Magnetism in spin models for depleted honeycomb-lattice iridates: Spin-glass order towards percolation

Eric C. Andrade and Matthias Vojta
Institut für Theoretische Physik, Technische Universität Dresden, 01062 Dresden, Germany
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Iridates are characterized by a fascinating interplay of spin-orbit and electron-electron interactions. The honeycomb-lattice materials \( \text{A}_2\text{IrO}_3 \) (A=Na,Li) have been proposed to realize pseudospin-1/2 Mott insulating states with strongly anisotropic exchange interactions, described by the Heisenberg-Kitaev model, but other scenarios involving longer-range exchange interactions or more delocalized electrons have been put forward as well. Here we study the influence of non-magnetic doping, i.e., depleted moments, on the magnetic properties of experimentally relevant variants of the Heisenberg-Kitaev and Heisenberg \( J_1-J_2-J_3 \) models. We generically find that the zigzag order of the clean system is replaced, upon doping, by a spin-glass state with short-ranged zigzag correlations. We determine the spin-glass temperature as function of the doping level and argue that this quantity allows to experimentally distinguish the different proposed spin models when the doping is driven across the site percolation threshold of the honeycomb lattice.

The interplay of strong spin-orbit coupling and electronic correlations is at the heart of many recent developments in condensed-matter physics, involving, e.g., correlated topological insulators, fractional Chern insulators, and spin-orbit Mott insulators [1-5]. On the materials side, oxides with partially filled 5d shells, such as iridates and osmates, are considered promising candidates in order to realize the theoretically proposed phenomena.

In this context, the insulating iridates \( \text{A}_2\text{IrO}_3 \) (A=Na,Li) have attracted enormous attention over the past few years [6-11]. In these materials, the \( \text{Ir}^{4+} \) ions are arranged in a layered honeycomb-lattice structure. Due to the combined effect of strong spin-orbit coupling and Coulomb interactions, the \( \text{Ir} 5d^9 \) states, with one hole in the \( t_{2g} \) manifold, have been proposed to realize \( J_{\text{eff}} = 1/2 \) spin-orbit Mott insulators [12-13], similar to other layered iridates [4,5]. Furthermore, Ref. [14] suggested that the magnetism of the \( J_{\text{eff}} = 1/2 \) moments is dominated by strongly spin-anisotropic compass interactions, which by itself lead to the spin-liquid model on the honeycomb lattice proposed by Kitaev [15]. Supplemented by an additional spin-isotropic Heisenberg interactions, the resulting Heisenberg-Kitaev (HK) model has been shown to host both spin-liquid and conventionally ordered phases [14,16,21].

Experimentally, both \( \text{Na}_2\text{IrO}_3 \) and \( \text{Li}_2\text{IrO}_3 \) have been found to undergo a magnetic ordering transition at \( T_N \simeq 15 \text{K} \) [9,10]. In \( \text{Na}_2\text{IrO}_3 \) the low-temperature spin configuration has been identified as collinear “zigzag” order [9,10], with ferromagnetic zigzag chains arranged antiferromagnetically in the honeycomb plane. This state is indeed a ground state of the HK model, where it results from a competition of antiferromagnetic Kitaev and ferromagnetic Heisenberg interactions [19]. Alternatively, Heisenberg and HK models with longer-range interactions have been considered: specifically, a Heisenberg \( J_1-J_2-J_3 \) model with sizeable second and third-neighbor coupling has been found to describe the available data as well [9,22]. Finally, a more itinerant scenario in terms of molecular orbitals has also been proposed [24], although a detailed description of the magnetic properties in this model is lacking to date.

In this paper, we propose magnetic depletion, i.e., the random substitution of magnetic \( \text{Ir}^{4+} \) by non-magnetic ions, as a powerful tool to study the magnetism of \( \text{A}_2\text{IrO}_3 \) and to discriminate between the various proposed scenarios for magnetism. A key insight is that, within local-moment models, depletion will inevitably turn the zigzag ordered state into a spin (or spin-orbit) glass: Both the HK and \( J_1-J_2-J_3 \) models are frustrated, and the combination of disorder and frustration generically causes spin-glass behavior [24]. We calculate the freezing temperature, \( T_g(x) \), as function of doping level \( x \) and show that its behavior across the site-percolation threshold, \( x_p = 30.3\% \), strongly differs between the HK and \( J_1-J_2-J_3 \) models.

