## Effects of Disorder on Quantum Phase Transitions and Quantum Dynamics

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#### ABSTRACT

We present experimental studies of the effects of disorder on the quantum phase transitions of antiferromagnetic LiErF<sub>4</sub> and of the dynamic behavior of LiHo<sub>0.2</sub>Y<sub>0.8</sub>F<sub>4</sub>, which hosts a spin glass ground state due to the combination of substitutional disorder and magnetic frustration. Both compounds are insulating dipolar-coupled magnets that can be effectively treated as spin <sup>1</sup>/<sub>2</sub> systems.

Two distinct quantum phase transitions can be induced in the easy-plane antiferromagnet LiErF<sub>4</sub>, applying a magnetic field in the plane or perpendicular to it. The isotopic distribution of natural Er permits us to probe these transitions in the clean and dirty regimes. <sup>167</sup>Er has a natural abundance of 23% and is the only stable isotope with a non-zero nuclear spin. At low temperatures, the nuclear spin slaves to the electronic spin and reduces the effective field felt by the electronic spin, thereby inducing random mass disorder in the dirty (low-temperature) regime. We use specific heat measurements to identify the temperature scale of the crossover between the dirty and clean regime as T=150 mK, and make ac magnetic susceptibility measurements to characterize the effects of disorder on the two quantum phase transitions. When the field is applied along the c-axis, the critical behavior is consistent with a violation of the Harris criterion in the clean regime and a change of universality class in the dirty regime. When the field is applied along the a-axis, the critical behavior is unchanged by the crossover between clean and dirty regimes.

We use ac susceptibility measurements to conduct thermal memory dip experiments on the spin glass state of  $LiHo_{0.2}Y_{0.8}F_4$  in zero magnetic field and find no apparent rejuvenation or memory. We perform an analogous "quantum memory dip" measurement which uses a transverse magnetic field rather than temperature to enter the spin glass state, and we find strong rejuvenation. The relaxation rate of the susceptibility decreases as the transverse field increases. This counterintuitive result is attributed to an increase in the variance of the random longitudinal field associated with increasing the transverse field and is supported by simulations. Finally, we perform a "negative field cycle" experiment which finds erasure of memory in the spin glass state. We establish a theoretical framework of quantum resonant tunneling to explain our results, rather than the conventional picture of a hierarchical free energy landscape associated with classical spin glasses.

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#### Chapter 1

#### INTRODUCTION

#### 1.1 Classical Phase Transitions

Statistical mechanics is the study of taking an astronomically large number of degrees of freedom and reducing them to a small set of variables that maintain strong predictive power. Phase transitions have proven to be a particularly rich subset of this research. Classical phase transitions occur when a high temperature disordered state transitions to a low temperature ordered state. This phenomenon can be understood from the basic relation of Helmholtz free energy,

$$F = E - TS,$$

which can be minimized when a system is coupled to a heat bath. Here E is the internal energy of the system, T is temperature, and S is entropy. Ordered states have small E and small S, while disordered states have large E and large S. As temperature is increased, the entropy term most usually dominates over internal energy and the disordered state becomes energetically favorable.

A deeper understanding of phase transitions is gained by the introduction of an order parameter. This quantity is zero in the disordered state and finite in the ordered state. The definition of the order parameter is system specific. In general, it describes the symmetry of the disordered state that is broken upon entering the ordered state. The phase transition between ferromagnetic (ordered) and paramagnetic (disordered) phases provides a conceptually simple system to demonstrate this concept. In the paramagnetic phase, spins have an equal probability of pointing in any direction, while in the ferromagnetic phase it is energetically favored for spins to align. The magnetization, m, is the order parameter for this transition because it captures this loss of symmetry.

Landau found that when the system is near the critical temperature, Tc, which separates the ordered and disordered states, an approximation of the free energy can be made by expanding in powers of the order parameter (Landau et al., 2011). This theory assumes that the order parameter is uniform across the whole system and thereby ignores any order parameter fluctuations. Phase transitions where this approximation is applicable are described as mean field. We now sketch the ferromagnetic-paramagnetic phase transition in the Landau framework. The free energy expansion is given by

$$F = am + bm^2 + cm^3 + dm^4.$$

Here, a, b, c, d are variables that depend on system specific parameters and temperature and magnetic field conditions. Since the free energy must be independent of the sign of magnetization when there is no external magnetic field, we can set a=c=0. We can also set d>0 because d<0 would cause a divergence of the free energy. We can now solve for the order parameter by minimizing the free energy.

$$F = bm^{2} + dm^{4}$$
$$0 = \frac{dF}{dm} = 2bm + 4dm^{3} \rightarrow m = 0, \pm \sqrt{\frac{-b}{2d}}$$

As seen in Fig.1.1, for b<0, m takes a finite value and implies  $b \sim (T - T_c)$ . We can



Figure 1.1: Plot of the free energy vs. magnetization for  $T>T_c$ ,  $T=T_c$ , and  $T<T_c$ .

now describe the magnetization in the ordered state as  $m \sim (T_c - T)^{1/2}$ . This power law functional dependence is characteristic of a type of phase transitions in which the order parameter smoothly goes to zero called continuous phase transitions. The power law behavior is due to the underlying non-analyticity in the free energy and occurs in all physical quantities near the phase transition. Continuous phase transitions are of fundamental interest in physics because the critical exponents are independent of specific microscopic details of the system. Some properties which do affect the critical exponents are symmetries, dimensionality of the system, and dimensionality of the order parameter. When phase transitions share these properties, they are described as belonging to the same universality class which are defined by their unique set of critical exponents. Whether disorder is a property that alters a universality class will be the focus of Chapter 3. The critical exponents and their relationship to physical quantities are defined in Table 1.1.

