Physica B 608 (2021) 412875

Contents lists available at ScienceDirect

Physica B: Physics of Condensed Matter

journal homepage: http://www.elsevier.com/locate/physb

Anomalous frequency dependence of magneto-electric effect in doped DTN

L. Yin [a], J.-S. Xia [a], N.S. Sullivan [a,*], J.N. Fry [a], H.-P. Cheng [a], M. Yazback [a], V. Zapf [b], A. Paduan-Filho [c]

[a] Department of Physics, M^2QM, University of Florida, Gainesville, FL, USA
[b] Los Alamos National Laboratory, USA
[c] Instituto de Fisica, Universidade de Sao Paulo, 05315-970, Sao Paulo, Brazil

ARTICLE INFO

Keywords:
Molecular magnet
Magneto-electric
Bose glass

ABSTRACT

The anomalous frequency dependence observed for the magneto-electric effect in the Bose glass state of dichloro-tetrakis-thoiurea-nickel doped with bromine is analyzed in terms of the hierarchical droplet model of spin glasses. In this model low energy barriers must be overcome before accessing higher energy states leading to scaling laws for the spin correlation functions and an associated frequency dependence for transition rates.

1. Introduction

There is considerable interest in exploring molecule-based magnets [1–4] for which polarizable components can lead to new magneto-electric effects. In addition to their fundamental interest these systems have potential for the development of new high sensitivity detectors and for the manipulation of spin states that could lead to new candidates for qubits in quantum information. We have been particularly interested in systems for which an applied magnetic field can modify the lattice structure, and because of the presence of polarizable components lead to the generation of a macroscopic electric polarization.

The quantum magnet dichloro-tetrakis thiourea-nickel, generally referred to as DTN, is a particularly clean example of this class of materials as the electrically polarizable thiourea molecular groups have been shown to have significant magneto-electric responses [5,6]. While the phase diagram for the magnetically ordered states of DTN is well known [7–9] the effect of the addition of disorder to this system for which the interactions have high anisotropy is less well understood. Ru et al. [10] have shown that a Bose-glass glass state is introduced if the Cl linkers are replaced at random with larger Br atoms. For Br concentrations of 8%, there are critical magnetic fields at 1.2 T and 12 T for transitions to and from the antiferromagnetic state with the Bose glass featuring before and after those transitions, respectively. The phase diagram is shown in Fig. 1.

One of the striking anomalies is the observation of a strong magnetic field induced dielectric susceptibility near the transitions, as illustrated by the broken lines A and B in Fig. 2 [11,12]. As shown in Fig. 2 there is a quadratic dependence for the magnetic field induced change in polarization for fields $0.9 < B < 11.3$ T (consistent with Zapf et al. [5]) followed by an appreciable drop at the transition to the Bose glass state (dashed line in Fig. 2). The second peak (line B) in the change in polarization of Fig. 2 is attributed to a transition to a Mott state [10].

One of the most remarkable features of the measurements is the unusual frequency dependence of the change in the peak of the induced dielectric susceptibilities shown by line A in Fig. 2 at the transition to the Bose glass state. The purpose of this report is to compare that frequency dependence in disordered DTN with the dependence calculated using the droplet model for spin glasses.

2. Results

In view of the disorder introduced in the spin-spin interactions and the consequent frustration that results, the first attempt to understand the frequency dependence is to invoke the dynamics of spin glass models, in particular those of Fisher and Huse [14] who realized that because of the hierarchical nature of the dynamics in spin-glasses, you need to overcome low energy barriers before reaching the high energy barriers. As the thermal excitations allow new energy barriers in configuration space to be overcome, the previous induced polarizations or memory of the low temperature state is erased for the barriers that are traversed. In a time t the energy barriers crossed will be those satisfying $0 < E < E_{max}(t)$ where $E_{max}(t) = k_b T \ln \Gamma_0 t$. Γ_0 is an attempt rate determined by the coupling between spins. Any barriers crossed result in a

* Corresponding author.
E-mail address: sullivan@phys.ufl.edu (N.S. Sullivan).

