An intermediate state between the kagome-ice and the fully polarized state in $Dy_2Ti_2O_7$

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$Dy_2Ti_2O_7$ is at present the cleanest example of a spin-ice material. Previous theoretical and experimental work on the first-order transition between the kagome-ice and the fully polarized state has been taken as a validation for the dipolar spin-ice model. Here we investigate in further depth this phase transition using ac-susceptibility and dc-magnetization, and compare this results with Monte-Carlo simulations and previous magnetization and specific heat measurements. We find signatures of an intermediate state between the kagome-ice and full polarization. This signatures are absent in current theoretical models used to describe spin-ice materials.

I. Introduction

Spin-ice materials are deceptively simple in their constitution: classical Ising spins with nearest-neighbour ferromagnetic interactions forming a pyrochlore lattice. This crystal structure can be thought as an alternating stack of kagome and tri-

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angular lattices along the [111] direction. The spins sit at the vertices of tetrahedra and can point either to their center or towards the outside. The magnetic frustration can be seen at the level of a single tetrahedron: the energy is minimized by having two spins pointing inwards and two outwards. This is the *ice rule*, which corresponds exactly to the Pauling rules for protons in water ice; like the latter, it also leads to zero-point entropy, a characteristic signature of spin-ice systems [1].

We have chosen to work on $Dy_2Ti_2O_7$ as the cleanest example of a spin-ice material. Its ground state properties can be well described by a model with only an effective nearest neighbour exchange interaction J_{si} of $\approx 1.1\,K$ [2]. Within this framework, when one applies an external magnetic field H in [111] below 1 K, the polarization of the system will happen in two steps. First, the spins in the triangular lattice that lie parallel to [111] will orient along the magnetic field, removing *part* of the residual entropy but with no change in the configurational energy [3,4]. When the magnetic moment of this sublattice has saturated, the magnetization M cannot be further increased without breaking

the spin-ice rule. This leads to a plateau as a function of field at $M = 3.33\,\mu_{\mathrm{B}}$/Dy-ion, characteristic of the *kagome ice* state. At higher fields, the spins in the kagome lattice are finally fully polarized, leading to a sudden but continuous increase in M towards its saturation. This behavior was predicted theoretically and found in Monte Carlo simulations [5,6]. In spite of this, something different happens in real spin-ice materials.

Since the magnetic moment of the magnetic ions in spin-ice materials is quite large – the one associated with Dy^{3+} ions in $Dy_2Ti_2O_7$ is near $10\mu_B$– , long range dipolar interactions have to be considered [7]. These interactions do not alter the zero field ground state [8], but have a big effect on its excitations. In relation to this, the transition to the fully polarized state —which is the main concern of this paper— experiments a qualitative change. T. Sakakibara and collaborators [9] studied experimentally the magnetization with $H//$ [111] to temperatures much smaller than J_{si}. After a well defined plateau at $\approx 3.33\,\mu_{\mathrm{B}}$/Dy-ion, they observed a very sharp increase in the magnetization. The presence of hysteresis was a convincing argument that the real system reaches the fully polarized state through a metamagnetic first order phase change at the lowest temperatures. The change in M becomes continuous at the critical end-point $T_c = 360 \pm 20\mathrm{mK}$ and $\mu_0 H_c \approx 0.93\,\mathrm{T}$ [9].

The change in character of this transition — from a crossover to a discontinuity when dipolar interactions are included— was later understood in terms of the defects associated with the breaking of the ice rules, or *monopoles*. The nearest neighbors model corresponds to the case of free non-conserved monopoles sitting in a diamond lattice. Including dipolar interactions implies turning on a Coulomb interaction between these charges, allowing them to condense through a real first order transition [10]. Numerical simulations (including Ewald summations to take into account long range interactions) proved this picture right, and provided an additional validation to the dipolar model [10]. The Mvs. H curves obtained in these simulations are quite symmetrical around H_c. The jump in the magnetization $\Delta M(T)$ when crossing the first order transition line grows very abruptly with decreasing temperature: for T only $\approx 10\%$ below T_c, $\Delta M(T)$ amounts to $\approx 90\%$ of the total change in magnetization from the kagome ice to full saturation. In

other words, almost full order is achieved in the system for temperatures just below T_c and a magnetic field of 1 T.