Exponent	Relation
β	$m \sim  T - T_c ^{\beta}$
α	$C \sim  T - T_c ^{-lpha}$
γ	$\chi \sim  T - T_c ^{-\gamma}$
ν	$\xi \sim  T - T_c ^{-\nu}$
δ	$m(T = T_c) \sim h^{1/\delta}$
η	$\lim_{x \to \infty} G^c(T = T_c, x) \sim x^{-d+2-\eta}$
Z.	$ au \sim \xi^z$

Table 1.1: Definitions of critical exponents. Here m is the order parameter, C is heat capacity,  $\chi$  is the susceptibility of the order parameter,  $\xi$  is the correlation length, and  $\tau$  is the characteristic time of order parameter fluctuations.  $G^{c}(T, x) = \langle m(T, x)m(T, 0) \rangle - \langle m(T) \rangle^{2}$  is the connected correlation function.

The correlation length is a key quantity which diverges at continuous phase transitions. Fluctuations of the order parameter occur on all length scales less than the correlation length. When the correlation length diverges, fluctuations occur on all length scales and the system becomes scale-invariant. This observation justifies the use of the mathematical machinery of renormalization group theory which includes the effects of fluctuations and provides several scaling relations between critical exponents.

$$\gamma = \beta(\delta - 1)$$
$$\alpha + 2\beta + \gamma = 2$$
$$\gamma = (2 - \eta)\nu$$
$$\nu d = 2 - \alpha$$

Here the exponents are as defined in Table 1.1, and d is the dimension of the system. These relations reduce the number of critical exponents needed to define a universality class.

#### **1.2 Quantum Phase Transitions**

Quantum phase transitions are induced by introducing quantum fluctuations into the system at T=0 (by contrast to thermal fluctuations at a classical phase transition). This is accomplished by tuning an athermal parameter, g, in a Hamiltonian,

$$H = H_1 + gH_2,$$

with the requirement that  $[H_1, H_2] \neq 0$ , preventing  $H_1$  and  $H_2$  from sharing a common set of eigenstates. A finite g will induce fluctuations, and if g is sufficiently large, these fluctuations will induce a phase transition. While a quantum phase transition occurs at zero temperature, the effects of quantum fluctuations persist to finite temperature. A T-g phase diagram consists of three regimes: the classical regime where thermal fluctuations dominate, the fan of quantum criticality where thermal and quantum fluctuations are relevant, and the quantum disordered regime where quantum fluctuations dominate (Sondhi et al., 1997) (see Fig. 1.2).



Figure 1.2: General phase diagram of a quantum phase transition.

#### **1.3 Transverse Field Ising Model**

Common physical parameters used to tune g include pressure, magnetic field, and composition. We will use the example of the transverse field Ising model to further illustrate the properties of quantum phase transitions. In this model, spins are confined to the Ising axis (z-axis) and a magnetic field is applied along the x-axis. Its Hamiltonian is expressed as

$$H_{trans} = \frac{-A}{2} \sum_{i \neq j} \sigma_i^z \sigma_j^z - h \sum_i \sigma_i^x.$$

Here A is the exchange energy,  $\sigma_i$  are the standard Pauli matrix at site i, and h is the magnetic field. In this model, h is an athermal tunable parameter since  $[\sigma_i^z, \sigma_i^x] \neq 0$ . It is instructive to examine the two limiting cases. For h=0, the ground state will be the standard ferromagnetic or antiferromagnetic state depending on the sign of A. In the ferromagnetic case:

$$\left|\uparrow\right\rangle_{global} = \prod_{i} \left|\uparrow\right\rangle_{i},$$

where  $|\uparrow\rangle_i$  is the eigenstate of  $\sigma_i^z$ , and  $|\uparrow\rangle_{global}$  is the state vector of the entire system. When h >> A, the ground state will be a product state of the eigenstates of  $\sigma_i^x$ ,

$$|\rightarrow\rangle_{global} = \prod_{i} |\rightarrow\rangle_{i} = \prod_{i} \frac{|\uparrow\rangle_{i} - |\downarrow\rangle_{i}}{\sqrt{2}}$$

The paramagnetic nature of  $|\rightarrow\rangle_{global}$  can be seen by noting that it maintains spininversion symmetry (i.e.  $|\uparrow\rangle_i \leftrightarrow |\downarrow\rangle_i$  does not alter the state). The quantum paramagnetic state fundamentally differs from a classical paramagnetic state in that it is coherently fluctuating in a superposition of states, while a classical paramagnetic state incoherently fluctuates from coupling to a thermal bath.

When h is tuned away from these limiting cases, the spins will become nontrivially entangled on a length scale,  $\xi$  (Sachdev, 2011; Sachdev & Keimer, 2011). Spins within a correlated volume,  $\xi^d$ , can be renormalized and treated as an effective spin. The ground state can be expressed as a simple product state of these effective spins. Explicitly, this takes the form  $|\uparrow\rangle_{global} = \prod_{\xi_j} |\uparrow\rangle_{\xi_j}^{eff}$  and  $|\rightarrow\rangle_{global} =$  $\prod_{\xi_j} |\rightarrow\rangle_{\xi_j}^{eff}$  for the ferromagnetic phase and paramagnetic state, respectively. When h is tuned such that spin-inversion symmetry is lost, a quantum phase transition occurs. As in the case of the classical phase transition,  $\xi$  will diverge at the quantum critical point, and the entirety of the system will become non-trivially entangled. The introduction of a finite temperature and consequently thermal fluctuations results in the quantum critical fan shown in Fig. 1.2. This behavior can be understood by considering the effect of incoherence due to thermal fluctuations on the entangled spins within  $\xi^d$ . On short length and time scales, the behavior of spins within  $\xi^d$  is equivalent to spins truly at the quantum critical point. As temperature is increased and thermal fluctuations become stronger, the entanglement is cut off at shorter length and time scales. If this cutoff length scale is smaller than  $\xi$ , the whole system will behave as if it is at the quantum critical point.