https://doi.org/10.1016/j.physb.2021.412875
Received 6 October 2020; Accepted 25 January 2021
Available online 3 February 2021

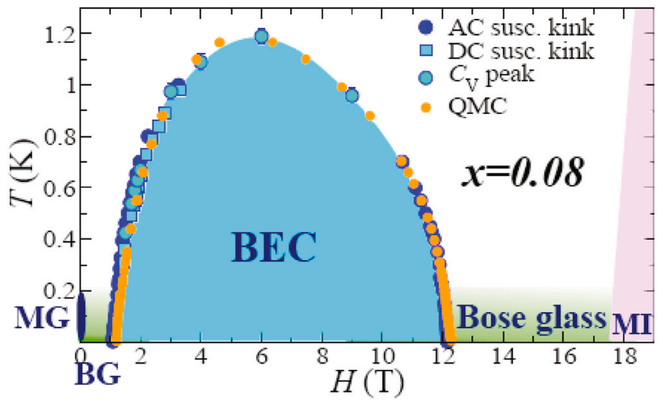

Fig. 1. Phase Diagram of Br-doped (8%) DTN as determined from magnetic susceptibility measurements [10]. At the extremes of magnetic field MI and MG refer to a Mott insulator and Mott glass, respectively.

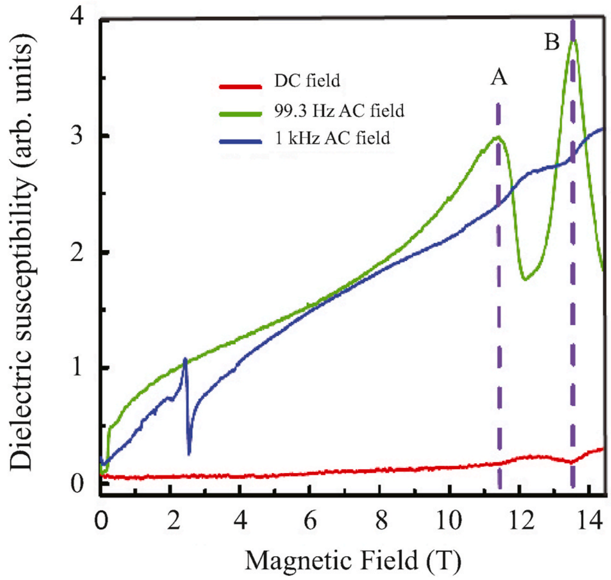

Fig. 2. Observed field induced change in the impedance of the capacitance cell for Br-doped DTN (8%) sample [13]. The broken line at A corresponds to the transition to the Bose glass state. The line at B is attributed to a higher field transition to a Mott insulator.

susceptibility change

$$\Delta\chi = A\int_0^{E_{max}} \rho(E)\, dE \tag{1}$$

where $\rho(E)$ is the density of states for the spin system, and A is a constant that depends on the cell geometry and the magneto-electric component of the sample's susceptibility. Assuming a constant density of states, ρ_0, as often observed in spin glass systems, we find

$$\Delta C = k_b T \rho_0 \ln\frac{f}{\Gamma_0}. \tag{2}$$

The experiments measured the change in impedance of the capacitive cell and the overall frequency dependence of the detected signal is therefore

$$\Delta S = -\frac{2A\rho_0}{C_0}\frac{k_b T}{f}\left|\ln\frac{f}{\Gamma_0}\right| \tag{3}$$

where C_0 is the capacitance of the empty cell.

3. Discussion

The first attempt to analyze the observed data provided only a poor approximation to the observed frequency dependence and it was realized that the scaling arguments postulated by Thill et al. [15] should be used to calculate the dynamics of anisotropic spin glasses. This would lead to a change given by

$$\Delta S = -\frac{2A\rho_0}{C_0}\frac{k_B T}{f}\left|\ln\frac{f}{\Gamma_0}\right|^{\alpha} \tag{4}$$

where the exponent α is small in the case of spin glasses. In order to explore this possibility the frequency dependence ΔS was calculated for $\alpha = 0.5$, 0.65 and 1.0. The results are shown in Fig. 3.

