Charge ordering in a pure spin model: dipolar spin-ice

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We study the dipolar spin-ice model at fixed density of single excitations, ρ, using a Monte Carlo algorithm where processes of creation and annihilation of such excitations are banned. In the limit of ρ going to zero, this model coincides with the usual dipolar spin-ice model at low temperatures, with the additional advantage that a negligible number of monopoles allows for equilibration even at the lowest temperatures. Thus, the transition to the ordered fundamental state found by Melko et al in 2001 is reached using simple local spin flip dynamics. As the density is increased, the monopolar nature of the excitations becomes apparent: the system shows a rich ρ vs. T phase diagram with “charge” ordering transitions analogous to that observed for Coulomb charges in lattices. A further layer of complexity is revealed by the existence of order both within the charges and their associated vacuum, which can only be described in terms of spins—the true microscopic degrees of freedom of the system.

Defects are the entropic antagonists of the perfectly ordered state, while at the same time they are inextricably linked to it. Topological defects are particularly stable forms of disorder which, when dense, can lead to higher hierarchies of order. Thus, for example, the interaction between vortices in a superconductor can form an Abrikosov lattice or other forms of vortex matter; these phases, in turn, will have their own topological defects. The Berezinskii-Kosterlitz-Thouless transition (BKT), dealing with the unbinding of vortex-antivortex pairs is another example. Among the endless variety of these defects, a new kind of fractional point-like topological excitation—magnetic charges or monopoles—was proposed theoretically and tested experimentally in the spin-ice compounds. Given their analogy with electrical charges, a rich behaviour is to be expected at low temperature (T) for high monopole number density (ρ). These are two conditions that are very difficult to achieve simultaneously in spin-ice, and require a very fine tuning of the parameters of the Hamiltonian. In this work we take the alternative path of studying the full ρ – T phase diagram in a spin ice system by externally fixing the density of magnetic monopoles.

Controlling the density of topological defects is a clean way of highlighting their essential role in determining some ordered phases. During the eighties and nineties, for example, the importance of vortex strings in the 3D XY-model and of “hedgehog” point defects in the Heisenberg model phase transition was clearly shown using this strategy. We take a similar approach in this letter: we fix the number of defects, but keep the model unbiased and simulate the spin-ice system not in terms of the effective degrees of freedom (the monopoles), but in terms of the individual spins. The strength and beauty of the monopolar picture of this magnetic system appears reinforced by our finding of two phases, which can be understood in terms of the different types of ordering of the attracting monopoles (i.e. charge-like degrees of freedom). Adding to this remarkable result, our perspective shows in a unified view the presence of more subtle forms of order: they are related to the many different ways in which both the monopole-free system (the monopole vacuum) and a perfect crystal of single monopoles can be assembled in terms of their constituent spins. These spin degrees of freedom that are not taken into account in the monopolar picture can be thought in this context as internal degrees of freedom of the monopolar charges and vacuum. The close relationship between these findings and previous results in spin ice is discussed.

The magnetic properties of spin-ice (SI) materials at low temperatures are well described by the dipolar model, in which nearest neighbours exchange, J, and long ranged dipolar interactions with coupling constant D —both measured in Kelvin— are taken into account in the Hamiltonian

\[
\mathcal{H} = \frac{D}{3D} \sum_{<ij>} S_i S_j + \sum_{(i,j)} \left( \frac{\mathbf{e}_i \cdot \mathbf{e}_j}{|\mathbf{r}_{ij}|^3} - \frac{3(\mathbf{e}_i \cdot \mathbf{r}_{ij})(\mathbf{e}_j \cdot \mathbf{r}_{ij})}{|\mathbf{r}_{ij}|^5} \right) S_i S_j \right). \tag{1}
\]

Here, the magnetic moments \( \mu_i \) occupy the sites \( i \) of a pyrochlore lattice, separated by distances \( |\mathbf{r}_{ij}| \). They reside in the vertices of corner-sharing tetrahedra (see Fig. 1) of side \( a \) and behave as Ising-like spins \( \mu_i = \mu S_i \hat{e}_i \), with \( S_i = \pm 1 \), constrained to point along the \( \langle 111 \rangle \) directions \( \hat{e}_i \). When the effective nearest neighbours interaction \( J_{\text{eff}} = J/3 + 5/3D > 0 \), \( D = \mu_0 \mu^2 / 4 \pi a^3 \), the spin-ice rule is enforced: two spins should point in and two out of a tetrahedron to minimise its energy. This rule, combined with the lattice geometry makes SI a magnetic...
analogue of water ice, with a similar residual entropy [11]. A violation of the local law implies the creation of a defect, or monopole, sitting in the tetrahedron with a magnetic charge proportional to the divergence of the spin vectors [6]. The number of defects at fixed temperature is thus regulated by the magnitude of $J_{eff}/D$. In the currently known SI materials, it leads to moderately correlated monopole fluids [13, 14]. Material design or the application of external pressure can be used to strengthen the correlations, revealing new aspects on these systems that we set out to determine by numerical simulations.