#### **1.4 Critical Exponents of Quantum Phase Transitions**

Quantum phase transitions are also categorized into university classes which are defined by a set of critical exponents; however, the set of exponents is larger than classical universality classes because criticality must be considered as a function of temperature and the athermal tuning parameter. The control parameter susceptibility,  $\chi_r = \frac{\partial^2 f}{\partial r^2}$ , is an additional observable described by a power law relation and is analogous to the heat capacity of classical phase transitions. For example, compressibility is the control parameter susceptibility of a pressure-induced quantum phase transition. Its power law behavior is described by two exponents:

$$\chi_r(h, T = 0) \sim |h - h_c|^{-\alpha}$$
$$\chi_r(h = h_c, T) \sim T^{-\alpha_T}.$$

For a full description, see the theoretical work developed by Kirkpatrick and Belitz (Kirkpatrick & Belitz, 2015). In this framework, there are scaling relations that are analogous to the classical case. Unlike in classical phase transitions, the statics and dynamics are coupled together in quantum phase transitions as a consequence of the Heisenberg uncertainty principle. The presence of the dynamical critical exponent z in some of the quantum scaling relations is an effect of this coupling. Two examples of this are

$$\alpha = 2 - \nu(d + z)$$
$$\alpha_T = 2/\nu z - d/z - 1$$

#### **1.5 Hamiltonian of LiReF4 Material System**

To study magnetic systems in the real world, we must choose a material system. In this work, we focus on the LiReF<sub>4</sub> family of materials, where Re is a rare earth with an electronic moment. These crystals have a scheelite structure (I4<sub>1</sub>/a) (Salaün et al., 1997). There are four rare earths sites per unit cell with a  $\overline{4}$  symmetry. In particular, we examine materials with rare earths of Holmium and Erbium that have partially-filled 4f valence states and are therefore strongly localized. The spin

Rare Earth	Valence	S	L	J	$g_L$
Но	$4f^{10}$	2	6	8	1.25
Er	$4f^{11}$	3/2	6	15/2	1.2

states of the ions are determined by Hund's rules and are well described by the Russel-Saunders coupling scheme.

Table 1.2: Description of the spin states of Holmium and Erbium.

The Hamiltonian of these materials is naturally more complicated than the transverse field Ising model previously discussed. It's given by

$$H = H_Z + H_{cf} + H_{hf} + H_D.$$

Here  $H_Z$  describes the Zeeman energy,  $H_{cf}$  describes the crystal field splitting,  $H_{hf}$  the hyperfine interaction, and  $H_D$  describes the dipolar-dipolar interaction between spins. An exchange energy term is omitted because highly localized 4f electrons have little orbital overlap and therefore a negligibly small exchange interaction.

The Zeeman term, which couples the electronic moment with a magnetic field, is given by

$$H_z = -\sum_i \mu_B(L(i) + 2S(i)) \cdot H = -\sum_i g_L \mu_B J(i) \cdot H,$$

where J(i) is the total angular momentum at the ith site,  $\mu_B = 0.6717 K/T$  is the Bohr magneton, H is an external magnetic field, and  $g_L$  is the Lande g-factor. The Lande g-factor is given by

$$g_L = \frac{S(S+1) - L(L+1)}{2J(J+1)} + 3/2.$$

The crystal field splitting is due to the effect of the electrostatic field from neighboring ions:

$$V_{CF}(r_i) = \frac{1}{4\epsilon_0} \sum_j \frac{q_j}{|r_i - r_j|}.$$

This potential breaks the symmetry of the 4f electron cloud which lifts the 2J+1 degeneracy of the electronic state and induces anisotropy. In the Hamiltonian, the potential is described using the formalism of Steven's operators (Stevens, 1952). The formalism expresses the potential in terms of tesseral harmonics (i.e. real spherical harmonics) and replaces the Cartesian coordinates with the total angular momentum spin operators (e.g.  $x \rightarrow J_x$ ):

$$H_{cf} = \sum_{i} \sum_{lm} B_l^m O_l^m(J(i)).$$

Here  $O_l^m$  is the spherical harmonic term and  $B_l^m$  is its energy coefficient.  $B_l^m$  is determined experimentally by inelastic neutron scattering and bulk magnetization measurements. These parameters are listed for Ho and Er in Table 1.3. The largest term for both materials is  $B_2^0$  and equals  $-57.9\mu$ eV and  $58.1\mu$ eV for LiHoF<sub>4</sub> and LiErF<sub>4</sub>, respectively. Its significance can be seen by considering  $O_2^0 = 3J_z^2 - J(J+1)$ . The difference in sign of  $B_2^0$  results in  $J_z = J$  to be energetically favorable for Ho and  $J_z = 0$  to be favorable for Er. Accordingly, LiHoF<sub>4</sub> is an Ising magnet and LiErF<sub>4</sub> is an easy plane magnet. Exact diagonalization of  $H_{cf}$  for a single ion using the parameters listed in Table 1.3 shows that both materials have a ground state doublet and that the first excited state is separated from the ground state by 11 K and 26 K for Ho and Er, respectively (see Fig. 1.3). This provides an energy scale in which the materials can be treated as an Ising and easy plane magnet.

	LiHoF <sub>4</sub>	LiErF <sub>4</sub>
$B_2^0$	57.9	58.1
$B_4^0$	0.309	0.536
$B_{4}^{4}(c)$	3.51	5.53
$B_6^0$	0.540e-3	0.00625e-3
$B_{6}^{4}(c)$	63.1e-3	106 e-3
$ B_{6}^{4}(s) $	17.1e-3	23.8e-3

Table 1.3: Crystal field parameters of LiHoF<sub>4</sub> and LiErF<sub>4</sub> taken from (Babkevich et al., 2015) in units of  $\mu$ eV. All original calculations in this work use these crystal field parameters.

