0 \), which contains a spin-liquid, plaquette RVB (PRVB) phase for \( J'/J \lesssim 0.93 \), an AF-ordered phase in the approximate interval \( J'/J \in [0.93, 1.68] \), and a further spin liquid, the dimer RVB (DRVB) phase, at larger \( J'/J \gtrsim 1.68 \) [14]. Expansions about the plaquette and dimer limits will be compared with simulations using the stochastic series-expansion quantum Monte Carlo (SSE QMC) algorithm [15], on 1/5-depleted, square lattices of up to 30×30 sites, and at temperatures down to \( T = 0.02J \). This algorithm involves expansion of the partition function in inverse temperature, employs local and global system updates, and is significantly more efficient than conventional QMC schemes. In the presence of non-magnetic impurities, ensemble averages over typically 500 random realizations were taken to ensure numerical errors smaller than the symbol sizes in Figs. 2 and 3.

![Figure 2](image_url)

**FIG. 2.** (a) Ensemble of decoupled plaquettes: temperature dependence of \( T\chi(T) \) at impurity concentrations \( \rho = 0.0, 0.05, ..., 0.4 \). Solid lines are exact results, and symbols are QMC simulations. \( T\chi(T) \) is normalized by the number of spins in the system. (b) As (a), for decoupled dimers. Insets: dependence of zero-temperature Curie constant \( C \) on \( \rho \). Solid lines denote decoupled plaquette and dimer limits, and dashed lines the results from perturbation expansion with (a) \( J'/J = 0.1 \) and (b) \( J'/J = 0.1 \).

Considering first an ensemble of completely decoupled 4-spin plaquettes, a small number of randomly placed, non-magnetic dopants creates free spin-1/2 moments, corresponding to the doubly degenerate \( S^z = \pm 1/2 \) ground state of 3-spin Heisenberg clusters [16]. Each of these “pruned” plaquettes gives a paramagnetic contribution to the susceptibility \( \chi(T) \) at low temperature. Upon further doping, clusters containing \( n < 3 \) spins are also created, with distributions \( P(n) \) [7], but only unpaired spins contribute to the low-\( T \) Curie tail. Fig. 2(a) shows \( T\chi(T) \) for various impurity concentrations. Without impurities, this quantity extrapolates to zero as the temperature is lowered, indicative of the spin gap in the clean system. With impurities, the zero-temperature Curie constant is given by

\[
C = \lim_{T \to 0} [T\chi(T)] = \frac{1}{4} \left( \frac{P(1) + 1/3P(2) + P(3)}{1 - \rho} \right),
\]

and depends on concentration as shown in the inset of Fig. 2(a). For all \( \rho \), three distinct temperature regimes are observed. (i) For \( T \gg \Delta_{\text{max}} \) (not shown) the spins are essentially independent, each contributing \( \frac{\mu^2}{4k_B} \) to \( C \). \( \Delta_{\text{max}} = 1.5J \) is the largest energy level separation in any cluster. (ii) For \( \Delta_{\min} < T < \Delta_{\text{max}} \), some spins freeze into singlets, gradually reducing the overall magnetic response by a factor of approximately \( \rho \) as \( T \) decreases. \( \Delta_{\min} = 0.25J \) is the smallest energy spacing in any cluster. (iii) For \( T < \Delta_{\min} \), plateaus appear in \( T\chi(T) \) when the contributing clusters reach their ground states.

With finite inter-plaquette coupling, spin-1/2 moments on adjacent plaquettes may combine to form new RVB clusters with smaller spin gaps, involving larger numbers of spins. In the susceptibility, this effective recombination reduces \( C \) from its value for decoupled, pruned plaquettes, further suppressing \( T\chi(T) \) at very low \( T \). This cluster formation may be quantified from the distribution functions for neighboring plaquettes, evaluated perturbatively in \( J'/J \). These functions have a non-trivial dependence on the relative positions of the dopant vacancies in adjacent clusters. Close to the PRVB limit, the inset of Fig. 2(a) illustrates this reduction of \( C \), which is strongest at smaller \( \rho \) where more spins are available to form larger RVB clusters. Fig. 2(b) shows analogous results for the DRVB limit.