Specific heat C_p measurements confirmed the existence of a critical end-point —a sharp peak is clearly seen very near the precise spot in field and temperature specified by Sakakibara *et al.* [11]. However, the identification of a single first-order line below T_c is less clear. The $C_p(T)vs.H$ curves show peaks at the fields $H_c(T)$ identified in [9] as the first-order line, albeit of much smaller amplitude than that at T_c. Additionally, below 300 mK, a second peak at higher fields is discernible [11]. Even at the lowest temperatures (100 mK), magnetic fields above 2 T are needed to coerce the specific heat down to 0. This suggests that, in spite of the absence of thermal excitations, the system does not reach full polarization immediately after the first order transition from the kagome ice, and an intermediate state establishes between these two well-known phases. This specific heat features were confirmed by *ac*-susceptibility measurements on the same samples [12]. In all cases, the sample sat at a fixed platform with respect to the magnetic field and therefore the alignment with respect to the [111] direction was within a few degrees. An angular dependent study of the magnetization with Sato and coworkers [19] showed these asymmetries, and additional features in the polarization transition were seen at small angles away from [111]. The implications of these results in the current understanding and modeling of the spin-ice materials have not been considered.

In this paper, we study in detail this additional intermediate state, and show that it cannot be explained by any of the models currently used to study spin-ice materials. Working at small angles away from [111], we looked for a magnetic signature by repeating the static magnetization measurements in several samples. In addition, improving the sensitivity by three orders of magnitude, we measured ac-susceptibility at different frequencies, which also allowed us to do a characterisation of the dynamics of the observed transitions. In order to gain further insight into this possible intermediate state, we performed Monte Carlo simulations of the experimental situation using the currently accepted models including Ewald summations and exchange interactions up to the third nearest neighbor [13, 14].
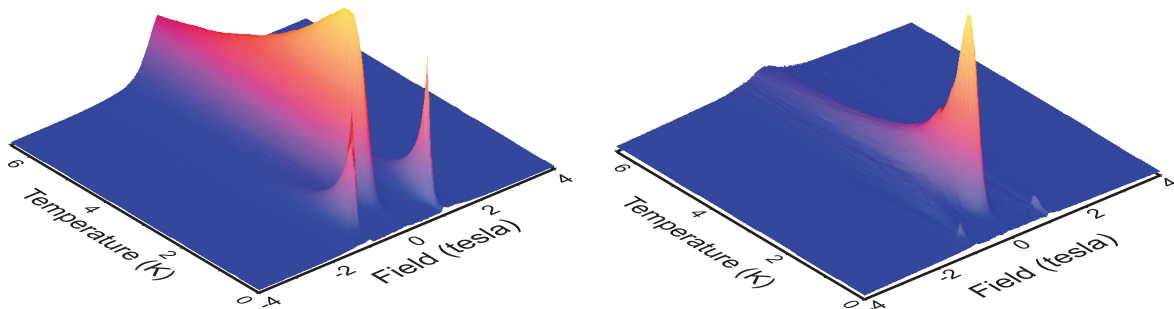
Figure 1: Real (left) and Imaginary (right) parts of the ac-susceptibility as a function of temperature and magnetic field, for temperatures between 50 mK and 6000 mK and magnetic fields between -4 and 4 T. The oscillatory field was of amplitude 0.05 Oe and at a frequency of 87Hz. The zero-field Schottky-type anomaly corresponding to the onset of spin-ice correlations, and the peaks corresponding to the critical point at ± 1 T and ≈ 400 mK are clearly seen.

II.   Methods

For our work, we measured several $Dy_2Ti_2O_7$ single crystals grown in Kyoto and in St Andrews with the floating-zone method. Samples were oriented using Laue diffraction and cut into 3 mm long prisms of square or octagonal section of approximately $1 \, mm^2$, with the [111] direction along the long axis to reduce demagnetising effects with the field in the vicinity of [111] ($\approx 5^o$). The experiments were performed in a dilution refrigerator in St Andrews. Samples were thermally grounded to the mixing chamber through gold wires attached into them with silver paint. For susceptibility, we used a drive field of $3.3 \cdot 10^{-5}$ T r.m.s., and counter-wound pickup coils each consisting of approximately 1000 turns of $12 \, \mu m$ diameter copper wire. The filling factor of the sample in the pick up coil was of approximately 90%. We measured using drive fields of frequencies varying from approx. 10 Hz to 1.0 kHz. Low temperature transformers mounted on the 1 K pot of the dilution refrigerator were used throughout to provide an initial signal boost of approximately a factor of 100. The magnetization was measured using a home-built capacitance Faraday magnetometer [15].

