Phase diagram of the dilute magnet $LiHo_xY_{1-x}F_4$

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We study the effective long-range Ising dipole model with a local exchange interaction appropriate for the dilute magnetic compound $LiHo_xY_{1-x}F_4$. Our calculations yield a value of 0.12 K for the nearest-neighbor exchange interaction. Using a Monte Carlo method, we calculate the phase boundary $T_c(x)$ between the ferromagnetic and paramagnetic phases. We demonstrate that the experimentally observed linear decrease in T_c with dilution is not the simple mean-field result, but a combination of the effects of fluctuations and the exchange interaction. Furthermore, we find a critical dilution $x_c=0.21(2)$, below which there is no ordering. In agreement with recent Monte Carlo simulations on a similar model, we find no evidence of the experimentally observed freezing of the glassy state in our calculation. We apply the theory of Stephen and Aharony to $LiHo_xY_{1-x}F_4$ and find that the theory does predict a finite-temperature freezing of the spin glass. Reasons for the discrepancies are discussed.

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I. INTRODUCTION

The rare-earth compound $LiHo_xY_{1-x}F_4$ has been widely used as a model magnet displaying a wide range of phenomena. At $T_c=1.53$ K, the predominant long-range dipolar interaction causes a second-order classical phase transition to a ferromagnetic state.[1] By applying a transverse magnetic field, the order can be destroyed in a $T=0$ quantum phase transition at about 4.9 T.[2] Positional disorder can be introduced by substituting the magnetic Ho^{3+} ions with nonmagnetic Y^{3+} ions. The disorder has been shown to cause a transition to glassy behavior at high dilution.[3]

A main attraction of $LiHo_xY_{1-x}F_4$ is that the microscopic model is well known.[3,4] The ground state of the Ho^{3+} ion in the crystal field is an Ising doublet, with the first excited state 11 K above the ground state. At the temperature range we consider here ($T<1.5$ K), $LiHoF_4$ should be a very good realization of a dipolar Ising model

$$H=\frac{J}{2}\sum_{i\neq j}\frac{r_{ij}^2-3z_{ij}^2}{r_{ij}^5}\sigma_i^z\sigma_j^z+\frac{J_{\mathrm{ex}}}{2}\sum_{i,\mathrm{NN}}\sigma_i^z\sigma_{\mathrm{NN}}^z, \qquad (1)$$

where J is the dipolar coupling constant, J_{ex} the nearest-neighbor (NN) exchange constant, r_{ij} the interspin distance, and z_{ij} the interspin distance along the Ising axis. The summation is done over all Ho^{3+} ions, which form a tetragonal Bravais lattice with four ions per unit cell. When diluted, a fraction x of the sites are occupied by nonmagnetic yttrium and not included in the above sum. The size of the unit cell is (1, 1, 2.077) in units of $a=5.175$ Å. If we express the interspin distance in units of a, then the dipolar coupling constant $J=(g\mu_B/2)^2/a^3=0.214$ K.[4] The exchange coupling J_{ex} has been experimentally determined to be about half of the nearest-neighbor dipolar coupling.[5] In our calculation, we have neglected the next-nearest-neighbor exchange interaction, which was found to be about 5% of the nearest-neighbor dipolar coupling.[5] In addition, we have left out the hyperfine coupling between the nuclear and electronic spins, as well as the random fields generated by the breaking of crystal symmetries due to the dilution. The effects of these terms on our results will be discussed.

A goal of the extensive experimental studies[3] of the dilute magnet $LiHo_xY_{1-x}F_4$ is to establish the material as a spin-glass prototype with canonical glass properties, and with a well-understood microscopic theory. This would allow comparison between different analytical approaches to spin-glass systems, as well as provide an important experimental benchmark. Currently, it is widely believed that the above dipolar Ising model captures the essential behavior of $LiHo_xY_{1-x}F_4$ observed in numerous experiments, yet a direct calculation of the phase diagram is lacking. The goal of this study is to fill this void and determine the phase diagram for the dilute dipolar Ising model appropriate for $LiHo_xY_{1-x}$ by a direct nonapproximate Monte Carlo calculation. In the process, we also address the fundamental question of whether a disordered classical dipolar ferromagnet supports a long-ranged spin-glass phase.