The remarkable peak observed for $f = 207 \pm 25$ Hz or 1300 rad/s is at first sight surprisingly low. This low value is due to the fact that of all the possible transitions only a few conserve energy. This is discussed in the next section.

4. Transition rates

In order to understand the low value of Γ_0 we need to estimate the rate at which one cluster of frustrated Ni spins in disordered DTN can transition to another state. This rate involves transitions over potential energy barriers in a complex distribution of spin states such as one encounters in spin glasses. The assumption is that these transitions are driven by the magnetic dipole-dipole interactions between Ni spins near the Br impurity atoms.

We first need to consider the crystal field due to the distortion around the Br impurity. Following the technique of Margenau [16] and Landesman and Winter [17,18] used for calculating the dynamics around ^{3}He impurities in solid ^{4}He we express the crystal field as

$$H_K = \sum_{j<k} K_0\left(1 - 3\cos^2\theta\right) r_{jk}^{-3}\tau_j^{\dagger}\tau_k \tag{5}$$

where $\tau_j^{\dagger}$ creates a spin up state for a neighboring Ni spin. The amplitude is

$$K_0 \tilde{\ } mc_s^2/4\pi \tilde{\ } 190\,\mathrm{K}, \tag{6}$$

where m is the Br mass and $c_s \sim 5\ 10^2$ m s^2 is an estimated velocity of sound in the crystal. θ_{ij} is the azimuthal angle specifying the orientation

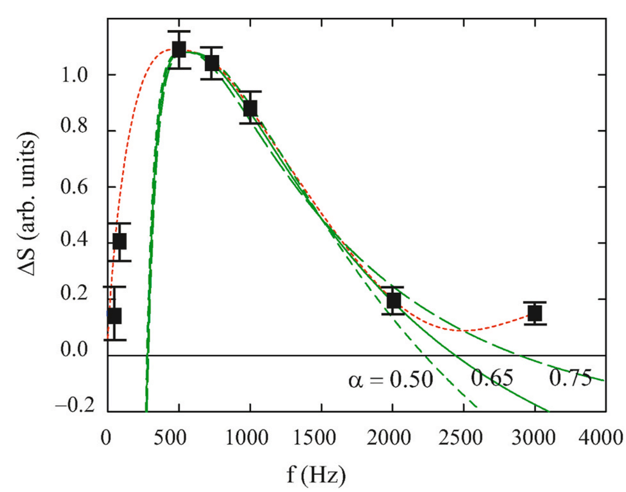

Fig. 3. Comparison of the calculated change in dielectric cell impedance with the experimental observations [11,13] (solid squares) for $\alpha = 0.5$ (broken green line), 0.65 (solid green line), and 0.75 (dashed green line). The dotted red line is just a guide to the eye for the experimental points. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

of the vector r_{jk} with respect to the c-axis of the crystal. In the following we will neglect this angular factor as it contributes only a term of order unity.

The transition rate Γ_0 for spin-spin transitions induced by the magnetic dipole-dipole interactions is determined by the dipolar correlation functions for spins in the neighborhood of the impurities. The dipolar interactions between spins at sites i and j can be written as

$$H_{DD} = \frac{\mu_0 \hbar^2 \gamma^2}{4\pi\sqrt{5}} \sum_m \sum_{ij} \frac{(-)^m}{r_{ij}^3} Y_2^{-m}(\Omega_{ij}) T_{ij}^m \tag{7}$$

μ_0 is the Bohr magneton, γ is magnetogyric ratio, Y_2^m are the spherical harmonics with Ω_{ij} giving the polar angles for the orientation of r_{ij} with respect the reference axis, the c-axis of the crystal. The T_{ij}^m are the tensorial equivalents of the spherical harmonics, Y_2^m, in the space $S = 1$.