The hyperfine term is only relevant for isotopes with a finite nuclear moment. Ho has one stable isotope, Ho-163. It has a nuclear spin of I=7/2. Erbium has several stable isotopes; however, Er-167 is the only stable isotope with a finite nuclear moment of I=7/2. This isotope has a natural abundance of 23%. The hyperfine coupling is given by

$$H_{hf} = A_{hf} \sum_{i} J(i) \cdot I(i)$$

The hyperfine coupling is antiferromagnetic for both systems. The coupling strength is 40 mK (Magariño et al., 1980) and 6 mK (Sattler & Nemarich, 1971) for Ho and Er, respectively. At low temperatures, the hybridization of electronic and nuclear states becomes significant, and the ground state doublet should be thought of as a manifold of 16 electronuclear states.

Finally, we consider the dipole-dipole interaction which takes the standard form

of

$$H_D = -\frac{J_D}{2} \sum_{i \neq j} D_{ij}^{\mu\nu} J^{\mu}(i) J^{\nu}(j).$$

Here  $J_D = \frac{\mu_0}{4\pi} (g_L \mu_B)^2$ , and  $D_{ij}^{\mu\nu} = \frac{3(r_i^{\mu} - r_j^{\mu})(r_i^{\nu} - r_j^{\nu}) - |r_i - r_j|^2 \delta_{\mu\nu}}{|r_i - r_j|^5}$ . Dipolar-dipolar coupling is a long-range interaction which falls off as  $1/r^3$ .



Figure 1.3: (left, middle) Calculation of the lowest three eigenstates of a single ion of Ho and Er in a magnetic and crystal field. (right) The splitting between the ground state and first excited state which determines the strength of the quantum fluctuations in the system.

#### 1.6 6 Low Energy Effective Hamiltonian

Now that we have fully characterized the Hamiltonian of the LiReF<sub>4</sub> materials, we can map it to a low energy effective model . This process maps the subspace of the ground state electronic doublet onto the transverse field Ising model (Chakraborty et al., 2004). Later extensions were also developed to fully include the electronuclear levels (McKenzie & Stamp, 2018). We now sketch this process for the simpler purely electronic case. For a single ion with no hyperfine coupling the Hamiltonian is given by

$$H_{\text{singleion}} = H_Z + H_{cf}.$$

This matrix is constructed using the (2J+1)x(2J+1) matrices of the spin operators  $J_x$ ,  $J_y$ , and  $J_z$ . The lowest three eigenstates are shown in Fig. 1.3 as a function of field. The effect of including the Zeeman term is to mix the excited states into the ground state doublet of  $H_{cf}$  and thereby induce quantum fluctuations. We can immediately write down an effective Hamiltonian using the subspace spanned by the two lowest lying eigenstates. If we define these eigenstates as  $|\leftarrow\rangle$  and  $|\rightarrow\rangle$ , the Hamiltonian takes the form

$$H_{eff} = E_{COM}(H) - \frac{1}{2}\Delta(H)\sigma^{x}.$$

Here  $E_{COM}(H) = 1/2(E_1(H) + E_2(H))$ ,  $\Delta(H) = E_2(H) - E_1(H)$ , and  $E_1(H)$  and  $E_2(H)$  are the energy of the two lowest lying states at given field. A key difference between the two materials is the functional dependence of  $\Delta(H)$ . At low fields,  $\Delta$  increases quadratically in LiHoF<sub>4</sub> and linearly for LiErF<sub>4</sub>. This difference is an effect of the ground state of Ho and Er being non-Kramers and Kramers doublets, respectively (Wendl et al., 2022).

We now cast the dipole-dipole term into this low energy subspace. This is accomplished by projecting the spin operators into the subspace, and then substituting these effective operators into the original dipole-dipole term. First, the unitary transformation used to diagonalize the single ion Hamiltonian  $\tilde{H}_{singleion} = U_1 H_{singleion} U_1^{\dagger}$  is applied to the spin operators  $\tilde{J}^{\mu} = U_1 J^{\mu} U_1^{\dagger}$ . These matrices are truncated to a 2x2 subspace,  $\tilde{J}^{\mu}_{trunc}$ , which only includes the two lowest eigenstates. A final rotation is applied to the truncated operators to diagonalize  $J^z_{final} = U_2 J^z_{trunc} U_2^{\dagger}$  for LiHoF<sub>4</sub> and to diagonalize  $\tilde{J}^x_{trunc}$  for LiErF<sub>4</sub>. It is standard to express these spin operators in terms of Pauli matrices,

$$J^{\mu}_{final} = C_{\mu} + \sum_{\nu=x,y,z} C_{\mu\nu}(B)\sigma^{\nu}.$$

When these effective operators are substituted into the dipole-dipole term, a good approximation is found as

$$H_D^{eff} = -\frac{J_D}{2} \sum_{i \neq j} C_{\mu\mu} C_{\nu\nu} D_{ij}^{\mu\nu} \sigma^{\mu}(i) \sigma^{\nu}(j).$$

For the Ising case, this approximation can be further simplified by ignoring the off-diagonal dipole terms (Chakraborty et al., 2004),

$$H_D^{eff} = -\frac{J_D C_{zz}^2}{2} \sum_{i \neq j} D_{ij}^{zz} \sigma^z(i) \sigma^z(j).$$

The effect of transitioning to this low-energy subspace is to renormalize the electronic moment and is typically captured by defining an effective g-factor,  $g_{||} = 2g_L C_{zz}$  and  $g = g_{\perp} = 2g_L C_{xx}$  for LiHoF<sub>4</sub> and LiErF<sub>4</sub>, respectively.

