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Dipolar spin systems: models for $LiHoF_4$ and $LiHo_{0.3}Y_{0.7}F_4$

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Abstract. Models for the spin systems in $LiHoF_4$ and the randomly diluted spin system $LiHo_{0.3}Y_{0.7}F_4$ are investigated by a Monte Carlo simulation. The models are described by long-range dipolar Hamiltonians. The experimentally observed ferromagnetic ground state for $LiHoF_4$ is reproduced in the simulations provided the 'sample' is of prolate ellipsoidal shape with an axis ratio of four or more. The transition temperature $T_c(L)$—where L is an effective length—is obtained from the position of the maximum of the heat capacity for a number of sample sizes. The critical temperature, $T_c(L = \infty)$, obtained by extrapolation of $T_c(L)$, is in fair agreement with the experimentally observed critical temperature. The randomly diluted spin systems are obtained by removing spins from the undiluted sample. Two different dilution methods are considered. Both produce an incompletely ordered ferromagnetic ground state in agreement with experiment. Comparison with simulations on a modified long-range model indicates that the absence of a perfect ferromagnetic ground state is due to frustration effects inherent in the dipolar Hamiltonian. The estimates for the zero-temperature magnetisation and the critical-temperature depression agree with the experimental results. Some simulations that include a magnetic field along the c axis have also been performed on the diluted spin system. The results show that the ferromagnetic ground state is obtained for a sufficiently strong magnetic field. Experiments to test this prediction are suggested.

1. Introduction

Some of the materials $LiRF_4$, where R is a magnetic rare-earth ion, exhibit interesting critical behaviour. Experiments on $LiTbF_4$, for example, show that the spin system exhibits the critical behaviour of a long-range uniaxial ferromagnet (Als-Nielsen 1976, Holmes *et al* 1975), and excellent agreement with the exact renormalisation group relations is obtained (Als-Nielsen 1976).

Much attention—both theoretical and experimental—has also been given to the properties of compounds randomly diluted with non-magnetic Y^{3+} ions, such as $LiTb_pY_{1-p}F_4$ and $LiHo_pY_{1-p}F_4$. Theoretical studies (Aharony 1976) predict that on dilution new critical behaviour is expected below a threshold concentration. On the experimental side it appears that the material $LiHo_{0.3}Y_{0.7}F_4$ has some peculiar low-temperature properties. Neutron diffraction experiments show that the spins order ferromagnetically. However, the zero-temperature magnetisation $\Phi(0)$ is only around 60% of the value expected from considerations of the total number of paramagnetic ions (Kjaer 1984, Kjaer *et al* 1989). It is the purpose of this paper to probe the reasons for

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this anomaly. The investigation is performed using Monte Carlo (MC) techniques to simulate the spin system in $LiHo_{0.3}Y_{0.7}F_4$. In order to show that simulations are in fact useful for such complicated systems with long-range interaction, we first consider simulations of a model for the undiluted material $LiHoF_4$. It appears that the critical temperature of $LiHoF_4$ may be reproduced fairly well under certain conditions indicating that, despite its obvious limitations due to finite-size effects, the simulation technique is useful.

The model for $LiHoF_4$ requires long simulations. Different random distributions of the spins may lead to very different estimates for $\Phi(0)$, calling for an average over many spin distributions. The simulations have, therefore, been performed for ten different spin distributions and the average value of $\Phi(0)$ is found to accord with the experimental value. None of the samples investigated leads to an estimate for $\Phi(0)$ equal to unity, the characteristic of a perfect ferromagnetic ground state. The absence of a perfect ferromagnetic ground state is due to competing interactions in the dipolar Hamiltonian (frustration effects) rather than to, e.g., some peculiarity of the random distribution of the spins. This statement is based on the observation that simulations—on the *same* random spin distribution, but using a long-range isotropic Hamiltonian (i.e. without competing interactions)—easily produce a ferromagnetic ground state.

Simulations have also been performed on a model for $LiHoF_4$ in a magnetic field along the fourfold axis (c axis). It is shown that a sufficiently strong magnetic field will lead to a perfect ferromagnetic ground state.

The layout of this paper is as follows. In § 2 some relevant experimental data for $LiHoF_4$ and $LiHo_{0.3}Y_{0.7}F_4$ are presented. The models for these materials are given in § 3 along with some details of the simulations. Section 4 contains the results of the simulations. Finally, in § 5 we discuss our findings and suggest new experiments on the diluted model.

