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Dimensional analysis, spin freezing and magnetization in spin ice

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Abstract

Dimensional analysis is shown to give an insight into the non-ergodic behaviour of spin ice below its apparent ‘spin freezing’ temperature. Expressions are derived for the temperature-dependent magnetic susceptibility that are found to be highly consistent with the previously reported field cooled and zero field cooled magnetization of the spin ice dysprosium titanate, Dy₂Ti₂O₇, as well as with the theory of a ‘magnetolyte’, including Debye–Hückel screening and Wien dissociation. The spin freezing is inferred to reflect the inability of the quasi-free magnetic charges or ‘monopoles’ that comprise the magnetolyte to fully screen an applied magnetic field on the timescale of an experiment. The apparent freezing temperature (\(T_f \approx 0.65\) K) is identified as the point where the Debye screening length becomes greater than the Bjerrum association distance for charge pairs. Combining these dimensional arguments with Onsager’s theory of the Wien effect, it is shown that magnetization data at relatively high field (Snyder et al 2004 Phys. Rev. B 69 064414) may be used to estimate the elementary magnetic charge of spin ice, as well as the temperature-dependent monopole density. Evidence is presented of a non-equilibrium population of monopoles below \(T \approx 0.2\) K. It is shown how Onsager’s microscopic theory of field-induced monopole pair separation naturally suggests the ‘magnetization jumps’ in Dy₂Ti₂O₇ observed at applied fields of the order of \(\sim 0.1\) T. It is concluded that the results of dimensional analysis, when combined with Onsager’s theory, provide an accurate, albeit approximate, description of the properties of Dy₂Ti₂O₇, that could be improved by the development of a lattice theory of the Wien effect, or tested on other spin ice materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction


Thus, the low field susceptibility of the spin ice Dy₂Ti₂O₇ shows three limiting regimes: a high temperature Curie–Weiss regime [12], and two low temperature regimes, corresponding to field cooled (FC) magnetization, which is roughly constant with temperature, and zero field cooled (ZFC) magnetization, that is an increasing function of temperature [11]. Each of the three regimes appears to have a well-defined linear susceptibility, that we label as \(\chi_{\text{high-}}\), \(\chi_{\text{ZFC}}\) and \(\chi_{\text{FC}}\) respectively. The FC–ZFC splitting at \(T_f = 0.65\) K [11] might be termed a ‘spin freezing’, but recent experiments have shown that the spins are far from static in this regime [8, 10]. The zero field cooled susceptibility, \(\chi_{\text{ZFC}}\), is well described by the Wien effect and by monopole creation at \(T = 0.36\) K [10] which give rise to a very small but linear magnetic response, \(\chi_{\text{ZFC}} \ll 1\) (in SI units). In contrast, the data of Snyder et al [11] show that the
FC susceptibility, $\chi_{\text{FC}}$, is of order unity: $\chi_{\text{FC}} \sim 1$, and hence up to several powers of ten greater than $Z_{\text{ZFC}}$.

Here it is shown that an insight into this difference may be gained by straightforward dimensional analysis. It will be shown that the results provide a natural connection with the theory of the Wien effect in spin ice, which has been argued to determine the limiting susceptibility in weak applied field [8, 10]. Comparison of the dimensional analysis result with the Wien effect expression implies an equation for the susceptibility or magnetization that can be used over a much larger range of applied magnetic field than hitherto considered.

2. Dimensional analysis of the susceptibility

In the SI system, the susceptibility is dimensionless so according to the Buckingham $\pi$ theorem it may be represented as a function of independent dimensionless groups $\Pi_i$ ($i = 1, 2, \ldots$).\(^1\) We define the following quantities for the spin ice thermodynamic system: $Q$ is the ‘elementary’ magnetic charge [5], $N_{\text{Dy}}$ is the number of Dy atoms, $2N_f$ is the number of monopoles, and $V$ the volume. The magnetic moment per Dy is $\mu = aQ/2$ where $a$ is the (diamond) lattice constant [5]. Note that it is important to include the numbers $N_{\text{Dy}}$ and $N_f$ in the dimensional analysis as they are measures of quantity: they may be correctly incorporated in terms of concentrations i.e. numbers per unit volume. Also the magnetic charge is included as an extra dimension, in addition to mass, length and time.