III.   Results and Discussion

Figure 1 shows the real ($\Delta \chi'$, left) and imaginary ($\Delta \chi''$, right) parts of the ac-susceptibility χ as a function of temperature and magnetic field in the whole area of interest. The excitation frequency in this case is $\omega = 87$ Hz; the main features we describe in the following are qualitatively independent of ω. At zero field, there is a very noticeable peak in both $\Delta \chi'$ and $\Delta \chi''$ for $T \approx 2$ K. This corresponds to the Schottky-type anomaly associated with the onset of spin-ice correlations of the system. The magnetic field axis spans from -4 to 4 T, and we can clearly see in the real part two peaks (at positive and negative fields) corresponding to the critical point at $\approx \pm 1$ T and ≈ 400 mK. For temperatures below 400 mK, we see a much smaller feature in $\Delta \chi''$, which has a correspondence in $\Delta \chi''$: a ridge with an amplitude that decreases as a function of temperature. The magnitude of the latter is comparatively very small. At low temperatures and for fields 0.3 T $< |\mu_0 H| < 0.9$ T, and 2 T $< |\mu_0 H|$, the susceptibility is very low, in accordance to the kagome ice plateau and the saturation in the magnetization, respectively.

We now concentrate on the real part of the susceptibility at temperatures below J_{si}. In Fig. 2, we can see a series of curves at fixed temperatures (from 50 to 500 mK) and fields between -3.5 and 3.5 T. The excitation field used was 0.05 Oe, and the frequency 87 Hz. The curves have been offset by 30% for clarity. The field was swept from negative to positive values. Before the kagome ice state is established, the low field susceptibility ($|\mu_0 H| < 0.3$ T) at temperatures below 600 mK is strongly dependent on the magnetic field sweep rate and direction (increasing or decreasing), both signs
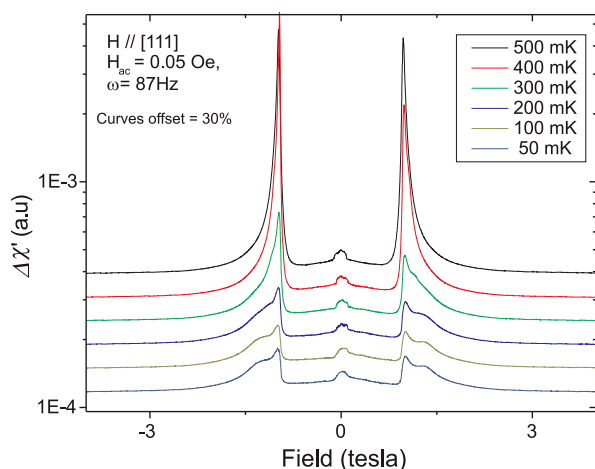
Figure 2: Low temperature real part of the ac-susceptibility as a function of field at fixed temperatures as indicated in the plot. The excitation field was 0.05 Oe at a frequency of 87Hz. The curves are offset by 30% for clarity. As temperature is lowered from 400 mK, the peak at approx. 1 T at 400mK rapidly decreases in amplitude, and splits into two peaks at lower temperatures.

of out-of-equilibrium behavior. At higher magnetic fields, we only observe a small difference in the height of the peaks at around $\pm 1\,\mathrm{T}$, depending on whether the transitions are swept upwards or downwards in field. The position changes very little, and the shape of the features is unaltered. As we lower the temperature, the peak at $\approx 1\,\mathrm{T}$ decreases markedly in amplitude, but without a corresponding change in its high field side shoulder. Below $400\,\mathrm{mK}$, it eventually splits into two distinct features. Their separation in the field axis ($\approx 0.1\,\mathrm{T}$ at 300 mK) is consistent with previous measurements for a similar sample orientation with respect to [111] [19]. While the first set of peaks has a correlate in the imaginary part of $\Delta\chi$ (not shown here), no feature is discernible in $\Delta\chi''$ for the peaks at higher fields.