$$T_{ij}^0 = S_i \cdot S_j - 3S_{zi}S_{zj} \tag{8}$$

$$T_{ij}^1 = \sqrt{\frac{3}{2}}(S_{zi}S_j^+ + S_{zj}S_i^+) \tag{9}$$

$$T_{ij}^2 = -\sqrt{\frac{3}{2}}(S_i^+ S_j^+) \tag{10}$$

The dipolar correlation function can then be written as

$$G_m(t) = \frac{4\pi}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma^4}{N} \sum_{(ij)(kl)} \frac{Y_2^{m*}(\theta_{ij})\, Y_2^m(\theta_{kl})}{r_{ij}^3\, r_{kl}^3} \Gamma_{(ij)(kl)}(t) \tag{11}$$

where (ij) and (kl) are distinct neighbors. The spin correlation tensor is given by the average

$$\Gamma_{ij,kl}(t) = \langle T_{ij}^m(0)\, T_{kl}^m(t)^\dagger \rangle \tag{12}$$

The characteristic relaxation time, τ_c, can now be determined using Kubo theory [19,20]. We consider the time derivative $\ddot{\Gamma}_{ij,ij}$, and assuming an exponential decay deduce the characteristic rate from

$$\tau_c^{-1} = \frac{1}{G(0)} \int \ddot{\Gamma}(t)\, dt. \tag{13}$$

The details are given in the Appendix. We find

$$G(t) = \langle H_{DD}^2 \rangle F(t) \tag{14}$$

where H_{DD} is the strength of the dipole-dipole interaction, and the relaxation function is

$$F(t) = \exp\left[-2\pi x_{\mathrm{Br}} \Lambda \left(\frac{3}{2}K_0 t\right)^{3/4}\right] \tag{15}$$

With $\Lambda = 1.555$, using $H_{DD} = 1.5\,10^8\ \mathrm{s}^{-1}$ and $K_0 = 4.2\,10^{12}\ \mathrm{s}^{-1}$ we obtain a calculated relaxation rate of

$$\tau_c^{-1} = \frac{\langle H_{DD}\rangle^2}{K_0} \frac{\Gamma\left(\frac{7}{3}\right)}{(2\pi x_{\mathrm{Br}}\Lambda)^{4/3}} = 8.8\,10^3\ \mathrm{s}^{-1}, \tag{16}$$

which is to be compared with an observed rate of $1.3\ 10^3\ \mathrm{s}^{-1}$. The difference between the calculated value and the observed transition rate is not surprising given the approximations made, especially that for the estimation of K_0.

5. Conclusion

A reasonable quantitative fit to the anomalous frequency dependence of the magneto-electric effect in Br-doped DTN was obtained using the hierarchical droplet model of Fisher and Huse that was originally invoked for spin glasses. The common feature of the current Bose glass system and the spin glass system being the influence of disorder on a frustrated spin system. The best fit for the droplet scaling parameter (determined by quantum fluctuations) is $\alpha = 0.65$. Estimates of the magnetic spin-spin interactions lead to a characteristic frequency $\Gamma_0 = 8.8\ 10^3\ \mathrm{s}^{-1}$ compared to an experimental value of $\Gamma_{0e} = 1.3\ 10^3\ \mathrm{s}^{-1}$. The low value of Γ_0 (compared to H_{DD}) results from the reduced number of available states for magnetic transitions in the frustrated spin system.

Author contributions

L. Yin, J.-S Xia: Experimental investigation, Data curation. N. S. Sullivan, V. S. Zapf: Conceptualization, Methodology, Writing – original draft preparation. H.-P. Cheng, J. Fry: Writing, reviewing, editing. A. Paduan-Filho: Sample preparation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported as part of the Center for Molecular Magnetic Quantum Materials, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0019330. A.P-F acknowledges support from the Brazilian agencies CNPq and FAPESP (Grant N. 2015-16191-5).