The experimentally obtained phase diagram is shown in Fig. 1. For $x>0.5$, the boundary between the paramagnetic and ferromagnetic phases can be fitted to a straight line passing through the origin, corresponding to the mean-field result $T_c(x)=xT_c(1)$. As the dilution is increased, the boundary falls below the mean-field result and glassy behavior ensues. At one point ($x=0.167$) freezing of the spin glass was observed, and at further dilution ($x=0.045$) the glassy state did not

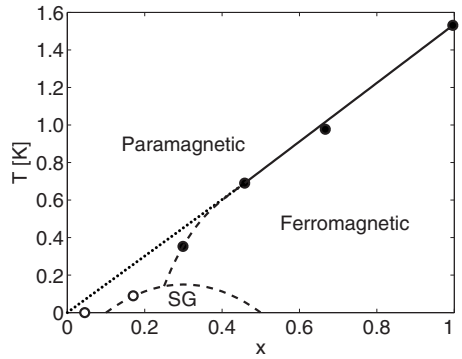

FIG. 1. Experimental phase diagram from Ref. 3. Open circles denote glassy behavior; SG=spin glass.

appear to freeze. This so-called antiglass phase shows a behavior distinct from traditional spin glasses and has been the subject of numerous investigations.[6–8] In contrast to these earlier experiments, very recent experiments suggest that there is no phase transition to an ordered spin glass at low temperature.[9]

We are aware of two earlier theoretical investigations of randomly parked dipoles. The conclusion of the first study,[10] considering bond-diluted dipoles, was that, depending on the lattice structure, spin-glass ordering may be favored over ferromagnetic ordering at low T. The ordering (spin glass or ferromagnetic) persists for any finite dilution x, in disagreement with the antiglass phase. The second study[11] predicts that a site-diluted bcc lattice is ferromagnetically ordered above $x=0.21$ with a spin-glass phase below $x=0.21$. It is also interesting to note that a study of the three-dimensional Ruderman-Kittel-Kasuya-Yosida Ising spin glass, with an interaction of mixed sign proportional to $1/r^3$, finds that this system lies on the boundary between a finite-temperature and a $T_c=0$ spin glass.[12]

Numerical Monte Carlo studies of dipoles on a dilute bcc lattice[11] find a transition to ferromagnetic ordering at $x=0.3\pm0.1$, but are unable to determine whether there is a low-T spin-glass transition. A more recent Monte Carlo study of Ising dipoles[13] on a cubic lattice at dilutions $x=0.045$, 0.12, and 0.20 fails to find a finite-temperature spin-glass transition. Note that the dipolar model on a cubic lattice is not a ferromagnet at higher temperatures, unlike $LiHoF_4$. In conclusion, the most relevant theoretical and numerical studies to date disagree with experiments on the existence and extent of the glassy low-T part of the phase diagram. This could be partially explained by the subtleties of the dipolar interaction since numerical and theoretical predictions depend on the lattice structure and boundary conditions used.[14,15] Our goal is therefore to tailor our calculations to $LiHo_xY_{1-x}F_4$ in order to be able to compare the entire phase diagram with experiments.

II. COMPUTATIONAL METHODS

We have studied the dipolar Ising model given by Eq. (1) using a Monte Carlo method. Due to the long-range nature and angular dependence of the Hamiltonian, this is a challenging problem. Luttinger and Tisza[14] demonstrated that lattice sums depend on the sample shape, while Griffiths later showed[16] that physical properties are independent of sample shape due to breakup into sample-shape-dependent domains. In $LiHoF_4$ there is clear experimental evidence for long needle-shaped domains.[17,18] In order to compare calculations to experiments, the domain structure has to be taken into account, and there are, at present, two different approaches.[15] Previously the domain structure of $LiHoF_4$ was taken into account by performing the Monte Carlo simulation over a spherical cavity embedded in a cylindrical domain.[4] The part of the domain external to the cavity is treated in mean-field theory and gives rise to an effective field acting on the sphere.