In Fig. 3, we have plotted the position of these peaks as a function of field and temperature (white circles), and the position of the critical point (black circle). We have taken the specific heat data from reference [11] and determined the position of the peaks in C *vs. H* for different temperatures. These are plotted in this same graphic as red symbols.
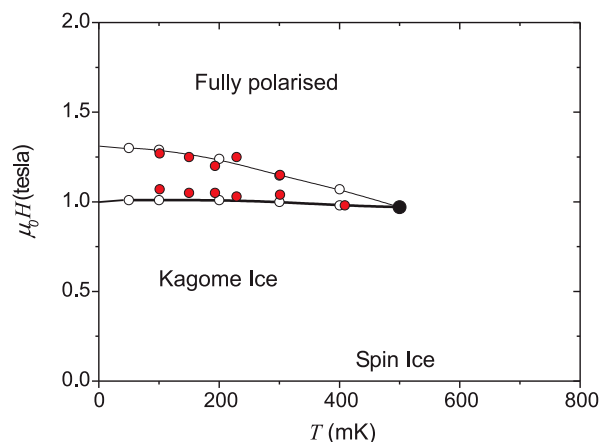

Figure 3: Phase diagram with field slightly tilted from [111] ($\theta \leq 5^o$). An intermediate phase is seen between the kagome-ice and fully polarized regions. The black circle is the critical point as identified from a peak in the real part of the ac-susceptibility, χ'. The dotted white circles correspond to a small doubled peaks seen in χ' with a corresponding feature in the imaginary part χ'', while the white circles denote small peak in χ' with no signature in χ''. The red circles are taken from peaks in the specific heat (C) measurements of reference [11]. The main divergence of C seen in reference [11] and identified as a critical point coincides with the critical point (black circle).

The coincidence between these two experiments of different quantities, on different samples, laboratories and experimental setup is remarkable.

As mentioned before, this secondary peak at higher fields is absent in the dM/dH data presented on Ref. [9]. We measured the magnetization using a Faraday balance on the same samples and under similar temperature and field conditions than before [16]. The main body of Fig. [17] shows our dM/dH as a function of field, compared with curves of $\Delta\chi$ at $T = 100\,\mathrm{mK}$ and frequencies spanning two orders of magnitude (from $\omega \approx 10$ to $1000\,\mathrm{Hz}$). For clarity, we have multiplied $\Delta\chi$ by a factor of twenty. The peak in dM/dH is markedly asymmetric, with an extended tail in the high field side but no additional feature is seen at high fields, in coincidence with Sakakibara's observations. On the other hand, the second peak is clearly seen for low temperature ($T < 400\,\mathrm{mK}$) at all measured frequencies in
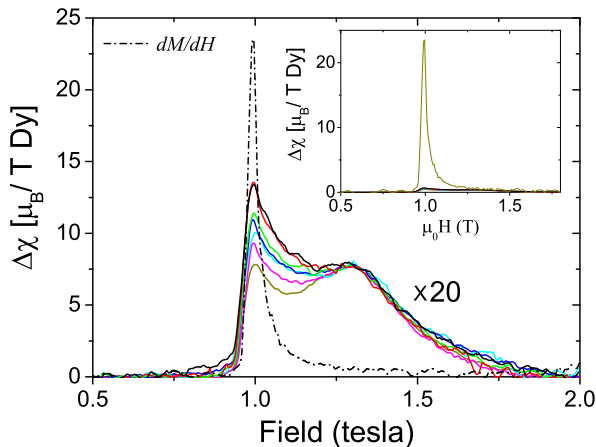
Figure 4: dM/dH (dotted line) and real part of ac-susceptibility measured at different excitation frequencies, from top to bottom: 19, 37, 77, 136, 277, 561, and 1117 Hz, and for $T = 100$mK. For ease of comparison, the latter have been multiplied by a factor 20, and normalized to the amplitude of second peak (no imaginary part has been measured for this feature). The inset shows both sets of data in the same scale.

the ac-susceptibility. While these two experiments seem to be in mutual contradiction, the issue can be easily explained in terms of the resolutions of both techniques. The inset of Fig. 4 shows both sets of data on the same scale; we can see that the high field shoulder on the dM/dH peak directly corresponds (in the limit of long measurement times or low frequencies) to the second peak detected with ac-susceptibility.