In Fig. 3, the \( T \)-dependence of the uniform susceptibility is shown at various doping levels in the three regimes of \( J'/J \). In Figs. 3(a) and (c), results from SSE QMC simulations (symbols) are plotted along with those
from perturbative expansions about the limits of completely decoupled plaquettes and dimers (solid lines). At \( \rho = 0 \), \( T_{\chi}(T) \) clearly displays activated behavior in the two gapped regions, but a linear form in the long-range-ordered phase.

**PRVB:** At small \( \rho \), a plateau develops in \( T_{\chi}(T) \) at low temperatures, \( T \sim \Delta_{\text{min}} \), indicating a freezing of the plaquettes into their ground state configurations. For a finite inter-plaquette coupling, the additional reduction of \( C \) observed at ultra-low temperatures indicates that the plaquette spins become correlated on an ultra-low energy scale \( J_{\text{eff}} \). At sufficiently small \( \rho \), this energy can be estimated \[ \xi_{\text{AF}}(T) \] by assuming RKKY-like interactions between the impurity spins, yielding

\[
J_{\text{eff}} \approx J \exp \left( -\frac{(1 - \rho)}{\xi_{\text{AF}}(\rho, T)} \right),
\]

where \( \xi_{\text{AF}} \) is the short-range AF correlation length in the spin-liquid regime. Approaching \( T = 0 \), the Curie constant extrapolates to \( C = \rho/12 \), a reduction of roughly 1/3 compared to the plateau value \[ \xi_{\text{AF}}(0, T) \]. At larger impurity concentrations, the onset of this ultra-low-\( T \) regime moves up, consistent with \( T \sim J_{\text{eff}} \) (Eq. 3). At still higher doping, the picture of isolated impurity spins, and RKKY interactions mediated via the spin-liquid RVB background, breaks down. The regimes of moment formation and correlation overlap, and the plateau feature in \( T_{\chi}(T) \) becomes less pronounced. On doping towards the percolation threshold \( \rho_{c} \), the magnetic response is dominated by the largest percolation clusters, typically containing several pruned plaquettes. From simulations in the classical limit \[ \xi_{\text{AF}} \], we find \( \rho_{c} = 0.26(9) \) for the 1/5-depleted lattice. Studies of percolation thresholds in regular square lattices \[ \xi_{\text{AF}} \] suggest that the value of \( \rho_{c} \) for the quantum spin system differs by less than 1% from the classical value \( \rho_{c} = 0.407 \). In this regime the plaquette plateaus disappear, a trend accentuated as the long-range-ordered regime is approached \( (J'/J \to 0.93) \), where \( \xi_{\text{AF}} \) increases and (Eq. 3) the onset of the ultra-low-\( T \) regime moves to lower energies.

**DRVB:** As in the PRVB regime, non-magnetic impurities introduce local moments in the gapped, spin-liquid state. A dimer “plateau” is reached at \( T \sim J_{\text{eff}} \), and further moment recombination occurs at ultra-low temperatures, leading to an additional reduction of \( T_{\chi}(T) \) as \( T \to 0 \). The plateaus disappear on approaching the transition to the AF phase, \( J'/J \to 1.68^{+} \).

**AF:** In contrast to gapped spin liquids, isolated, non-magnetic impurities do not introduce quasi-free local moments, because all spins remain aligned with the staggered AF background \[ \xi_{\text{AF}} \]. However, the low-temperature susceptibility does have a divergent contribution, albeit with \( C \) rather smaller than in the spin liquids at given \( \rho \), arising from free moments isolated from the AF system by dopants.

**FIG. 4.** Staggered magnetization as a function of impurity doping for coupling ratios \( J'/J \) in the PRVB (dashed), ordered (solid) and DRVB (dotted) regimes. The inset shows the evolution of \( m_{s} \) with \( J'/J \) at a fixed doping \( \rho = 8\% \); arrows indicate the phase boundaries of the pure system.