#### **1.7 Phase Diagrams of** LiHoF<sub>4</sub> **and** LiErF<sub>4</sub>

With the full effective electronic Hamiltonian defined, we can now examine the ordered state of the two materials. While the crystal field term determines the

anisotropy of the system, it does not define the orientation of the spins within the Ising axis or easy plane. The symmetry of the ordered state is established by the dipole-dipole interaction. Since the sign of the coupling is dependent on the relative orientation of the dipoles and its magnitude on the spacing, the ordering can be non-trivial. In the case of LiHoF<sub>4</sub>, the ordered state is an Ising ferromagnet. However, the ordered state of LiErF<sub>4</sub> has a more complex structure, as shown in Fig. 1.4. When the spins are confined in the a-b plane, ferromagnetic and antiferromagnetic components of the dipole-dipole interaction are relevant. The ordered state has a bilayered antiferromagnetic structure which is composed of planes of ferromagnetic spins that alternate in sign along the c-axis. As seen in Fig. 1.5, the transition



Figure 1.4: Spin structures of the ordered states of LiHoF<sub>4</sub> and LiErF<sub>4</sub>. The black spheres represent the rare earth ions, and the arrows represent the electronic moment.

temperature is about four times larger for LiHoF<sub>4</sub> thanLiErF<sub>4</sub>. The critical field of LiHoF<sub>4</sub> is larger than LiErF<sub>4</sub> by over a factor of 10. This result is in line with the much stronger field dependence of  $\Delta$  in LiErF<sub>4</sub> seen in Fig. 3.

A key feature in the phase diagram of LiHoF<sub>4</sub> is the change in curvature occurring at  $\sim 800$ mK. Mean field calculations of the phase diagram using only the electronic degrees of freedom agree with the experimental phase diagram nicely above this temperature and then underestimate the critical field. Calculations which also include the nuclear degrees of freedom find agreement for all temperatures. This is



Figure 1.5: Temperature-field phase diagram of LiHoF<sub>4</sub> and LiErF<sub>4</sub>. Plots are produced following references (Bitko et al., 1996) and (Kraemer et al., 2012)

a result of the hyperfine coupling reducing the effective field felt by the electronic spins. The effect of hyperfine coupling on  $\text{LiErF}_4$  is more subtle and will be the focus of Chapter 3.

#### **1.8** Spin Glass State in $LiHo_xY_{1-x}F_4$

Composition is another knob that can tune the Hamiltonian of the LiReF<sub>4</sub> material family. Y is an ideal element for substitution with Re because its ionic radius is approximately equal to Ho and Er (Salaün et al., 1997). Therefore, it does not affect the material symmetry and has negligible effect on its lattice constants. Y has no electronic moment. The primary effect of its substitution is to increase the average distance between Re ions, which reduces the average strength of the dipole-dipole interaction. This behavior can be written more quantitatively as  $\langle D_{ij}^{\mu\nu} \rangle \sim x$ , where x is the concentration of Re in LiRe<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub>. The linear dependence on concentration is due to the dimensionality of the material and the scaling of dipole-dipole dipole interaction,  $D_{ij}^{\mu\nu} \sim 1/r^3$ . Substitution will also introduce disorder into the system that causes random longitudinal and transverse magnetic fields. These fields are produced by the dipolar interaction. In a pure sample in which all the spins are aligned, dipolar transverse fields are zero at a given site due to cancellation from all neighboring spins. When a neighboring spin is missing, this cancelation will be imperfect. This is sketched in Fig. 1.6.

In this work, we will only focus on the substitution of Y into LiHoF<sub>4</sub>. A phase diagram of T-x is shown in Fig. 1.7. As x decreases from 1, the T<sub>c</sub> decreases linearly in x. This follows from  $T_c \sim D_{ij}^{\mu\nu} > x$ . Below  $x \sim 0.25$ , the ground



Figure 1.6: Diagram of ferromagnetically ordered electronic spins (red arrows) and their dipolar fields (blue arrows) acting on a central spin. (left) Pure sample where transverse dipolar fields cancel. (right) Sample with Y substitution (black sphere) where cancelation is incomplete.

state transitions from ferromagnetic state to a spin glass state. In spin glasses, large amounts of disorder and frustration result in a complex free energy landscape with many deep local minima. This limits the accessible phase space, and the system becomes non-ergodic. Accordingly, relaxation occurs on very long time scales. The spins within the spin glass state are frozen into a random orientation. This naturally raises the question of what order parameter is capable of distinguishing a paramagnetic and spin glass state. The frozen behavior can be captured by taking a time average of a spin state over some time, t, which is long on a microscopic scale. Then  $\langle S_i \rangle_t$ , which describes a single spin averaged over this time, will be non-zero in the glass state and average to zero in the paramagnetic state. The Edwards-Anderson order parameter is most commonly used to describe the spin glass state. It takes a thermal ensemble rather than a time average; however, it essentially captures the same physics being a higher-order correlation function (Mydosh, 1993). It additionally averages over different realizations of the disorder. In our system, this would be an average over different configurations of Ho and Y. The order parameter is expressed as

$$q_{EA} = << S_i >_T^2 >_c .$$

Here  $<>_T$  indicates a thermal average and  $<>_c$  indicates a configuration average.



Figure 1.7: T-x phase diagram of  $LiHo_xY_{1-x}F_4$  taken from (Ancona-Torres et al., 2008) Substitution of Y for Ho reduces the critical temperature of the ferromagnetic state. At x<0.25, the ground state transitions to a spin glass phase.

Finally, we can consider the effect of applying an external transverse field to the spin glass state. As is in the case of the pure sample, the transverse field introduces quantum fluctuations which suppress the ordered state. The applied transverse field acts in combination with intrinsic random transverse fields. The T-H phase diagram for LiHo<sub>0.2</sub>Y<sub>0.8</sub>F<sub>4</sub> and LiHo<sub>0.17</sub>Y<sub>0.83</sub>F<sub>4</sub> are shown in Fig. 1.8. Since the glass temperature,  $T_g$ , of LiHo<sub>0.2</sub>Y<sub>0.8</sub>F<sub>4</sub> is greater than LiHo<sub>0.17</sub>Y<sub>0.83</sub>F<sub>4</sub> at zero field, we would naively expect it to have a larger critical field as well. However, its critical field is smaller by a factor of two. This implies that the random transverse fields in LiHo<sub>0.17</sub>Y<sub>0.83</sub>F<sub>4</sub>.



Figure 1.8: T-H phase diagram for x = 0.167 and x = 0.2 taken from (Ancona-Torres et al., 2008) The transverse field suppresses the ordering temperature of the spin glass for both concentrations.