Models. We focus on two models which have been considered to describe the zigzag ordered state of \( \text{Na}_2\text{IrO}_3 \). The first is the HK model,

\[
\mathcal{H} = J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + 2K \sum_{\langle\langle ij \rangle\rangle} \vec{S}_i^\gamma \vec{S}_j^\gamma, \tag{1}
\]

the second the \( J_1-J_2-J_3 \) model

\[
\mathcal{H} = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle ik \rangle\rangle} \vec{S}_i \cdot \vec{S}_k + J_3 \sum_{\langle\langle\langle il \rangle\rangle\rangle} \vec{S}_i \cdot \vec{S}_l. \tag{2}
\]

Here, the sums run over pairs of nearest, second, and third neighbor sites, respectively, while \( \gamma = x, y, z \) in Eq. \( \mathcal{H} \) labels the three different links for each spin in a honeycomb lattice. The parameter regimes of interest are defined through the presence of zigzag magnetic order as realized in \( \text{Na}_2\text{IrO}_3 \) [9,10]. The HK model’s couplings may be parametrized as \( J = A \cos \phi \) and \( K = A \sin \phi \), where \( A \) is an overall energy scale. Its full phase diagram was first mapped out in Ref. [19] with the zigzag phase...
The honeycomb layers are spanned by the primitive lattice vectors with aperiodic stacking of the honeycomb structure. For A-B-type stacking of the honeycomb layers, the magnetic susceptibility is given by the HK model equations for unit-length spins on lattices of size \( L \times L \times L_z \), typically with \( L_z = L/2 \) and periodic boundary conditions. The honeycomb layers are spanned by the primitive lattice vectors \( \vec{a}_{(2)} = (3/2, \pm \sqrt{3}/2) \), with each unit cell containing two sites. Depletion is simulated by randomly removing a fraction \( x \) of spins, with \( x \) varying between 5% and 40%, with the total number of spins \( N_s = (1-x) \times 2L^2L_z \). We perform equilibrium MC simulations using single-site updates with a combination of the heat-bath and microcanonical (or over-relaxation) methods. We consider typically \( 5 \times 10^5 \) MC steps per spin for the measurements, after discarding an equal amount of steps for equilibration. To efficiently sample all spin configurations we also employ the parallel-tempering algorithm\(^{28,29} \). Disorder averages are taken over \( N_s \) samples, with \( N_s \) ranging from 1000 for \( L = 6 \) to \( N_s = 50 \) for \( L = 16 \). In all our results we set the Boltzmann constant \( k_B = 1 \) and quote all energies in units of \( J \equiv J_1 \), the nearest-neighbor Heisenberg exchange.

We extract the ordering (or freezing) temperature \( T_g \) from the crossing points of \( \xi(T) / L \) for different \( L \), according to the scaling law \( \xi(T) = f(L^{1/\nu}(T - T_g)) \), where \( \xi \) is a correlation length, \( f(x) \) a scaling function, and \( \nu \) the correlation length exponent. This procedure is especially suitable to detect spin-glass freezing, as shown in previous studies of the 3d Edwards-Anderson model\(^{30-32} \). The main source of numerical error in \( T_g \) is from the \( L \to \infty \) extrapolation of the crossing point location required for small \( L \).

The magnetic correlation length \( \xi_S \) is calculated from a fit of the static magnetic structure factor, \( S(q) \), close to the ordering wavevector \( \vec{Q} \) (the three independent \( \vec{Q} \) vectors corresponding to the zigzag order are \( (\hat{b}_1 + \hat{b}_2)/2, \hat{b}_1/2, \) and \( \hat{b}_2/2 \), where \( \hat{b}_{1(2)} = 2\pi(1/3, \pm 1/\sqrt{3}) \) are the reciprocal lattice vectors). Analogously, the spin-glass correlation length \( \xi_{SG} \) is obtained from the spin-glass susceptibility \( \chi_{SG} (q) = N_s \sum_{\alpha, \beta} \left[ \left\langle q^{\alpha, \beta} (\vec{q}) \right\rangle \right]_{av} \), where \( q^{\alpha, \beta} (\vec{q}) = N_s^{-1} \sum_i S^{(1)}_i \cdot S_i^{(2)} \), with \( (\vec{q}) \) the spin-glass order parameter. Here \( \alpha \) and \( \beta \) are spin components, \( (\vec{r}) \) denotes identical copies of the system (‘replicas’) containing the disorder configuration, \( \langle \cdots \rangle \) denotes MC average, and \( [\cdots]_{av} \) average over disorder.