At high temperature it seems reasonable to assert that monopoles are irrelevant to the problem and that the linear susceptibility should depend on $\{\mu_0, \mu, (kT), (N_{\text{Dy}}/V)\}$ (note that dependence on $a$ is implicit in $(N_{\text{Dy}}/V)$). In this case only one independent dimensionless group can be formed:

$$\Pi_1 \sim \left(\frac{\mu_0 \mu^2 N_{\text{Dy}}}{kT V}\right).$$

If we further insist that the susceptibility is intensive, we immediately recover the Curie Law:

$$\chi_1 \sim \frac{\mu_0 \mu^2 N_{\text{Dy}}}{kT V}.$$  \hspace{1cm} (2)

At sufficiently low temperature a monopole description is more appropriate [5–7]. The monopoles should be well separated and it seems reasonable to suppose that the rare earth moment $\mu$ and the quantities $a$ and $N_{\text{Dy}}/V$, which parameterize the structured quasiparticle vacuum, are irrelevant. In this case the thermodynamic properties should only depend on the set $\{\mu_0, Q, (kT), (N_f/V)\}$. Again, there is only one dimensionless group that can be formed of these quantities, and by asserting the intensity of the susceptibility we find:

$$\chi_2 \sim \frac{\mu_0 Q^2 N_f}{kT V^2}.$$  \hspace{1cm} (3)

\(^1\) There is an analogy here with dimensional analysis for the ratio $F/NkT$, which is also a dimensionless quantity: here $F$ is the free energy arising from Coulomb interactions in an electrolyte [13]. As spin ice is a magnetic electrolyte or ‘magnetolyte’, we would expect the two problems to be very similar.

Formula (3) implicitly assumes that the internal field is equal to the applied field. However, in a system of charges this need not be so, leaving one further case to be considered. If the charges are sufficiently conducting then they should be able to screen the applied field completely, so that the internal field is zero. In this limit the ‘true’ susceptibility $M/H_{\text{external}}$ is unmeasurable because $H_{\text{external}}$ is zero. The apparent susceptibility $M/H_{\text{external}}$ depends only on sample shape because $H_{\text{external}} = D M$ (for an ellipsoidal sample, where $D$ is the demagnetizing factor). The result of dimensional analysis is simply:

$$\chi_3 \sim 1.$$  \hspace{1cm} (4)

Now it is instructive to rewrite the susceptibilities equations (2)–(4) all in the following form:

$$\chi_i \sim \frac{\mu_0(Q_l)^2 N_l}{kT V}.$$  \hspace{1cm} (5)

where $l_i$ is a characteristic length and $i = 1, 2, 3$. This is appealing because, at a physical level, the temperature, charge and chemical potential (which controls the monopole concentration) are certainly the most important parameters in the problem.

When we do this we find that the $l_i$ correspond to the characteristic lengths of basic electrolyte theory [13]:

$$\chi_1 \sim \frac{\mu_0(Q_0)^2 N_{\text{Dy}}}{kT V},$$  \hspace{1cm} (6)

$$\chi_2 \sim \frac{\mu_0(Q_f)^2 N_f}{kT V},$$  \hspace{1cm} (7)

$$\chi_3 \sim \frac{\mu_0(Q_l)^2 N_l}{kT V}.$$  \hspace{1cm} (8)

Here $l_1 = a$ is the effective ionic diameter or contact distance of the lattice Coulomb gas, $l_2 = l_f = Q/Q^2/8\pi kT$ is the Bjerrum association length, and $l_3 = l_D = \sqrt{\frac{3kT}{\mu_0 Q^2 N_f}}$ is the Debye screening length [10].

The expression for $\chi_2$, an increasing function of temperature, is particularly noteworthy. It contains the magnetic charge $Q$ but not the lattice constant $a$. In a conventional magnet $Q$ and $a$ must always appear in combination via the magnetic moment $\mu$, but spin ice is very unusual in the sense that this need not be so: dipole excitations fractionalize to form magnetic monopoles and $\chi_2$ is an unambiguous signature of the existence of these objects. The expression for $\chi_2$ is essentially that we have previously derived from the linear Wien effect using Onsager’s continuum theory [10]:

$$\chi_{\text{ZFC}} = \frac{\lambda_0 Q^2 N_f}{2\pi^2 kT V} = \frac{\mu_0(Q_l)^2 N_l}{kT V^2},$$  \hspace{1cm} (9)

which suggests the basic importance of this susceptibility expression. As the Onsager theory applies to a non-equilibrium steady state, it is consistent to apply equation (9) to a non-equilibrium susceptibility, $\chi_{\text{ZFC}}$. To make contact with previous work [7, 10], the charge density per unit volume
may be substituted for the charge density per Dysprosium
\[ n_f = N_f / V \times V / \text{Dy} \] where, to a first approximation,
\[ n_f = \exp(\eta / T) \] is the expected free charge density in zero field and \( \eta \approx -4.5 \text{ K} \) is the monopole chemical potential divided by Boltzmann’s constant.