Here we choose the other approach, which is to impose periodic boundary conditions and evaluate the effective interaction between spins i and j as a sum over all periodic images of spin j. It is important that the thermodynamic limit reflects the domain shape. For a needle-shaped domain, which is relevant for $LiHoF_4$, this means carrying out the sum along the Ising axis prior to the sum in the radial direction. A significant speedup in evaluation of the sums can be achieved using the Ewald summation method, which splits the sum into two rapidly converging parts, one in Fourier space and one in real space. The advantages with periodic boundary conditions over the cavity method are twofold. The cavity method neglects all fluctuations outside the spherical cavity, while the periodic images include at least part of the fluctuations in the domain. The cavity method was also shown to lead to nonmonotonic system-size dependence in some quantities,[4] which is not the case for periodic boundary conditions.

Due to the long-range interactions, the time required for one Monte Carlo step scales as N^2, as opposed to N for the short-range case. Adding the computational expense of performing disorder averages over several hundred copies of the system makes the efficiency of the Monte Carlo method particularly important. We have therefore compared the efficiency of the single-spin-flip Metropolis method with continuous-time Monte Carlo simulation,[19] the stochastic series expansion cluster algorithm,[4] and the Wang-Landau method,[20] which gives explicit access to the density of states. In agreement with other studies, we found that the Wang-Landau method converges very slowly for large system sizes. The cluster algorithm allows for inclusion of a transverse field, but in the present low-temperature classical simulations it becomes inefficient, since all spins tend to join a single cluster. The continuous-time Monte Carlo method also proved less efficient than the traditional single spin flip, which therefore was used throughout this study.

In order to determine the extent of the ferromagnetic phase, the critical temperature T_c is determined as a function of disorder x. In the Monte Carlo simulation, this is accomplished by calculating the Binder ratio for the magnetization,

$$g_m = \left\langle 1 - \frac{\langle M^4 \rangle}{3\langle M^2 \rangle^2} \right\rangle_d . \tag{2}$$

In addition to the thermal average, an average over quenched disorder configurations d is calculated. The critical temperature was extracted from the intersection of the Binder ratio for different system sizes. We used system sizes up to 10^3 unit cells, containing 4000 spins. Disorder averages were performed over a few hundred disorder configurations. A typical run consisted of 2×10^6 Monte Carlo steps, of which the first 10^6 steps were discarded.

III. RESULTS

In mean-field theory there are two phases, a low-temperature ferromagnetic phase and a high-temperature paramagnetic phase separated by a phase boundary $T_c(x)=xT_c(1)$. For the present model, $T_c(1)=2.41$ K in simple mean-field theory,[4] significantly higher than the experimental value of 1.53 K. The effects of fluctuations can be included

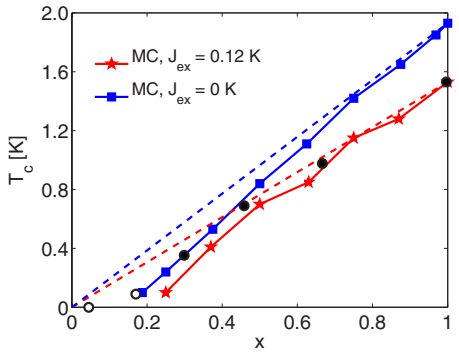

FIG. 2. (Color online) T_c as a function of dilution from experiments (circles) and Monte Carlo calculations. The dashed lines represent mean-field solutions.

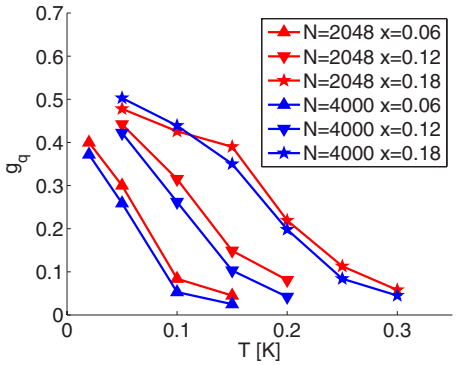

FIG. 3. (Color online) Overlap Binder cumulants in the limit of high dilution.