**Clean HK model.** The 2d disorder-free HK model has been studied by exact diagonalization in Refs.\(^{13,19} \) by auxiliary-fermion functional renormalization group in Ref.\(^{17} \) and by classical MC simulations in Refs.\(^{20,21} \)

A comparison of the phase diagrams shows that the classical-spin HK model reproduces\(^{21} \) all phases of the spin-1/2 model except for the quantum spin liquid, with \( T = 0 \) phase boundary locations in reasonable agreement between quantum and classical models. The results in Refs.\(^{20,21} \) also indicate the presence of two thermal transitions upon cooling from the high-temperature paramagnetic phase to any of the low-temperature phases with semicircular order (as the zigzag phase). The system first enters a critical phase at \( T_u \), with power-law spin correlations, and a state with true long-range order is reached only below \( T_l < T_u \). This behavior parallels that of a six-state clock model in 2d\(^{33} \), as suggested by the sixfold degeneracy of the ordered states in the HK model.

For selected values of \( \phi \), we have verified that our MC simulations, applied to the 2d HK model (\( J_\perp = 0 \)), reproduce the results of Ref.\(^{21} \). In particular, the specific heat, Fig.\(^{2}a \), shows a broad peak far above both \( T_u \) and
in the same sample, Fig. 3. Moreover, the vacancies locally select specific stripe orientations [35], which ultimately leads to spin-glass behavior [24]. Since both models are frustrated, the introduction of vacancies locally results in the combination of disorder and frustration, in favor of spin-glass magnetism. However, the glassy temperature is strictly zero in two dimensions [37, 38], even in the case of Ising symmetry.

We have first studied the 2d case (\(J_z = 0\)) and found – in both models and at any \(x > 0\) – indications of neither conventional nor spin-glass order at finite temperature. This is expected: conventional order is suppressed, due to the combination of disorder and frustration, in favor of spin-glass magnetism. However, the glassy temperature is strictly zero in two dimensions [37, 38] even in the case of Ising symmetry.

For finite interlayer coupling, \(J_z/J = 0.01\), the situation changes, with sample results shown in Fig. 4. While conventional long-range order is absent for any \(x > 0\), spin-glass order emerges instead at low \(T\). The latter is signified by a well-defined common crossing point in \(\xi_S/L\) and a corresponding scaling, Fig. 4(c)-(d) [39]. In contrast, existing crossing points of \(\xi_S/L\) display a systematic downward shift with increasing \(L\), indicative of short-range zigzag correlations, Fig. 4(b). We note that we do not reach the limit \(L \gg \xi_S(T = 0)\) where crossing points would be absent entirely.

Short-range magnetic order also manifests itself in the specific heat, Fig. 4(a). The peak in \(C(T)\) is broad and occurs at a temperature considerably larger than the freezing temperature (here \(T_{peak} \approx 2T_g\)), indicating that this short-range order builds up at temperature considerably higher than \(T_g\). We stress that this behavior is a hallmark of glassy systems [29] [38], and it is, in principle, disconnected from the non-trivial behavior of the 2d disorder-free HK model [27], Fig. 2(a).

To account for the possibility of different (non-zigzag) dilution-induced magnetic ground state, we monitored \(S(\vec{q})\) in the reciprocal space, but (within our resolution) we detected peaks only at the \(\vec{Q}\) vectors corresponding to the zigzag order. However, these peaks grow slower than the system size, Fig. 4(b), again indicating static short-range magnetic order in the clean HK model for several system sizes \(L\). (a,c): 2d. (b,d): 3d with \(J_z/J = 0.01\). (a,b): Specific heat as a function of the temperature \(T\). (c,d): \(\xi_S/L\) as a function of \(T\). The vertical dashed lines indicate the position of \(T_1\) and \(T_N\) in the 2d and 3d cases, respectively.

Figure 2: Sample ground-state spin configuration of the classical HK model at \(x = 20\%\) depletion, with one \(L = 12\) layer shown. The arrows denote the \(x\) and \(z\) components of the \(\vec{S}\); the circles indicate the vacancy positions. The arrow lengths indicate the weight of the projection onto the \(x-z\) plane and the colors the in-plane orientation. Short-range zigzag order with glassy domain formation is visible. Inset: Ideal zigzag order with the spins aligned along \(S^z\).