Through this analysis, we can see that the experimental volume of data concerning this transition seems to be compatible. Between $\approx 300mK$ and the lowest temperatures (50 mK in Ref. [9]), only $\approx 60\%$ of the total change in magnetization occurs when traversing the first order transition line. The remaining 40% is delivered *gradually* when the field is further increased to values well above $1.5H_c$, in a fashion that does not seem to depend much on temperature (see Fig. 3 on Ref. [9]). This gradual (as opposed to discontinuous) change is behind the asymmetric shape of the magnetization curves, and the second set of peaks in C_p and $\Delta\chi$.

The theoretical prediction for the transition between kagome-ice to fully polarized state with field

in [111] was of a single transition—the "dimer to monomer" transition of refs. [6, 18]. A small additional perpendicular field – present in the experiments at small angles away from [111]– induces order in the dimers in the kagome-ice state, but does not change the prediction of a single transition into the fully polarised "monomer" state [18]. This might hold true when further interactions are added, such as dipolar or further neighbor exchange interactions. In order to investigate this, we performed a numerical check. We did extensive Monte Carlo simulations of the dipolar model including Ewald summations to account for the dipolar long range interactions. We also added exchange interactions up to third nearest neighbors (taking the exchange constants and other parameters within the constraints given by refs. [13, 14]). We explored a wide range of field angles around [111], but were unable to detect a double feature in C_V at low temperatures compatible with the experimental observations. It is then worth stressing that the very observation of a second feature –even when taking into account a possible sample misalignment– asks for new ingredients in the Hamiltonians that are regularly used to describe spin-ice materials.

Given these considerations, it is difficult to discuss on the nature of this intermediate state. It is tempting to think of some sort of "charge" ordering in the diamond lattice (2-in 2-out tetrahedra within a majority of 3-1 and 1-3), previous to the final Zn-blende arrangement, where only $\approx 40 - 50\%$ of the sites are occupied by single monopoles. Note that this does not rule out the possibility of still storing some residual entropy, since there are different spin configurations that generate the same charge within a given tetrahedron. We have not found previous data of the evolution of the entropy as a function of field at temperatures well below T_c. However, the very asymmetric shape of the entropy at 350 mK obtained using the magnetocaloric effect shows that at this temperature the system is already experiencing a strong first order metamagnetic transition, as mentioned in Ref. [20]. This work shows that a big fraction of the residual entropy stored in the kagome planes remains in the system well above H_c [20], suggesting that the intermediate state is indeed a partially disordered one.

IV. Conclusions

In conclusion, we observe an intermediate state between the kagome-ice and the fully polarized state when the field is slightly tilted from the [111] direction. The signature of a double step we find in ac-susceptibility and magnetization measurements is also present in earlier calorimetric measurements, and suggested by magnetocaloric effect experiments. This feature cannot be captured by the models regularly used to describe spin-ice systems, fact that asks for further model refinements. At present, this data stands as a challenge for the development of a realistic theoretical model of spin-ice materials.

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[16] Since we are using two different probes, the exact position and orientation of the sample with respect to the magnet differs slightly between the

ac-susceptibility and the magnetization measurement, and a positive shift of 0.02 T in the magnetization measurement was necessary to make the critical field of the first order transition coincide.

[17] The jump in magnetization ΔM is essentially independent of temperature at low T. Since ΔM is the integral of the susceptibility, one would naively expect that area below the peak in χ' (Fig. 2) to be also independent of T. But this is true only for the dc susceptibility, or, more accurately, for χ' measured at frequencies lower than the inverse of the longest relaxation time. The fact that we can measure an out of phase response $\Delta\chi''$ reveals we are actually measuring dynamic response, i.e. that our frequencies are high and some relaxation processes do not contribute to $\Delta\chi'$. Since relaxation times grow on lowering the temperature, the area loss observed in this figures is quite natural.

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