2. Some experimental data

The material $LiHoF_4$ crystallises in the tetragonal Scheelite structure. The space group is $I4_1/a$ and there are four formula units per unit cell. The positions of the magnetic ions in the unit cell are shown in figure 1. The lengths of the unit-cell axes are at room temperature (Keller and Schmutz 1965)

$$a = b = 5.175 \text{ Å} \qquad c = 10.75 \text{ Å}. \tag{2.1}$$

$LiHo_{0.3}Y_{0.7}F_4$ has the same structure with almost the same unit cell. The lengths of the unit cell axes at 1 K are (Kjaer 1984, Kjaer *et al* 1988)

$$a = b = 5.146 \text{ Å} \qquad c = 10.76 \text{ Å}. \tag{2.2}$$

The free Ho^{3+} ion has a $^5I_8$ ground term which in $LiHoF_4$ is split by the crystal field into a series of levels. The ground state is a doublet and the first excited state lies 9–10 K above the ground state (Hansen *et al* 1975, Janssen *et al* 1985). The crystal field in $LiHoF_4$ forces the magnetisation to be along the tetragonal axis as indicated by the g-values, $g_\perp = 0$, and $g_\parallel = 14.0 \pm 0.2$ (Margariño *et al* 1980), $g_\parallel = 13.74 \pm 0.1$ (Beauvillain *et al* 1980) and $g_\parallel = 13.4 \pm 0.2$ (Janssen *et al* 1985) derived from EPR and susceptibility measurements, respectively. The diluted material with $p \sim 0.01$ has almost the same $g_\parallel$-value, 13.3 ± 0.1 (Margariño *et al* 1976), indicating that the crystal field at a Ho^{3+} ion depends very little whether the neighbours are Ho^{3+} or Y^{3+}. In this paper we use $g_\parallel =$

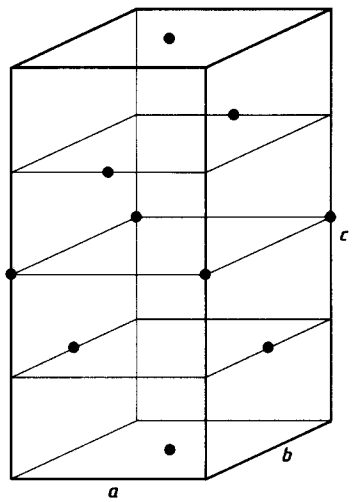

Figure 1. Positions of the Ho^{3+} ions in the unit cell of $LiHoF_4$.

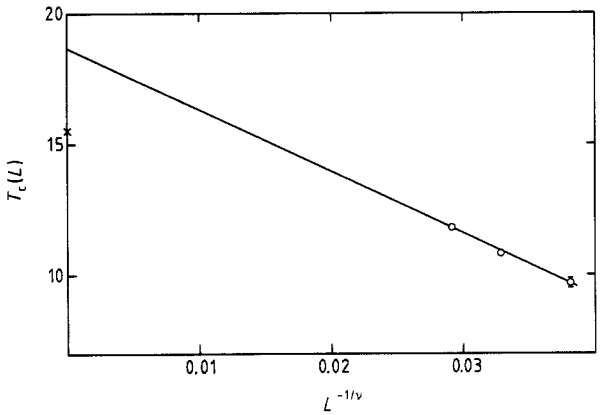

Figure 2. Transition temperatures (circles) obtained from simulations on a model for the spin system in $LiHoF_4$. L is an effective length of the sample, and $\nu = \frac{1}{2}$ is the critical exponent pertaining to the correlation length. X gives the experimental value of the critical temperature for $LiHoF_4$. L is the units of $a = 5.146$ Å and the temperature is in units of $\Omega = 0.102$ K.

13.8 for all values of p whenever we wish to convert our results into conventional units.

$LiHoF_4$ has a second-order phase transition at 1.55 K (Cooke *et al* 1975, Griffin *et al* 1980) between a ferromagnetic and paramagnetic phase. For $LiHo_{0.3}Y_{0.7}F_4$ the transition temperature is 0.36 K (Kjaer *et al* 1989). Thus the critical-temperature depression on dilution

$$R = T_c(LiHo_{0.3}Y_{0.7}F_4)/T_c(LiHoF_4) \tag{2.3}$$

is 0.23 which is substantially stronger than the mean-field prediction of 0.30. The zero-temperature magnetisation of $LiHo_{0.3}Y_{0.7}F_4$ is 67 ± 10% of the value expected from the amount of Ho^{3+} ions present in the sample (Kjaer *et al* 1989).