Returning to the issue of order by disorder, our simulations close to the AF regime of the pure system show that introduced moments do not simply recombine into larger RVB clusters, but form a long-range-ordered AF network at ultra-low temperatures. This doping-induced long-range order is best characterized by the staggered magnetization \( m_{s} \), which is shown in Fig. 4 as a function of non-magnetic impurity doping within each of the distinct phases of the system. As also in Fig. 5, these data were obtained by finite-size extrapolation at ultra-low temperatures, and thus represent the thermodynamic limit. In the long-range-ordered AF regime, we see that random static vacancies simply reduce the average staggered magnetization, driving it to zero beyond the percolation threshold \( \rho_{c} = 0.26(9) \). By contrast, in the spin-liquid regimes the doping-induced moments have effective interactions mediated by the RVB background, which are unfrustrated \[ \xi_{\text{AF}} \]. A long-ranged order may then be expected to emerge from the large-spin clusters at zero temperature. Indeed, the resulting AF network has an extensive staggered magnetization, which peaks around \( \rho = 0.08 \). This ordered AF phase coexists \[ \xi_{\text{AF}} \] with the gapped, spin-liquid state of the majority, undoped plaquettes or dimers (Fig. 3). The mechanism leading to this moment formation may be viewed as an order-by-disorder phenomenon. The inset of Fig. 4 shows the staggered magnetization as a function of the coupling ratio at the maximal doping. The disorder-induced, ordered moments in the spin-liquid regions are significant over a wide range of \( J'/J \), and become large near the phase boundaries of the pure system, where they cross continuously to the full moment of the intrinsically ordered regime.

Our results are summarized by the phase diagram in Fig. 5, where the shading illustrates the strength of the staggered magnetic order. The solid lines depicting phase boundaries may not be taken as true transitions at any finite doping: impurity-induced AF order within a spin li-
uid crosses smoothly to impurity-suppressed order within an AF, with no vanishing order parameter. Impurities may be considered as damaging both to the AF ordered phase, and the quantum spin liquid phase.

Experimentally, the situation in CaV$_4$O$_9$ may be more complex than that simulated here. Inelastic neutron scattering measurements [2] and subsequent refinements by comparison with simulations [3], show that the magnetic system is composed of metaplaquettes with $J_2 = J = 14$meV, which interact with their neighbors via mutually frustrating couplings $J_1 = J'_1 = 0.49$J, and with next neighbors by a further weak coupling $J'_2 = 0.25$J. Because of the frustrated nature of the subdominant interactions $J_1$, it would appear reasonable that the effective coupling $J'$ between metaplaquettes is small, and thus that the physical system is well in the PRVB regime; this deduction is consistent with the robust spin gap, $\Delta = 9.4$meV, of CaV$_4$O$_9$. Doping with non-magnetic impurities could be effected by random replacement of some spin-1/2 V$^{4+}$ ions by non-magnetic Ti$^{4+}$. Our simulations of the uniform susceptibility and staggered magnetization suggest that the weak AF order induced on doping should be detectable in 5-10% Ti-doped CaV$_4$O$_9$, by measurements of $\chi(T)$, Knight shift or magnetic Bragg scattering.

In summary, we have analyzed the behavior on doping by non-magnetic impurities of the spin-liquid and ordered AF phases of the Heisenberg model on a 1/5-depleted, square lattice of spins $S = 1/2$. In the spin liquids, introduction of impurities creates effectively free spins which combine through exponentially weak interactions to create a long-ranged AF order at $T = 0$, coexisting with the gapped, spin-liquid phase. In the intrinsically AF regime, impurities cause a progressive destruction of the long-range order until it vanishes at the percolation threshold. The SSE QMC algorithm which we employ proves to be a powerful and efficient means of simulating the properties of a spin system; these attributes are particularly important when many realizations of random impurity distributions are required. Finally, the unique magnetic plaquette structure of CaV$_4$O$_9$ provides a well-defined starting point for studying the effect of non-magnetic impurities in spin liquids, and provides valuable insight for other 2d RVB compounds, such as frustrated Heisenberg systems, where a recombination of pruned bonds into new RVB clusters is also expected to occur.

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![FIG. 5. Phase diagram for the 1/5-depleted, square-lattice antiferromagnet with doping by non-magnetic impurities.](image-url)

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