Now experimental evidence on the spin ice Dy\(_2\)Ti\(_2\)O\(_7\) [11, 12] shows that the experimental susceptibilities \( \chi_{\text{high}} \), \( \chi_{\text{ZFC}} \), \( \chi_{\text{FC}} \) agree quite well with these formulae for \( \chi_1, \chi_3, \chi_3 \), respectively, to within numerical prefactors of order unity. We illustrate the low temperature agreement using the (dc-) magnetization \( M \) data of Snyder et al [11] in figure 1. The experimental susceptibility is defined here as \( \chi \equiv M / H \) (rather than as \( \Delta M / H \)) and derived from the measured \( M(T) \).\(^2\) In order to estimate \( n_f \) the zero field expression, equation (10), has been corrected for the finite applied field \( (B = 0.05 \text{ T}) \) using the Onsager theory, as described in detail below.

Qualitatively, we may conclude that each of the limiting susceptibilities is controlled by a single length scale: \( a, l_T \) or \( l_D \). Although the detailed reality is more complex than this, as discussed further below, the association of each susceptibility regime with a single, dominant length scale, does present a clear picture of the essential physics of spin ice, that facilitates a simple explanation of the FC–ZFC splitting.

\(^2\) Dimensional analysis has nothing to say about the difference between \( M / H \) and \( \Delta M / H \); the fixing of the amplitude in equation (7) by comparison with the Onsager theory makes the former definition more appropriate here.

Thus, when a sample is cooled in a field, charges find equilibrium positions that make the internal field zero—presumably, in the limit of low temperatures, on the sample surfaces. However when a zero field cooled sample has a field applied to it, new charges have to be created by the Wien effect and initially the system displays \( \chi_2 \) rather than \( \chi_3 \). The Debye length, which enters \( \chi_3 \), is irrelevant to newly generated charges, as an ionic atmosphere has not yet formed around them.\(^3\) It appears that the Wien effect steady state is very long lived and that the rate of decrease of internal field is extremely slow, most likely because it takes a long time for charges to unbind and then migrate to the sample surfaces. Hence \( \chi_2 \) appears as a quasi-equilibrium susceptibility when measured in experiment.

To make this argument quantitative, for each characteristic length scale \( l_i \) we may define an associated relaxation time \( \tau_i \sim l_i^2 / D \) where \( D \) is the diffusion constant for the magnetic charges. At high temperature (~1 K) the Debye length \( l_D \) is shorter than the Bjerrum length \( l_T \), so the relaxation time \( \tau_D \), which is a measure of the time taken to regain local charge neutrality, is less than the relaxation time \( \tau_T \), which measures the timescale of free charge generation and recombination. Newly created charges may therefore be almost instantly screened. However, \( l_D \) increases much more rapidly with decreasing temperature than does \( l_T \), and below a certain temperature \( l_D \gg l_T \). If we define the observational timescale \( \tau_{\text{obs}} \), we can then have the situation that \( \tau_T < \tau_{\text{obs}} \ll \tau_D \), which means that charge generation and recombination remains ergodic even though equilibrium charge arrangements, and local charge neutrality, cannot be achieved.\(^4\) An estimate of the ‘spin freezing’ temperature \( T_i \) may be gained by equating \( \tau_D \) with \( \tau_T \), which implies \( l_T \approx l_D \). Solving this equation, we find \( T_i \approx 0.7 \text{ K} \), in agreement with the experimental estimate [11]. Finally, assuming a well-defined charge mobility \( u = D Q / kT \) and conductivity \( \kappa = u Q C_\text{F} \), we find that \( \tau_i \approx (l_i / \kappa) / k \), so the long ‘Debye’ relaxation time is associated with a large susceptibility (\( \chi_{\text{ZFC}} \sim 1 \)) while the shorter ‘Bjerrum’ relaxation time is associated with a smaller susceptibility (\( \chi_{\text{FC}} \sim 1 \)). Thus the scenario suggested by dimensional analysis appears to be fully consistent with experimental evidence.

3. Discussion and application to experimental data

Invoking the spin ice–water ice mapping [1, 2], the excitation of magnetic monopoles in spin ice is equivalent to the coupled equilibria:

\[ 2\text{H}_2\text{O}(s) = [\text{H}_3\text{O}^+\text{OH}^-] = (\text{H}_2\text{O}^+) + (\text{OH}^-), \] where the square brackets indicate a pair of ions or monopoles bound by their mutual Coulomb interaction, and the curved brackets represent free ions or monopoles. The bound pairs and free ions are separated by a maximum in the free energy.