using a Monte Carlo method, and a recent study using the cavity method found that $T_c(1)=2.03$ K.[4] In the present study, the periodic boundary conditions allow for fluctuations in the domain surrounding the Monte Carlo cell, and we find that $T_c(1)=1.91$ K for the clean system. The difference between the present and the experimental results can be attributed to an anti-ferromagnetic exchange interaction which was measured to about half of the nearest-neighbor dipolar interaction.[5] Treating J_{ex} as a free parameter we find that a value of $J_{ex}=0.12$ K, or about 38% of the nearest-neighbor dipolar interaction $J^1_{dip}=0.33$ K, lowers T_c to 1.53 K.

In Fig. 2, we display the $T_c(x)$ boundary for Monte Carlo simulation and mean-field theory and compare it to the experimental data from Ref. 3.

At low and intermediate dilution ($x>0.5$), the three experimental data points follow the linear mean-field solution. In the Monte Carlo data, deviations from the mean-field solution are clearly visible already around $x=0.7$ when the exchange term is neglected. However, including a nearest-neighbor exchange term of strength 0.12 K results in a linear decrease in T_c for $x>0.5$, in agreement with the experimental data. We therefore see that the effect of the local exchange term is not only to reduce the critical temperature in proportion to the dilution, as in the mean-field solution, but it also changes the functional form of $T_c(x)$. For higher dilution, the Monte Carlo data fall slightly below the available experimental data. In our present simulation, we have neglected the next-nearest-neighbor exchange interaction, which experimentally was found to be about 10% of the nearest-neighbor interaction. Given the nonlinear effect of the exchange term on the critical temperature, this could explain the observed difference at high dilution. In conclusion, we have demonstrated that the experimentally observed linear decrease in T_c is not the simple mean-field result, but rather a combination of the effects of fluctuations and the exchange interaction.

In agreement with the experimental data, our phase boundary appears to intersect the x axis at a finite value of the dilution. This is in sharp contrast to theoretical studies[10,11] that predict a phase boundary extending to the origin. Extrapolating our data, the phase boundary intersects the x axis at about $x_c=0.15(2)$ (no exchange) and at $x_c=0.21(2)$ (including exchange). This is close to $x=0.167$, where experiments observed freezing of a spin glass at $T_c=0.13$ K. In order to find signs of a spin-glass freezing we have performed independent simulations of two replicas (same quenched disorder) simultaneously, and the Edwards-Anderson overlap

$$q=\sum_i \sigma_i^{(1)}\sigma_i^{(2)} \tag{3}$$

has been recorded. For a spin-glass freezing to occur there should be an intersection of the overlap Binder cumulants g_q, but no intersection of the magnetic Binder cumulant g_m.

We show the results for the overlap cumulant in Fig. 3. The data shown are for the case of no exchange interaction, but we found similar results when including the exchange term. For $x=0.18$, the curves intersect around $T=0.12$ K, but the magnetic Binder cumulant also intersects at this point, and we conclude that the system is magnetized. When we increase the dilution, the curves do not intersect, and we conclude that there is no finite-temperature freezing of the spin glass above $T=0.05$ K. At temperatures lower than $T=0.05$ K, equilibration problems occur, and we cannot exclude the possibility of freezing. However, the experimentally observed freezing for $x=0.17$ occurred at $T=0.13$ K, and should be visible in our data.

In order to give further credibility to the phase diagram in Fig. 2 we plot the magnetization squared as a function of disorder in Fig. 4. We note that, except for the two most

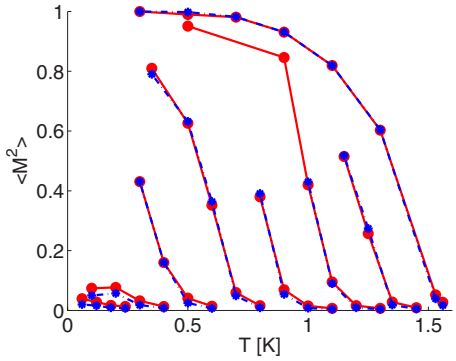

FIG. 4. (Color online) Magnetization squared for $x=n/32$ with $n=4$, 8, 12, 16, 20, 24, 28, and 32 (left to right) for $N=4000$ (dashed line) and 2048 (solid line).

diluted systems, the finite-size effects are very small for the system sizes considered ($N=4000$ and 2048). In the limit of high dilution, the magnetization decreases with increasing system size, indicative of the lack of magnetic order.