Here we have used the Monte Carlo technique to simulate the dipolar SI model (Eq. 1) with Ewald summations. We modified the dynamics so that we can have full and independent control over the temperature $T$, which we measure in units of $D$, and over the density of magnetic charges, $\rho$. Starting from a random configuration perfectly satisfying the ice rules, we first flip enough spins to reach the desired number of positive and negative single excitations per tetrahedra without allowing any double charge excitation. We then follow the usual single flip Metropolis algorithm with an additional constraint: we forbid spin flips which either create or destroy single defects, preserving detailed balance. In other words, we work in a statistical ensemble with constant number of single monopole defects, instead of fixed chemical potential $\mu$. Other details of the simulations can be found in the supplementary information section (Sup. Info.).

The curves in Fig. 1 represent our results for the molar specific heat $C_V$ as a function of temperature at low $\rho$ and linear lattice size $L = 3$ unit cells. The limit $\rho \ll 1$ is particularly important, since at very low $T$ we expect our monopole conserving model to coincide with the usual dipolar SI model. $\rho = 0$ is taken as the minimum non-trivial number of conserved monopoles (two, of opposite sign). At this concentration, the evolution of the system consists in the exploration of the states belonging to an almost perfect SI manifold (the exponentially degenerate set of two in / two out states) by means of the random wanderings of the two defects. Although no phase transition is expected in terms of charges, the specific heat in Fig. 1 shows a sharp peak for $\rho = 0$, centred at $T_V \approx 0.13D$. An identical feature in $C_V$ was found by R. Melko and collaborators in the usual SI dipolar model using a multiple spin flip “loop” algorithm [17]. They identified the peak at $T_V$ with a first order transition to a SI ordered ground state, and proposed an order parameter $\langle \Psi \rangle$ to account for this order [17]. In the present context, this ordering in the spin system with a virtual absence of monopoles should be interpreted as a change of the internal state of the vacuum of magnetic charges. The lower inset to Fig. 1 shows how $\langle \Psi \rangle$ grows below $T_V$ in our simulations. The quantitative agreement [12] – which holds also for other quantities, including the energy corrected for the presence of a pair of monopoles– confirms that this minimum number of conserved defects is sufficient to allow the dipolar model to equilibrate, even when the evolution is simulated through a simple single spin-flip algorithm. This result suggests that the extreme paucity in monopole excitations at low temperatures is a major factor in the spin freezing observed experimentally.

An inspection of Fig. 1 and its lower inset shows that – albeit to a smaller extent, and affected by difficulties in equilibrating and finite size effects– the vacuum of charges also orders below $T_V$ for non-negligible $\rho$. More interestingly, these concentrations show a second (wider) maximum in $C_V$, occurring at a temperature $T_C(\rho)$ higher than $T_V$. Both $T_C(\rho)$ and the height of the peak tend to increase with $\rho$, hinting a connection with the onset of ordering of the magnetic charges. We expect the Coulomb attraction to favour the clustering of monopoles in the zincblende structure, where one type of monopole has a greater tendency to occupy either the up or down tetrahedra sublattices. In analogy with the staggered magnetisation for antiferromagnetism, we use the staggered charge density, $|\rho_S(T)|$, to quantify this type of alternating or staggered charge order (SCO). We define $|\rho_S(T)|$ as the average of the modulus of the total magnetic charge in up tetrahedra per sublattice site per unit charge. Figure 2 shows $|\rho_S(T)|$ as a function of temp-
temperature for different sizes $L$ and fixed density $\rho = 0.1$. We can see that $|\rho_S(T)|$ tends to $\rho$ at low temperatures, decreasing to a small but finite value at high temperatures that scales as $L^{-3/2}$ (as expected for the average of the modulus of a random variable of zero mean value, see Sup. Info.). The transition becomes sharper with $L$, while the temperature of its steepest slope increases. The top inset to Fig. 2 shows the fluctuations in energy ($C_V$) and in $|\rho_S(T)|$ ($\chi_S$) measured at the temperature $T_C(L)$ at which they peak. Both tend to increase proportional to the volume of the system, while $T_C(L)$ vs. $1/L$ displays a linear behaviour (lower inset), indicating a first-order phase transition. We have also measured histograms for the local monopole number density, $\rho_{loc}$, which become bimodal below $T_C$, with peaks near $\rho_{loc} = 1$ and $\rho_{loc} = 0$. This signals that in addition to developing a staggered ordering with a net charge in each sublattice, the system phase separates into a dense arrangement of monopoles (a ionic crystal of magnetic charges) and a “fluid” phase with a very low local concentration of monopoles.