3. Model and simulational details

The interaction among the spins in $LiHoF_4$ and in $LiHo_{0.3}Y_{0.7}F_4$ is modelled by a dipolar Hamiltonian, where only the z components of the spins are considered because the strong crystal field confines the spins to the $c(z)$ axis.

$$H = \frac{g_\parallel^2 \mu_B^2}{2} \sum_{i=1}^{N} \sum_{j=1(\neq i)}^{N} S_{zi} \frac{r_{ij}^2 - 3z_{ij}^2}{r_{ij}^5} S_{zj} \tag{3.1}$$

where $\boldsymbol{r}_{ij} = (x_{ij}, y_{ij}, z_{ij})$ denotes the vector connecting the ith and the jth spins. S_{zi} is the conventional spin-$\frac{1}{2}$ angular momentum operator of the ith spin and μ_B is the Bohr magneton. It is convenient to rewrite (3.1) as

$$H = \frac{g_\parallel^2 \mu_B^2}{8a^3} \sum_{i=1}^{N} \sum_{j=1(\neq i)}^{N} \sigma_i \frac{1 - 3e_{z,ij}^2}{a_{ij}^3} \sigma_j \equiv \Omega \sum_{i=1}^{N} \sum_{j=1(\neq i)}^{N} \sigma_i C_{ij} \sigma_j \tag{3.2}$$

where $\boldsymbol{e}_{ij}$ denotes a unit vector along $\boldsymbol{r}_{ij} \equiv a\boldsymbol{a}_{ij}$. $\sigma_i = \pm 1$ is a convenient variable describing the state of the ith spin. Ω sets the energy scale and has a value 0.102 K in units of k_B.

The simulations use a conventional Monte Carlo importance sampling technique (MCIST). The number of spins considered is quite small because each spin interacts with all the other spins. In practice, not more than approximately 400 spins can be handled on the computer we have at our disposal. Free-boundary conditions are applied. Prior to the simulations a large cubical sample with spins at all Ho^{3+} positions is generated. We use the lattice parameters given in (2.2), neglecting the small difference in lattice constants for $LiHoF_4$ and $LiHo_{0.3}Y_{0.7}F_4$. Ellipsoids with different principal axis ratios are cut out of this sample. All spins within the ellipsoid are used in the simulation of $LiHoF_4$. The randomly diluted spin system is obtained by removing the required number of spins from the undiluted system. The simplest and most straightforward way to perform the dilution is to remove 70% of all spins at random. However, for the small system sizes considered here, this method is likely to produce some *ab* planes without a single spin. An alternative method consists in a random removal of spins from each (*ab*) plane giving all planes a concentration of spins close to 30%. Both dilution methods will be considered in the following.

The smallness of the ellipsoids makes a detailed study of the scattering function $S(\boldsymbol{Q})$ impossible, since the $\boldsymbol{Q}$-space resolution is of the order of the inverse sample length which at best is $\simeq 0.056$ Å^{-1}, whereas the experimental resolution can be made better than 5×10^{-4} Å^{-1} (Als-Nielsen 1976, Kjaer *et al* 1989). The sample size limitations are of less importance for thermodynamic averages, such as the heat capacity

$$C = (\langle H^2 \rangle - \langle H \rangle^2)/(k_B T^2) \tag{3.3}$$

especially when schemes to extrapolate the data to the thermodynamic limit are applied.

The simulations start by creating a high-temperature configuration of the spin states by assigning the values 1 or -1 to the variables σ_i in a random fashion. This configuration is brought to equilibrium at a selected high temperature using the conventional MCIST. Generally, the starting configuration at a new temperature is taken to be the final configuration from a nearby higher temperature, corresponding to a cooling process. The quantities calculated include the heat capacity (3.3) and the ferromagnetic order parameter

$$\Phi(T) = \left\langle \left| \sum_{i=1}^{N} \sigma_i \right| \right\rangle \Big/ N. \tag{3.4}$$