A. Appendix

From the expression for the autocorrelation function we find

$$\ddot{\Gamma}_{ij,kl} = \langle [T_{ij}, H_{DD}]\, e^{-iH_K t}\, [T_{kl}, H_{DD}]\, e^{iH_K t} \rangle \tag{17}$$

and the fast time dependence can be expressed as

$$G(t) = \langle H_{DD}^2 \rangle \langle e^{i\sum_p (K_{ip} - K_{jp})t} \rangle \tag{18}$$

where $\langle H_{DD}^2 \rangle$ is the mean square of the dipole-dipole interaction and (ip) and (jp) are neighbors. The average over the exponential terms is only significant for small differences in K_{jp} and K_{ip}, and therefore to a good approximation we can write

$$G(t) \sim \langle H_{DD}^2 \rangle F(t) \tag{19}$$

where

$$F(t) = e^{i\sum_p 3K_0(p)t/r^A} = \prod_p \cos\omega_p t = \prod_p [1 + (\cos\omega_p t - 1)] \tag{20}$$

with $\omega_p = 3(a_0/r)^4 K_0$. By expanding the product and re-arranging, and using the fact that $\omega_p t$ is very small, we have

$$F(t) = \exp\left[\sum_p [\cos\omega_p t - 1] = \exp[N\langle\cos\omega_p t - 1\rangle]. \tag{21}$$

The integral is

$$I(t) \quad = \quad \langle\cos\omega_p t - 1\rangle = -2\,\langle\sin^2\left(\frac{\omega_p t}{2}\right)\rangle = -\frac{2}{V}\int d^3r\sin^2\left[\frac{3}{2}\left(\frac{a_0}{r}\right)^4 K_0 t\right] = \frac{2\pi}{V}\left(a_0^3\left(\frac{3K_0 t}{2}\right)^{3/4}\Lambda\right) \tag{22}$$

with

$$\Lambda = \int \frac{\sin^2 x}{x^{7/4}}dx = 1.555. \tag{23}$$

The relaxation function is then found to be

$$F(t) = \exp\left[-2\pi x_{\mathrm{Br}}\Lambda\left(\frac{3}{2}K_0 t\right)^{3/4}\right] \tag{24}$$

and from equation (13) the relaxation rate is given by

$$\frac{1}{\tau_c} = \frac{\langle H_{DD}\rangle^2}{K_0}\frac{\Gamma\left(\frac{7}{3}\right)}{(2\pi x_{\mathrm{Br}}\Lambda)^{4/3}} \tag{25}$$

References

[1] M.B. Stone, C. Broholm, D.H. Reich, O. Tchernyshyov, P. Vorderwisch, N. Harrison, Quantum criticality in an organic magnet, Phys. Rev. Lett. 96 (2006) 257203, https://doi.org/10.1103/PhysRevLett.96.257203. https://link.aps.org/doi/10.1103/PhysRevLett.96.257203.

[2] O. Sato, Switchable molecular magnets, in: Proc. Japan Academy. Series B, Physical and Biological Sciences, vol. 88, 2012, https://doi.org/10.2183/pjab.88.213.

[3] F. Kagawa, S. Horiuchi, M. Tokunaga, J. Fujioka, Y. Tokura, Ferroelectricity in a one-dimensional organic quantum magnet, Nat. Phys. 6 (2010) 169, https://doi.org/10.1038/nphys1503.

[4] J.S. Miller, Organic- and molecule-based magnets, Mater. Today 17 (5) (2014) 224–235, https://doi.org/10.1016/j.mattod.2014.04.023.

[5] V.S. Zapf, P. Sengupta, C.D. Batista, F. Nasreen, F. Wolff-Fabris, A. Paduan-Filho, Magnetoelectric effects in an organometallic quantum magnet, Phys. Rev. B 83 (2011) 140405, https://doi.org/10.1103/PhysRevB.83.140405.

[6] E. Mun, J. Wilcox, J.L. Mansin, B. Scott, P. Tobash, V. Xapf, The origin and coupling mechanism of the magnetoelectric effect in $TMCl_2$-$4SC(NH_2)_2$ (TM=Ni and Co), Adv. Condens. Matter Phys. 2014 (2014) 512621, https://doi.org/10.1155/2014/512621.