The top part of Fig. 3 shows $C_V$ as a function of temperature for a wide range of $\rho$, and $L = 4$. A small peak is still noticeable at $T_V$, even for high $\rho$. The height of the cusp at $T_C$ grows with $\rho$ for small concentrations, as a consequence of the increase in the relative fraction of crystalline phase being formed. At $\rho = 0.3$ the cusp becomes wider, and eventually resolves into two peaks for $\rho \geq 0.5$. This peak bifurcation corresponds to the decoupling between the onset of the staggered order and monopole crystallisation. The low temperature peak is linked with the second phenomenon, and has a very modest evolution with $\rho$, occurring always at a temperature (which we call $T_C$) below 0.32$D$. The opposite is true for the second cusp, that peaks at temperature $T_S$ going above 0.7$D$ for $\rho > 0.6$. To show this explicitly, we plot $\rho_S(T)$ in the bottom part of Fig. 3, for the same values of $\rho$ as the upper panel. We observe that while for small $\rho$ the temperature at which $\rho_S$ is steepest correlates with $T_C$, it clearly follows the behaviour of $T_S$ for $\rho > 0.3$. In other words, the position of the high temperature peak, $T_S$, marks the transition to a phase, with long-range staggered charge-ordering but no phase coexistence. It is only below $T_C$ that a magnetic crystal separates from a very low vapour pressure fluid. Between $T_S$ and $T_C$ the average local density is homogeneous, fluid-like, but with a finite tendency $\rho_S$ for positive and negative charges to occupy preferentially separate sublattices.

We summarize most of the results found on this work in Fig. 4. It shows, projected into the $\rho$ vs. $T$ plane, the phase diagram for our model, drawn on top of an interpolated contour plot of the specific heat data. The low temperature dome we have labeled as $T_C(\rho)$ corresponds to the first order transition below which a monopole crystal with staggered order coexists with a low vapour-pressure gas [18]; see also the mean field treatment in [20]. At lower temperature, $T_V$ indicates the spin ordering (“vacuum order”) first reported in [17]. Above $T_C(\rho)$ and small $\rho$, the system exists in a fluid phase characterised by a homogeneous average local density of monopoles and no long range charge order. As we increase the density we reach a bifurcation point near $\rho = 0.3$ where the crystallisation transition splits in two: $T_S(\rho)$ marks the onset of SCO with homogeneous local density, while the system phase separates at $T_C(\rho)$ [19].

Figure 4 has a startlingly similar counterpart in systems of simple electric charges in a lattice, where $T_S$ was identified as a second order Néel-like transition temperature, meeting at a tricritical point with a first order dome where a ionic crystal coexists with a low density disordered phase [20–22]. A finite size scaling analysis of our results confirms that $T_S$ is a second order transition within the 3D-Ising universality class (see Sup. Info. for details). Beyond these similarities, one fundamental difference is that in our case the true degrees of freedom are spins, and the presence of the charges—and their ordering—are emergent phenomena.

A broader view is gained by comparison with other spin systems. As in our case, the melting of the ionic crystal in the uniformly-frustrated XY spin model in the triangular lattice can take place in two stages. However, this is a two-dimensional system with a continuous symmetry and therefore one of these transitions is of a different character (BKT) [23]. The resemblance to our system is closer in the case of the Blume-Emery-Griffiths Model used to describe He$_3$-He$_4$ mixtures [1], and it extends even to the universality class expected for the tricritical point.

The approximate character of the monopole picture
implies that there can be order not only in the internal structure of the monopoles vacuum, but also within the magnetic charges themselves. Indeed, we checked that different spin configurations leading to the same monopole cluster can have different energies, and we were able to find a good candidate for the spins ground state of the magnetic crystal, by exploring all possible spin configurations within the conventional cubic unit cell that would generate a perfect zincblende structure. Among the 48 configurations satisfying this condition, 16 had minimum energy, differing from the next lowest energy level by about 6%. As illustrated in the top inset to Fig. 1, the symmetry-connected ground states are characterized by having zero magnetisation, with the magnetic moments of each of the four up tetrahedra pointing along the four possible (111) diagonals.

Our $\rho - T$ phase diagram in Fig. 4 can be related to that measured in Dy$_2$Ti$_5$O$_7$ and Ho$_2$Ti$_2$O$_7$ under a field $\mathbf{H}/[111]$. A field in this direction induces a polarized state with monopoles in a crystalline zincblende structure and $\rho = 1$. At low temperatures this phase is accessed through a first order metamagnetic phase transition for fields of the order of 1 tesla. This curve of metamagnetic transitions in the $H - T$ phase diagram corresponds to the dome of first order phase transitions in the $\rho - T$ phase diagram, $T_C$, in the same way that the first order transition line in the pressure – temperature diagram for a vapour-liquid transition becomes a region in the temperature–density plane. The tricritical point in the $\rho - T$ diagram corresponds to the critical point of the first order transition line in $H - T$ and the line of second order transitions $T_S$ marking spontaneous symmetry breaking is replaced by a line of crossovers in the $H - T$ plane, since $H$ is a symmetry breaking field.

In summary, using the dipolar SI model we have been able to explore the whole $\rho$ vs. $T$ phase diagram, observing charge-like ordering in a purely magnetic system. Our model excludes the possibility of double charges, a fact that limits its application to all possible SI materials and temperatures. However, it has served to explore a complex phase diagram, stressing in a unified view both the monopolar nature of the excitations and the unavoidable need to take into account their spin nature at very low temperatures (where the charge vacuum orders). The model also provides a simple route to avoid the dynamical freezing while retaining single spin-flip dynamics.

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