4. Results

4.1. The model for $LiHoF_4$

Ellipsoidal samples with various principal axis ratios, ξ, have been considered. The axes of the ellipsoids are parallel to the unit cell axes. $\xi > 1$ corresponds to a sample where the ellipsoidal axis along the c axis is longer than the axes in the *ab* plane. Simulations on a spherical sample ($\xi = 1$) with its polar axis parallel to the c axis show that the ground state is not a ferromagnet as $\Phi(0)$ is close to zero. The lack of ferromagnetism (for $\xi = 1$) may be understood by following a simulation at low temperatures starting from a ferromagnet. Consider a spin σ_i close to the surface at the equator of the sample. The local field on σ_i will lack contributions from spins along the c axis, contributions that would favour a ferromagnetic state, as $c_{ij} < 0$ for these spins. Instead, σ_i experiences a

relative excess of local field contributions from spins belonging to the same *ab* plane as σ_i. These spins will not favour a ferromagnetic state as $C_{ij} > 0$. In fact, $\Sigma_j C_{ij} > 0$, implying that when σ_i is accessed in the simulation it will reorient, thus destroying the ferromagnetic order. The analysis suggests that samples that are elongated along the *c* axis (prolate ellipsoids) are more likely to accommodate a ferromagnetic structure. This is borne out by simulations, which show that the ground state is a ferromagnet for $\xi \geqslant 4$. Of course, in mean-field language this is a consequence of the smaller demagnetisation factor in a more elongated sample. Inspection of the spin configuration for $1 \leqslant \xi \leqslant 2$ indicates that the ground state is a ferro-sandwich consisting of oppositely oriented domains. In each domain all spins are in the same state. The interfaces between the domains are parallel to a {110} plane. The sample sizes that can be handled in the simulations are not large enough for us to be able to make an estimate of the domain width in the thermodynamic limit. Experimentally, the width of the sheet-shaped domains is estimated to be around 5×10^4 Å (Battison *et al* 1975), which is much larger than the 41 Å sample diameter of the present MC study.

The 'critical' temperature $T_c(L)$ for the finite systems is estimated to be the temperature at which the heat capacity attains its maximum value. $T_c(L)$ is determined for three samples with an equatorial radius of $2a$ and $\xi = 4, 5$ and 6. These data may be used to estimate the critical temperature in the thermodynamic limit, $T_c(\infty)$. For systems with short-range interactions, such as the Ising model, it has been found (Fisher 1971, Fisher and Barber 1972, Landau 1976) that $T_c(L)$ is related to $T_c(\infty)$ as

$$T_c(L) = T_c(\infty) - qL^{-1/\nu} + \ldots \tag{4.1}$$

where L is the linear length of the system, q is a constant, and ν is the critical exponent pertaining to the correlation length. It is assumed that (4.1) holds also for the present model with long-range interactions where $\nu = \frac{1}{2}$, and furthermore that the L-values we consider are large enough to justify the neglect of the omitted higher-order terms in (4.1). The linear length L is determined as $L = V^{1/3}$, where V is the volume of the ellipsoid. The data are plotted in figure 2, which shows a linear relation, although the range of $L^{-1/\nu}$-values is fairly limited due to the practical limitations on sample size. The available data lead to the following estimate for the critical temperature, $T_c(\infty) = 18.5 \pm 0.5$ in units of Ω, or (1.89 ± 0.05) K. Thus the MC estimate of T_c is about 22% higher than the experimental value 1.55 K (Cooke *et al* 1975). Before comparing this estimate with the experimental value we note that the MC calculations took only the dipolar interaction into account, while there is some experimental evidence (Beauvillain *et al* 1978) to show that $LiHoF_4$—in addition to the dipolar interaction—has an antiferromagnetic exchange interaction that amounts to about 33% of the dipolar interaction. A simple mean-field theory predicts that T_c will be proportional to the ground-state energy, suggesting that for a pure dipolar system T_c would be 50% higher than the actual experimental value. Thus we must compare the experimental value, transformed to correspond to a system with dipolar interactions only (i.e. $1.55\ \text{K}/(1 - 0.33) = 2.33$ K) with our estimate of 1.89 ± 0.05 K. The difference may in part be accounted for by noting that the uncertainty in the $g_\parallel$-values may introduce a 6% error in the transformation from the temperature in units of Ω (c.f. equation (3.2)) to degrees Kelvin.