In order to compare our results to theory, we have applied the mean-field calculation of Stephen and Aharony[10] to $LiHoF_4$. The transition temperature for the competing ferromagnetic and spin-glass order parameters is given by the two equations

$$r_1 = 1 - \sum_j x \tanh(J_{ij}/T_c) = 0, \tag{4}$$

$$r_2 = 1 - \sum_j x \tanh^2(J_{ij}/T_c) = 0. \tag{5}$$

For high temperatures $r_2 > r_1$ and ferromagnetic order persists, while, depending on the lattice sums, r_2 may be smaller than r_1 for low temperatures, in which case spin-glass ordering occurs. We have evaluated the sums for the lattice appropriate for $LiHoF_4$ and found that the solution favors spin-glass order for $x_c < 0.57$.

IV. DISCUSSION AND CONCLUSION

One reason for the discrepancy between the experimental results and our calculations could lie in parts of the Hamiltonian that we have neglected. The hyperfine coupling between nuclear and electronic spins is important in the low-temperature regime and omitted in our analysis. However, a recent study[21] concluded that at zero transverse field the hyperfine coupling would only renormalize the Ising dipolar Hamiltonian, and therefore it should not affect the phase diagram qualitatively. In particular, it should not be a cause of the spin-glass freezing. Another effect omitted in our simulation is the generation of random magnetic fields due to the dilution, which breaks the crystalline symmetry.[21–23] However, the effect of this term should be to increase fluctuations and lower the critical temperature for both the ferromagnetic and the spin-glass phases. It has even been argued that off-diagonal dipolar terms destroy the spin-glass transition at any finite transverse field.[22] We conclude that not only should the omitted terms not cause a spin-glass transition, they also have the potential of destroying the long-range glass order.

The analytic studies[10,11] yield the mean-field result $T_c(x) \sim x$ in the limit of high dilution and therefore predict long-range spin-glass order extending all the way to $x=0$. This result differs from both the experimental and our numerical studies, which both predict a disordered system in the limit of extreme dilution. It therefore appears that fluctuations not accounted for in the theory are strong enough to cause a finite-dilution phase transition at zero temperature. It would be of great interest to find a theory that could account for the vanishing of the order in the extreme dilution limit. For the case of short-range interactions, the theory of percolation provides the answer, but in the present case of infinte-range interactions this picture is no longer valid.

Numerical difficulties could also explain the difference between our results and experiments. Glassy systems are notoriously hard to equilibrate. Energy barriers between low-lying states cause equilibration problems and make it hard to obtain reliable data for large enough system sizes. The nearest-neighbor Ising spin glass has been studied numerically for years, and only recently does a consensus seem to have developed concerning the glass transition. In our simulations, we see definite signs of equilibration problems at the lowest temperatures. In particular, we find that a decrease in $\langle M^2 \rangle$ as the temperature is lowered is a clear indicator that the simulation does not reach equilibrium. However, having repeated many of the simulations, we believe that the data we show here are reliable. The system sizes we consider (1000–4000 spins) are an order of magnitude larger than in the previous study considering dipoles on a cubic lattice,[13] but we cannot entirely rule out that finite-size effects are so strong in the high-dilution limit that even larger system sizes would be necessary to see the true thermodynamic behavior of the model.

In order to resolve the differences, it would also be important to have more extensive experimental data. We are only aware of two measurements[3,24] of the spin-glass transition in $LiHo_{0.167}Y_{0.833}F_4$, and more recent experiments do not detect any spin-glass transition.[9] In particular, it would be of great interest to have further data points in the region surrounding $x=0.167$ to establish the possible extent and shape of the spin-glass phase. Further experimental data combined with more extensive Monte Carlo simulation using parallel tempering, or other improved equilibration techniques, should be able to resolve the present differences.

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