Figure 3: MC results for the ordering into the zigzag state of the clean HK model for several system sizes \(L\). (a,c): 2d. (b,d): 3d with \(J_z/J = 0.01\). (a,b): Specific heat as a function of the temperature \(T\). (c,d): \(\xi_S/L\) as a function of \(T\). The vertical dashed lines indicate the position of \(T_1\) and \(T_N\) in the 2d and 3d cases, respectively.

Clean \(J_1-J_2-J_3\) model. We have also performed corresponding simulations for the \(J_1-J_2-J_3\) model. Here, \(T_N\) \(\rightarrow\) 0 for \(J_z \rightarrow 0\) due to the assumed continuous spin symmetry (practically, spin anisotropies will render \(T_N\) finite even in the 2d limit). \(T_N(J_z)\) then follows the well established scaling \(T_N(J_z) \propto -J/ln(J_z/J)\) at small \(J_z/J\) [34]. For \(J_z/J = 0.01\) we have \(T_N/J = 0.446(3)\).

Magnetic depletion. We now describe our central results, obtained for the depleted HK and \(J_1-J_2-J_3\) models, with a concentration \(x\) of randomly placed vacancies. Since both models are frustrated, the introduction of vacancies generate local non-collinearities in the spin order [34], which ultimately leads to spin-glass behavior [24]. Moreover, the vacancies locally select specific stripe orientations [36] causing different stripe domains to coexist in the same sample, Fig. 3.
range order with a vanishing magnetic order parameter.

Ordering temperature and percolation. An easily accessible quantity is the ordering (or freezing) temperature \( T_g \) as a function of \( x \). While one generally expects that \( T_g \) decreases with increasing \( x \), the behavior at large \( x \) contains information on the nature of the magnetic couplings: For a layered local-moment system with nearest-neighbor couplings, \( T_g \) will diminish near the threshold \( x_p \) for 2d site percolation, because for \( x > x_p \), the layers fragment into disconnected spin clusters, and for Heisenberg symmetry \( T_g(x)/T_g(x = 0) \) will vanish as \( x \to x_p \) in the limit of small interlayer coupling. In contrast, in systems with longer-range magnetic couplings, \( T_g \) will stay finite across \( x_p \). The parent compounds of cuprate superconductors beautifully exemplify this physics: the Néel temperature in Zn-doped La\(_2\)CuO\(_4\) vanishes essentially at the square-lattice percolation threshold of \( x_p = 40.5\% \) [10] — this proves that the cuprate magnetism is dominated by nearest-neighbor coupling.

Our results for \( T_g(x) \) are shown in Fig. 1[a]. As expected from the above discussion, \( T_g \) of the nearest-neighbor HK model rapidly drops slightly above the honeycomb-lattice \( x_p = 30.3\% \) and becomes smaller than our lowest simulation temperature \((J/80)\) for \( x \gtrsim 33\% \); for smaller interlayer coupling this vanishing appears closer to \( x_p \), as the ratio \( T_g(x)/T_g(x = 0) \) diminishes with \( J_\perp \), Fig. 1[c]. (Note that, due to the finite \( J_\perp \), \( T_g \) is expected to be non-vanishing up to the 3d percolation threshold, however, it is undetectably small for \( x \gtrsim 33\% \).)

In contrast, \( T_g \) of the \( J_1-J_2-J_3 \) model continues its approximately linear variation with \( x \) across \( x_p \) and extrapolates to our lowest simulation temperature at a much larger doping level of \( x \approx 45\% \).

Summary. We have studied the magnetism of local-moment models for \( \text{A}_2\text{IrO}_3 \) under magnetic depletion. A spin-orbit glass, with zigzag short-range order, emerges generically from the combination of strong spin-orbit coupling, frustration, and disorder. We have determined the glass (or freezing) temperature \( T_g \) as a function of the doping level \( x \), which at large doping differs qualitatively between the HK and \( J_1-J_2-J_3 \) models, Fig. 1[a].

We thus propose to employ magnetic depletion as a tool to assess the importance of longer-range magnetic couplings in the \( \text{A}_2\text{IrO}_3 \) compounds: If the experimental \( T_g \) were found to vanish near \( x_p \) this would strongly hint [11] at short-range HK physics being realized in \( \text{A}_2\text{IrO}_3 \), as originally proposed in Refs. [13] [19] Suitable dopants replacing Ir should have magnetically inert \( d \) shells, e.g., with a 5d\(^0\) or a 5d\(^6\) configuration; the latter is expected for Pt.

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