#### 1.9 Thesis Outline

In this chapter, I have outlined the general concept of classical phase transitions and quantum phase transitions and used the transverse field Ising model as an example to illustrate these concepts. I've described the LiReF<sub>4</sub> material system, its full Hamiltonian in a magnetic field for Re= Ho and Er, and how it can be mapped to a low energy effective Hamiltonian. Finally, I've described the effect of introducing disorder by substituting Re with nonmagnetic Y.

In Chapter 2, I describe theoretical and experimental details of heat capacity and a.c. magnetic susceptibility measurements, which are the two experimental probes used in this work.

In Chapter 3, I discuss the significance of hyperfine coupling on the field-induced quantum phase transitions of LiErF<sub>4</sub> with a natural abundance of isotopes. A natural abundance of Er has a nuclear moment on 23% of atoms which acts as a source of disorder in the system. I use heat capacity measurements to establish the temperature scale of hybridization between the electronic and nuclear states. I use a.c. magnetic susceptibility measurements to identity a change in the universality class of the quantum phase transition produced by applying a field parallel to the c-axis. The change in universality class corresponds to the temperature scale of electronuclear hybridization, strongly implying disorder as the cause of the change. I also examine the quantum phase transition produced by applying a field along the a-axis and find no evidence of a change in universality class.

In Chapter 4, I use a.c. susceptibility to measure magnetic relaxation in  $LiHo_{0.2}Y_{0.8}F_4$ . as a function of temperature and transverse magnetic field. I adapt standard experimental protocols used to study classical glasses for quantum spin glasses and discuss their results within a theoretical framework of quantum resonant tunneling rather than a complex free energy landscape picture.

In Chapter 5, I summarize the main conclusions drawn from my work and suggest directions for future work.

#### Chapter 2

#### EXPERIMENTAL METHODS

Magnetic susceptibility and heat capacity are fundamental measurements used to characterize magnetic systems. They are most commonly used for the basic task of identifying phase transitions; however, both methods can give deeper insights into magnetic systems. The dynamics of the system can be probed with magnetic susceptibility, and heat capacity illuminates the microscopic degrees of freedom of the system. Furthermore, the power law behavior of both quantities is essential in the identification of system's universality class.

#### 2.1 Magnetic Susceptibility

#### Theory

Magnetic susceptibility is defined as

$$\chi = \frac{\partial M}{\partial H}.$$

Experimentally, susceptibility is measured by applying a finite magnetic field to the sample and measuring its magnetic response. This can be achieved by applying a constant field (d.c.) or a time varying probe field (a.c.). A d.c. measurement generally measures the static response of the system; however, if the system has very slow dynamics ( $10^{-4}$  Hz to 1 Hz), the dynamics can be captured by quickly removing or applying a field and observing the time dependence of the magnetic relaxation (Topping & Blundell, 2018).

In the low frequency limit, the a.c. measurement also probes the static response of the sample. However, when the relaxation rate of the magnetic system is near the a.c. frequency, the dynamics of the system begin to be probed. The magnetic response of the sample may lag behind the probe field and the susceptibility will gain an out-of-phase dissipative component.

$$\chi = \chi' + i\chi'',$$

where  $\chi'$  is the in phase component and  $\chi''$  the out-of-phase component. This technique can be employed reliably over a frequency range of  $10^{-1}$  Hz to  $10^4$  Hz. To study relaxation over longer time scales, a finite d.c. field can be quickly applied,

and the relaxation process can be monitored through the time-dependent behavior of the a.c. susceptibility (Vincent, 2007).

#### Implementation

We employ a gradiometer technique to make a.c. susceptibility measurements in this work. The sample is placed in two concentric solenoids. An a.c. current is applied to the drive coil, the outer solenoid, to induce a magnetic response from the sample. The alternating drive field causes a time varying magnetic flux across the pick-up coil, the inner solenoid (see Fig. 2.1).



Figure 2.1: (left) pick-up coil form wrapped with 1000 turns of copper wire ( $\sim$  10 layers) with a 0.0003" diameter. Drive coil form wrapped with 630 turns of superconducting wire ( $\sim$  2 layers) with a 0.004" diameter. (right) Copper mount for sample and reference coil sets.

The pick-up and drive coil forms were machined out of PEEK (polyetheretherketone). An insulating material is chosen to limit eddy current from the a.c. magnetic field. Furthermore, it has a similar thermal expansion coefficient to the LiReF<sub>4</sub> family of materials, which reduces the chance of fracturing the sample when cooling. The length of the drive coils was  $\sim 3$  times the length of the pick-up to ensure a uniform a.c. field across the sample. The pick-up coil forms were wrapped with oxygen-free high thermal conductivity copper because it remains nonmagnetic at sub-Kelvin temperatures. The drive coils were wrapped with superconducting wire to eliminate resistive heating.

The flux across the pick-up coil is given by

$$\Phi = NA(H_{AC} + 4\pi M),$$

where  $\Phi$  is the flux, M is the magnetization of the sample, N is the number of turns of the pick-up coil, A is the area of the pick-up coil, and  $H_{AC}$  is the drive field. Accordingly, the voltage response across the pick-up coil is given by

$$\Delta V = -\frac{d\Phi}{dt} = -NA(\frac{dH_{AC}}{dt} + 4\pi\frac{dM}{dt}) = -NA\frac{dH_{AC}}{dt}(1 + 4\pi\frac{\partial M}{\partial H}) = -i\omega NAH_{AC}(1 + 4\pi\chi).$$

In principle, a single pick-up and drive coil are all that are necessary to measure susceptibility; however, it is often the case that  $4\pi\chi << 1$ . Considerable improvement to signal to noise is gained by using an identical pair of drive and pick-up coils with no sample as a reference. When a differential measurement is taken across the sample and reference pick-up coils, only the sample response remains.