4.2. *The model for $LiHo_{0.3}Y_{0.7}F_4$*

Thermodynamic quantities are much more time-consuming to calculate for the $LiHo_{0.3}Y_{0.7}F_4$ model than for the $LiHoF_4$ model because the ensemble averages vary

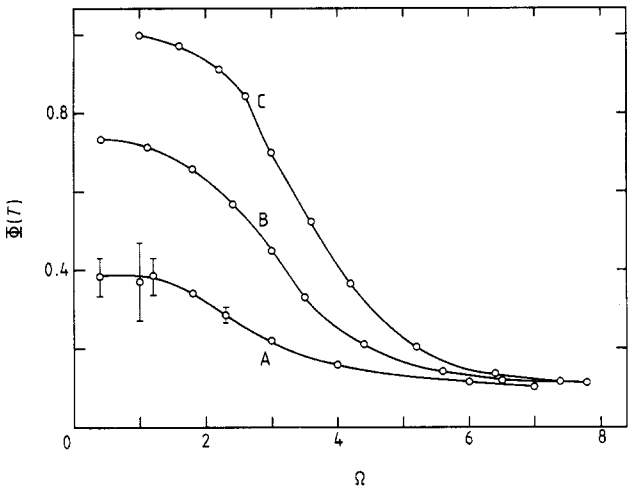

Figure 3. Ferromagnetic order parameters versus temperature. Curves A and B are obtained from simulations on a model for the randomly diluted spin system in $LiHo_{0.3}Y_{0.7}F_4$. A and B correspond to different distributions of the spins. Curve C is obtained from simulations on a modified long-range model with interactions favouring a ferromagnetic ground state. A and C are obtained from the same distribution of spins. The temperature is in units of $\Omega = 0.102$ K.

substantially with the random distribution of the spins. Several simulations have, therefore, been performed using different distributions for fixed sample sizes and thermodynamic functions are obtained as an average of the appropriate ensemble averages for each distribution. $T_c(L)$ has been determined in this way for two samples with equatorial radii $2a$ and $3a$, respectively, both with $\xi = 8$. The two $T_c(L)$ values are used in (4.1) to estimate the critical temperature in the thermodynamic limit

$$T_c(LiHo_{0.3}Y_{0.7}F_4, L = \infty) = (3.66 \pm 0.55)\,\Omega = (0.373 \pm 0.056)\,\text{K}. \tag{4.2}$$

A comparison of (4.2) with the experimental T_c, taking into account the antiferromagnetic exchange as in § 4.1, leads to the conclusion that (4.2) is smaller than the experimental value by 31%. The discrepancy is probably less because the ratio of exchange to dipolar energy in the ground state may very well be different in $LiHo_{0.3}Y_{0.7}F_4$ and $LiHoF_4$. In fact, we expect the antiferromagnetic exchange energy per spin to be smaller in $LiHo_{0.3}Y_{0.7}F_4$ than in $LiHoF_4$ because the former material is 'less ferromagnetic', implying a higher domain wall density, favourable for the antiferromagnetic exchange. Furthermore, even if $LiHo_{0.3}Y_{0.7}F_4$ were a perfect ferromagnet the exchange and dipolar energy scale differently on dilution, due to the difference between their ranges of interaction. The estimate in (4.2) leads to the following determination of the critical temperature depression on dilution (2.3)

$$R = 0.20 \pm 0.03 \tag{4.3}$$

which accords with the experimental value 0.23 (Kjaer *et al* 1989). In contrast, mean-field theory predicts that R equals the concentration of paramagnetic ions, i.e., $R = 0.30$.

The temperature variation of the ferromagnetic order parameter is shown in figure 3 for two different distributions of the spins (curves A and B) in a sample with equatorial radius $2a$ and $\xi = 8$. Obviously, $\Phi(T \rightarrow 0)$ is different from unity. In all, ten distributions are considered. The two dilution methods described in § 3 have both been used to create five of these distributions. In none of the ten samples investigated does $\Phi(0)$ equal unity showing that the ground state is not a perfect ferromagnet. The distribution of values of $\Phi(0)$ is very broad. On average there is no difference between the values of $\Phi(0)$ derived from simulations on distributions obtained from the dilution methods. Consequently, the average value for $\Phi(0)$ is taken as an average of the $\Phi(0)$ values for all ten samples.

The average is 0.61 ± 0.31 which is consistent with the experimental result 0.67 ± 0.10 (Kjaer *et al* 1989).