[7] S.A. Zvyagin, J. Wosnitza, C.D. Batista, M. Tsukamoto, N. Kawashima, J. Krzystek, V.S. Zapf, M. Jaime, N.F. Oliveira, A. Paduan-Filho, Magnetic excitations in the spin-1 anisotropic heisenberg antiferromagnetic chain system $nicl_{2}-4sc(nh_{2})_{2}$, Phys. Rev. Lett. 98 (2007), 047205 https://doi.org/10.1103/PhysRevLett.98.047205.

[8] L. Yin, J.S. Xia, V.S. Zapf, N.S. Sullivan, A. Paduan-Filho, Direct measurement of the Bose-Einstein condensation universality class in $nicl_{2}-4sc(nh_{2})_{2}$ at ultralow temperatures, Phys. Rev. Lett. 101 (2008) 187205, https://doi.org/10.1103/PhysRevLett.101.187205.

[9] R. Yu, C.F. Miclea, F. Weickert, R. Movshovich, A. Paduan-Filho, V.S. Zapf, T. Roscilde, Quantum critical scaling at a Bose-glass/superfluid transition: theory and experiment for a model quantum magnet, Phys. Rev. B 86 (2012) 134421, https://doi.org/10.1103/PhysRevB.86.134421.

[10] R. Yu, L. Yin, N.S. Sullivan, J.S. Xia, C. Huan, A. Paduan-Filho, N.F. Oliveira Jr., Haas, Stephan, A. Steppke, C.F. Miclea, F. Weickert, R. Movshovich, E.-D. Mun, B. L. Scott, V.S. Zapf, T. Roscilde, Bose glass and Mott glass of quasiparticles in a doped quantum magnet, Nature 489 (2012) 379, https://doi.org/10.1038/nature11406.

[11] J.S. Xia, L. Yin, N.S. Sullivan, V.S. Zapf, A. Paduan-Filho, Magneto-electric effect and dielectric susceptibility measurement technique at very low temperatures, J. Low Temp. Phys. 187 (2017) 627.

[12] L. Yin, Magnetic bose glass in br-doped ${N}i{C}l_{2}-4{SC}({NH}_{2})_{2}$: magneto-electric effect, Bull. Am. Phys. Soc. 8 (20) 5.

[13] L. Yin, J.-S. Xia, N.S. Sullivan, V.S. Zapf, A. Paduan-Filho, Magnetic bose glass in Br-doped $NiCl_2$-$4SC(NH_2)_2$: magnetoelectric effect, in: Proceedings Mar Meetig Am. Phys. Soc, Bull. Am. Phys. Soc., 2012, p. J8.5.

[14] D.S. Fisher, D.A. Huse, Equilibrium behavior of the spin-glass ordered phase, Phys. Rev. B 38 (1988) 386–411, https://doi.org/10.1103/PhysRevB.38.386.

[15] M. Thill, D. Huse, Equilibrium behaviour of quantum Ising spin glass, Phys. Stat. Mech. Appl. 214 (3) (1995) 321–355, https://doi.org/10.1016/0378-4371(94)00247-Q.

[16] H. Margenau, Theory of pressure effects of foreign gases on spectral lines, Phys. Rev. 48 (1935) 755.

[17] A. Landesman, J.M. Winter, Calculation of diffusion rate of ^{3}He impurities in ^{4}He, in: Proceedings Low Temperature Physics-LT13, Plenum, 1974, pp. 73–78.

[18] A. Landesman, Theory of magnetic relaxation for dilute ^{3}He atoms tunneling in hcp solid ^{4}He, Phys. Lett. 54 (2) (1975) 137–139, https://doi.org/10.1016/0375-9601(75)90839-7.

[19] R. Kubo, K. Tomita, A general theory of magnetic resonance absorption, J. Phys. Soc. Jp 9 (6) (1954) 888–919, https://doi.org/10.1143/JPSJ.9.888.

[20] B. Cowan, Nuclear Magnetic Resonance and Relaxation, Cambridge University Press, 2005, https://doi.org/10.1017/CBO9780511524226.