\(^3\) The non-appearance of \( a \) may seem surprising in view of the fact that charges are generated at a distance \( a \) apart. In fact, as already noted, \( a \) does appear in a bound pair contribution [10].

\(^4\) Topological constraints, which are not encompassed by this diffusion argument, may also play a role in fixing the amplitude of \( \tau_3 \).

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**Figure 1.** Field cooled (upper full curve, blue online) and zero field cooled (lower full curve, red online) susceptibility of Dy\(_2\)Ti\(_2\)O\(_7\), reproduced from the dc-magnetization data of [11] (note that the experimental data points are so numerous that they appear as a line, and that error bars lie within the thickness of this line). These experimental data are compared with equation (9) (see also equation (7)), multiplied by a factor of 0.4 (lower green curve) and the phenomenological expressions for arising from equation (8) (horizontal dotted line). It is concluded that analysis (equations (9), (8)), do agree with the experimental data to below.
so, regardless of their concentration, the bound pairs present a kinetic barrier that inhibits the generation of monopoles from the structured quasiparticle vacuum, represented by $2\text{H}_2\text{O}(s)$. As discussed elsewhere, Onsager’s theory of the Wien effect [14] may be used to calculate the partition between either free ions and bound pairs, or free ions and the vacuum, depending on the relative rates of the reactions in equation (11). It is assumed here that there is an effective partition between free ions and bound pairs, or free ions and the vacuum, and compared to the theoretical value [5] (long dashed curve, green online). The significant differences between theory and experiment at low temperature are argued to arise primarily from non-equilibrium effects.

order, or less than that of the free charges, as suggested by the results of [10]. In equation (9) the free monopole density $n_f(B, T)$ may be calculated using Onsager’s expression, equation (12). This predicts a nonlinear susceptibility as discussed further below.

Putting in the numbers we may first derive an equation for the magnetic charge:

$$Q = \left( \frac{1.04 \times 10^{-76} \chi_{ZFC} T^3}{n_f^{\text{On}}(B, T)} \right)^{1/6}. \quad (13)$$

Rather than solving equations (13) and (12) self-consistently, we apply the correction $n_l(0, T) \rightarrow n_l(B, T)$ by using the theoretical charge $Q = 4.266 \times 10^{-13} \text{ JT}^{-1} \text{ m}^{-1}$ [5] in Onsager’s expression and then testing if the data indeed collapses onto the theoretical value, according to equation (13), which is justified as the correction to the charge is only about 10%. The result is shown in figure 2, where a close agreement is observed at $T > 0.2$ K, and a gradual breakdown at lower temperature.

An alternative approach is to use equation (9) to derive an approximate estimate the charge density $n_l(B, T)$ from experimental data. Again putting the numbers into equation (9) we find:

$$n_l = T^3 \chi_{ZFC}/56.7, \quad (14)$$

from which we derive an estimate of $n_l$ from Snyder et al’s magnetization experiment [11]. The monopole density so derived is plotted in figure 3 on a semi-logarithmic scale, along with the expected value. It can be seen that the experimental estimate is of the order of the expected monopole density at high temperature, but exceeds it at low temperature. It is unlikely that there is a breakdown of equation (9) at such low charge concentrations. Rather, the difference between theory and experiment at low temperature seen in figures 2

Figure 2. ‘Elementary’ charge of a magnetic monopole in Dy$_2$Ti$_2$O$_7$ estimated from Snyder et al’s magnetization data [11], as described in the text (full curve, red online), and compared to the theoretical value [5] (long dashed curve, green online). The significant differences between theory and experiment at $T < 0.25$ K are ascribed to non-equilibrium effects (see text).

Figure 3. Density of magnetic monopoles per Dy, $n_l$, directly estimated from Snyder et al’s magnetization data [11] (full curve, red online), compared with the Onsager calculation (dashed curve, green online). Both experiment and theory ignore the contribution of bound monopole pairs. Differences between theory and experiment at low temperature are argued to arise primarily from non-equilibrium effects.
and 3, is likely to reflect a higher than expected charge density, indicating that the system is out of equilibrium [15]. If this is the case then the charge density should depend in part on experimental history.