The lack of a ferromagnetic ground state is not due to some peculiarity of the distribution of the spins in the sample. This statement is established by performing simulations on the *same* spin distribution using a modified long-range Hamiltonian

$$H = \alpha \sum_{i=1}^{N} \sum_{j=1\,(\neq i)}^{N} \sigma_i r_{ij}^{-3} \sigma_j \tag{4.4}$$

where α is a parameter that is fixed by demanding that a ferromagnetic spin configuration has the same energy at $T = 0$ for both (4.4) and (3.2). In (4.4) all couplings favour a ferromagnetic ground state as $\alpha < 0$, whereas—as noted previously—in (3.2) some of the C_{ij} do not favour a ferromagnetic order (frustration effects). The curves A and C in figure 3 represent simulations on the same distribution of spins with Hamiltonians given by (3.2) and (4.4), respectively. It appears that simulations using (4.4) lead to a perfect ferromagnet as $\Phi(0)$ is unity for curve C. This suggests that the value of $\Phi(0)$ being low for curve A is due to frustration effects inherent in (3.2). Furthermore, the amounts of statistics needed in the two simulations differ greatly. The error bars on curve A are estimated as the RMS deviations of three $\Phi(T)$ values calculated from simulations beginning with different spin configurations. In all, 5×10^5 MC steps per spin (MCS/spin) are used for each point. The corresponding error bars are much smaller for data points with $\Phi(T) \simeq 0.4$ on curve C and they are hidden in the size of the data symbol. Only 2.5×10^4 MCS/spin are used for this curve per point. These observations are also in line with the presence of frustration effects in (3.2).

4.3. The model for $LiHo_{0.3}Y_{0.7}F_4$ in a magnetic field

Since neither the simulations nor the experiments lead to a perfect ferromagnetic ground state, it seems useful to estimate the magnetic field strength needed to drive the spin system into a ferromagnetic state. The model has, therefore, been extended to describe an arrangement with a magnetic field along the c axis. The Hamiltonian used is

$$H = \Omega \left(\sum_{i=1}^{N} \sum_{j=1\,(\neq i)}^{N} \sigma_i C_{ij} \sigma_j - H \sum_{i=1}^{N} \sigma_i \right) \tag{4.5}$$

where H is a dimensionless magnetic field. Simulations on three different random spin distributions have been performed and $\Phi(0)$ has been determined to be a function of H in each case. It appears in all three cases that $\Phi(0)$ is close to 0.9 for $H \sim 1$ corresponding to 220 G in conventional units.

5. Summary and discussion

The findings of our simulations show that the ground state is dependent upon the form of the sample. Ellipsoidal samples elongated along the c axis with axis ratios, ξ, of four or larger lead to a ferromagnetic ground state, i.e. a single ferromagnetic domain, whereas samples with ratios, $1 \leqslant \xi \leqslant 2$, produce a ferro-sandwich with domain walls parallel to a {110} plane. The critical temperatures for finite samples (with a ferromagnetic ground state) are extrapolated to the thermodynamic limit. The estimate agrees fairly well with the experimental value, provided allowance is made for: (i) the antiferromagnetic exchange interaction absent in the simulations; (ii) the uncertainty in

the parameters used; and (iii) the accuracy of the mean-field relation between the ground-state energy and the critical temperature. An estimate for $T_c(LiHo_{0.3}Y_{0.7}F_4)$ has also been obtained. Making a meaningful comparison of this value with the experimental T_c is difficult because the average value of the dipolar and exchange energy in the ground state is unknown, preventing a mean-field calculation of an 'experimental' T_c for a purely dipolar $LiHo_{0.3}Y_{0.7}F_4$ system. The depression of the critical temperature on dilution agrees with the experimental value but disagrees with the mean-field prediction.

The simulations reproduce an imperfect ferromagnet in accordance with experiment. The average value of the zero-temperature magnetisation agrees with the experimental value. Comparison with simulations on a modified long-range model suggests that the absence of a perfect ferromagnetic ground state is due to frustration effects inherent in the dipolar model rather than to, e.g., some peculiarity in the random distribution of spins. It should be mentioned that an imperfect ferromagnetic ground state is observed also in simulations of a—far less complicated—nearest-neighbour model (Knak Jensen *et al* 1986). For this model the frustration is introduced through a random single-ion term in the Hamiltonian. Finally, simulations have been used to estimate the size of magnetic field needed to obtain a 90% magnetisation in $LiHo_{0.3}Y_{0.7}F_4$ at zero temperature. The estimate is approximately 220 G. It will be interesting to see if experiments will support this prediction. We would also encourage experiments to investigate the details of the domain structure in $LiHo_{0.3}Y_{0.7}F_4$.

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