$$\Delta V_{sample} - \Delta V_{ref} = -i\omega NAH_{AC}(1 + 4\pi\chi) - -i\omega NAH_{AC} = -i\omega NAH_{AC}4\pi\chi.$$

Furthermore, an additional measurement across only the reference pick-up coil can be made to eliminate all prefactors to the susceptibility.

$$\frac{\Delta V_{sample} - \Delta V_{ref}}{\Delta V_{ref}} = 4\pi\chi$$

A circuit diagram demonstrating our implementation of this technique can be seen in Fig. 2.2. An alternating voltage source from a lockin amplifier is used as a current source to drive the coils. A limiting resistor at room temperature, with  $R_{lim} >> R_{drive}$ , ensures that temperature variation in the resistance of the wires in a cryogenic environment does not strongly alter the magnitude of the current. A voltage measurement is also taken across a shunt resistor to monitor the current supplied to the drive coils. Sample and reference coils are wired antiparallel to each other to cancel each other. The differential signal across both coils and the signal from the reference coil are run through SR560 preamplifiers before a measurement is made with SR830 lockin amplifiers.



Figure 2.2: Circuit diagram used to measure the sample's a.c. susceptibility.

#### 2.2 Heat Capacity

#### Theory

Heat capacity is a measurement that is conceptually easy to understand, and experimentally difficult to perform. It is simply the amount of heat, Q, required to cause a unit change in temperature.

$$C = \frac{dQ}{dT}$$

It can be expressed equivalently in terms of entropy via the first law of thermodynamics, dQ = dE + pdV.

$$C_{v} = \frac{dE}{dT} = \frac{\partial E}{\partial S} \frac{\partial S}{\partial T} = T \frac{\partial S}{\partial T}$$

Then a measurement of C as a function of temperature can be used to extract a change in entropy.

$$\Delta S = \int_{T_1}^{T_2} \frac{\partial S}{\partial T} dT = \int_{T_1}^{T_2} \frac{C_v}{T} dT$$

This relation makes heat capacity a powerful probe to investigate microscopic degrees of freedom of a system. In practice, it can be difficult to distinguish entropic contributions from all of the degrees of freedom present in a real material. For experimental work at sub-Kelvin temperatures, effects from phonons, and crystal field splitting have typically frozen out, and we are left with only contributions from electronic and nuclear degrees of freedom. We need to model the nuclear contribution to isolate the electronic contribution. The nuclear spins obey a Schottky relation. For a two-level system with energy gap,  $\Delta$ , and N spins, this relation can be easily derived.

$$E_{two-level} = N \frac{\Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}$$

$$C_{two-level} = \frac{dE_{two-level}}{dT} = \frac{N}{k_B T^2} \frac{\Delta^2 e^{-\Delta/k_B T}}{(1 + e^{-\Delta/k_B T})^2}$$



Figure 2.3: (top) Occupation probability of the ground state and excited state of a two-level system as a function of temperature. (bottom) Heat capacity for a two-level system which peaks as the occupation of the ground state begins to saturate.

The Schottky relation can be generalized to an n-level system that corresponds to the nuclear spin present in any system of interest. Independent of n, for  $T >> \Delta$ , this relation simplifies to  $C \sim 1/T^2$  (Phillips, 1971).

We subtract the nuclear contribution from the total heat capacity to isolate the electronic contribution. This is the quantity of interest for investigating magnetic ordering in our systems. The exact functional dependence of the electronic contribution within the ordered state is non-trivial to calculate; however, for a second

order phase transition, the electronic heat capacity will obey a power law near the transition.

#### Implementation

A standard experimental procedure to measure heat capacity of a material is to start with a sample at a well-defined temperature, use a heater to apply a heat pulse, and measure the sample's temperature response with a thermometer. To extract the heat capacity from the temperature dependence of the sample, a thermal model must be assumed for how the heater and sample are coupled to the sample and how the sample is coupled to the thermal bath. Couplings are chosen such that the simplest possible thermal model is valid. In practice, this means the sample and heater are strongly coupled to the sample, and the sample is weakly coupled to the bath. We use a commercial calorimeter system produced by Quantum Design to achieve these requirements (see Fig.2.4). The fridge is thermally linked to a sample platform with a heater and thermometer deposited on it by their wires. The sample is coupled to this platform by N-Apzieon grease. We ensure this coupling is strong by measuring a sample that is as thin as possible ~ 20  $\mu$ . A thin sample (~ tens of microns) also helps limit the time constant of the response at low temperatures, which can grow rapidly in the milliKelvin regime.



Figure 2.4: Diagram of Quantum Design calorimeter. The sapphire platform has a heater and thermometer on the bottom. The wires of the heater and thermometer are used to hold the platform in free space. The sample environment is held at vacuum to ensure that these wires are the only link to the thermal bath.

The simplest possible model treats the sample and platform as a lump sum (see Fig. 2.5). In this case, the sample response is governed by the equation

$$C_{total}\frac{dT}{dt} = -K_w(T(t) - T_b) + P(t),$$

where  $C_{total} = C_{sample} + C_{platform}$ ,  $K_w$  is the thermal conductance of the heater and thermometer wires, T is the platform and sample temperature,  $T_b$  is the constant temperature of the bath, and P(t) is the power of the heat pulse. The solution to this differential equation is a simple exponential.

$$T(t) = \Delta T exp(-(K_w/C_{total})t) + T_b,$$

where  $\Delta T$  is the difference between the max temperature during the pulse and  $T_b$ . When the coupling between the sample and platform is weaker, a more complicated model must be used (see Fig. 2.5).



Figure 2.5: Schematic of two thermal models to describe a calorimeter. The simple model assumes the temperature of the platform and sample are equal, while the two-tau model considers the effect of a thermal resistance between the sample and platform.

$$C_{platform}\frac{dT_p}{dt} = P(t) - K_w(T_p(t) - T_b) + K_g(T_s(t) - T_p(t))$$

$$C_{sample}\frac{dT_s}{dt} = -K_g(T_s(t) - T_p(t)),$$

where  $K_g$  is the thermal conductance of the grease,  $T_p$  is the platform temperature, and  $T_s$  the sample temperature. The solution to these equations is a sum of two

exponentials that reduces to the simple model in the limit  $K_g >> K_w$  (Hwang et al., 1997).