We now propose a phenomenological model for the non-equilibrium charge population that implies a universal data collapse that could be tested using different experimental data sets. It is suggested that the low temperature data is out of equilibrium and that the initial experimental rate of cooling $r = -dT/dt$ and a magnetic relaxation rate constant $v$ are the key parameters that control the charge density at low temperatures. We thus define a single phenomenological parameter $\Delta = |r/v|$, with the dimensions of temperature, that in general will differ for different experiments. The parameter $\Delta$ has the property that it increases with increasing cooling rate, and decreases with increasing relaxation rate. It could, for example, represent a difference between the effective temperature that sets the monopole density and the “true” temperature $T$ set by the cryostat. However, it should be noted that it would be wrong to confuse the former temperature with the temperature sensed by the monopoles themselves: there is no reason that the monopoles could not be out of equilibrium as regards their density, but in equilibrium as regards their motion. For example, a kinetic blocking of the left hand equilibrium in equation (11) would severely alter the monopole population, but have no direct effect on the properties of the free charges.

The dimensions of $\Delta$ suggest the following phenomenological ansatz for the corrected monopole density:

$$ n_f = \exp(\eta/(T + \Delta)), $$

which has the required property of approaching the expected form at high temperature and gradually deviating from it as the temperature is reduced, to a degree determined by the value of $\Delta$. We observe that $n_f$ has the following property:

$$ \frac{dn_f}{dT} = f(n_f), $$

where $f(\cdots)$ denotes an explicit function of its argument. This result is interesting as it does not depend on the parameter $\Delta$. We generalize it to suggest that, for real data sets, $dn_f/dT$ should be a universal function of $n_f$, independent of the experimental details. It would be interesting to test this idea on different experimental data sets.

We finally consider how the susceptibility evolves as a function of strong applied fields. The susceptibility calculated using equation (9) and Onsager’s formula, equation (12) for $B = 0.002, 0.02$ and $0.2$ T is illustrated in figure 4. A strong nonlinear behaviour is observed at the highest field, where the susceptibility undergoes a rapid increase to its equilibrium value. Abrupt increases in the magnetization and nonlinearities in the susceptibility are indeed observed in Snyder et al’s data [11] at fields of this order, which presumably correspond to the jumps in the magnetic order parameter or magnetization, that have been directly observed, and characterized in detail, by neutron scattering [16, 17]. The neutron scattering measurements prove that these jumps do not arise from domain growth, but rather reflect the growth of a local magnetization. The discontinuity in the experimental magnetization occurs at approximately the point where the continuum Onsager theory breaks down. Thus the existence of bound pairs relies on there being a Coulombic barrier to dissociation: that is, a maximum in the combined potential of the Coulomb interaction and the applied field, with respect to a charge at the origin. It is straightforward to show that, at an applied field of $B = 0.1–0.2$ T along the [001] direction in Dy$_2$Ti$_2$O$_7$, the distance of the barrier from the central charge becomes less than the effective contact distance $a$ of the charges. Hence the Coulombic barrier abruptly disappears at $B \approx 0.15$ T and above this field there is no kinetic constraint on generating new charges, and the magnetization may very rapidly reach its equilibrium value. By this argument, it is clear that the lattice must be important, so it is unrealistic to expect the continuum Onsager theory to provide a very precise description of the real system in this range of field. Nevertheless the continuum model does predict nonlinearities in the same range of applied field as those observed experimentally [11, 16, 17]. After the completion of this paper, Slobinsky et al [18] reported a characterization of the magnetization jumps by bulk measurements, where they suggested that the discontinuity itself is a consequence of a ‘phonon bottleneck’. Their proposal is consistent with the ideas advanced here and in [8, 10], as the strong nonlinearity in the monopole density as a function of field, caused by Wien dissociation, is a necessary precursor to the phonon bottleneck proposed in [18].

4. Conclusions

In conclusion, it has been shown that dimensional arguments, when combined with Onsager’s theory of the Wien effect [14] facilitate an explanation of many experimental phenomena in spin ice in its non-equilibrium regime. These include the location of the freezing temperature [11], the magnitudes of the field cooled and zero field cooled magnetization [11], the
magnetization jumps [16, 17] and a non-equilibrium monopole population. The equations for the low temperature magnetic susceptibility proposed this paper are necessarily approximate as they ignore the lattice structure of spin ice and the explicit contribution to the magnetic susceptibility of bound charge pairs [10]. Nevertheless, the results obtained are seen to be accurate descriptions of experiment to within factors close to unity. This suggests that the basic equations and ideas presented here are correct and that an improved quantitative description could be obtained by including the bound pair contribution or by developing a lattice version of Onsager’s theory of the Wien effect. Even without this, it has been demonstrated that the equations are useful at a practical level. In particular they have been used to infer that at low temperatures ($T < 0.2$ K), the monopole population is out of equilibrium and hence much greater than expected. It would be interesting to experimentally test these ideas in greater detail, both on the canonical spin ices Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$, as well as on various newly discovered systems [19–21].

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References