Both of these models assume that the heat capacity is constant over the temperature change induced by the heat pulse. This is a problem near phase transitions, where heat capacity varies rapidly with temperature. Alternatively, we can assume that the heat capacity of the simple model varies with temperature and find

$$C_{total}(T) = \frac{-K_w(T)(T-T_b) + P(T)}{\frac{dT}{dt}}.$$

This relation is especially useful for studying power law behavior because data points need to be taken at high density near the transition.

#### Chapter 3

## EXPERIMENTAL CONSEQUENCES OF DISORDER AT AN ANTIFERROMAGNETIC QUANTUM PHASE TRANSITION

#### 3.1 Introduction

The introduction of disorder can have many effects on a classical phase transition (Vojta, 2019), including altering the universality class of a continuous transition (Pelissetto & Vicari, 2000), converting a transition from first to second order (Sang et al., 2014), and even changing the ground state of the system (Alba et al., 1982). Quantum phase transitions (QPT)s are expected to be affected more profoundly by disorder, with consequences for both the static and dynamical behavior (Bao et al., 1998; Jaramillo et al., 2010). When a d-dimensional quantum system is mapped to a (d+z) dimensional classical system, where z is the dynamical critical exponent, quenched disorder becomes correlated in the imaginary time dimension. However, systematic approaches to characterizing this hypersensitivity to disorder at a QPT pose distinct theoretical and experimental challenges.

Varying the importance of disorder typically entails studying a sequence of separate samples with a range of disorder, which can be difficult to synthesize controllably. Here, we adopt an alternate approach by investigating an erbium-based quantum magnet with quenched disorder provided by isotopic variation. Er-167, at 23% natural abundance, is the only stable isotope with non-zero nuclear spin. The energy scale of the hyperfine coupling makes it possible to vary the influence of the quenched disorder simply by changing the temperature.

LiErF<sub>4</sub> is an insulating tetragonal crystal with four erbium ions per unit cell (Fig. 3.1 left). Erbium's 4f electrons (J=15/2) provide large localized moments that are dipolar-coupled. The electronic ground state of an erbium ion is a Kramers doublet with a 26 K energy gap to its first excited state. This subspace can be treated as an effective spin-  $\frac{1}{2}$  system. The crystal field induces strong easy plane anisotropy with  $(g_{\perp}/g_{\parallel})^2 = 13.8$ . In-plane anisotropy, originating from order by disorder, causes the moments to point along the a or b-axis (Kraemer et al., 2012). These symmetries correspond to the  $XY/h_4$  universality class.

LiErF<sub>4</sub> orders antiferromagnetically (Beauvillain et al., 1977) with a bilayer structure at  $T_N = 373(5)$  mK (Kraemer et al., 2012). The observed  $T_N$  is approxi-



Figure 3.1: (left) Body-centered tetragonal unit cell of LiErF<sub>4</sub>. Lattice constants are a = 5.162 Å, c=10.70 Å. Er sites are represented as black spheres; Li and F sites are not shown. Arrows represent the double layer antiferromagnetic spin structure of the ordered state. (right) The data points mark the measured phase diagram as a function of temperature and c-axis magnetic field, obtained by sweeping temperature (open circles) and field (filled circles). Imagemap shows the susceptibility data from Fig. 3.3.

mately half of mean-field predictions, and its critical exponents have been reported as  $\beta = 0.15(2)$  and  $\alpha = -0.28(4)$ . These exponents are consistent with a 2D quasi-Ising description where the exponents lie in a universal window bounded by the exponents of the 2D Ising ( $\beta = 0.125$ ) and XY ( $\beta = 0.23$ ) models. The strength of the in-plane anisotropy tunes between these bounds (Taroni et al., 2008). This reduction in dimensionality is surprising for a material whose 2D nature is not evident from its structure; however, it has been observed in similar materials (Babkevich et al., 2016).

#### 3.2 Quantum Phase Transition with H||c

A QPT is induced by applying a magnetic field of order 4 kOe along the c-axis (Fig. 3.1 right).  $\beta_H = 0.31(2)$  was reported for this QPT which is near the values of both the 3D Ising ( $\beta_H = 0.3265(3)$ ) and XY ( $\beta_H = 0.349(2)$ ) models. This agrees with a d+1 mapping from the classical phase transition. Mean field calculations of the critical field are sensitive to which crystal field parameters are used; values ranging from 5.75 kOe (Kraemer et al., 2012) to 9.5 kOe (Babkevich et al., 2016) have been reported. However, all calculations overestimate the experimentally

observed critical field,  $H_c$ , and along with the dimensional reduction and the nonmean field critical exponents, point to the role of spin fluctuations at the transition.

For erbium sites occupied by Er-167 atoms, the nuclear moment (I=7/2) couples antiferromagnetically to the electronic moment with strength  $A_{hf}$ =6 mK (Sattler & Nemarich, 1971). This coupling splits the Kramers doublet into a multiplet. At the level of a single ion calculation, these states have a span of 160 mK (see Fig. 3.2). In LiHoF<sub>4</sub>, an Ising ferromagnet within the same family of materials, the hyperfine coupling slaves the nuclear spins to the electronic spins at sufficiently low temperature, increasing the critical field (Bitko et al., 1996) and allowing a new class of low energy, electronuclear excitations (Libersky et al., 2021), but does not alter its universality class (McKenzie & Stamp, 2018). The increase in  $H_c$  is a general effect due to a reduction in effective field felt by the electronic spins (Chakraborty et al., 2004). Since Ho has only one stable isotope, no disorder is introduced by the nuclear moment.

Mean field calculations on LiErF<sub>4</sub> that include nuclear moments on 23% of sites find a similar increase in Hc of ~ 500 Oe (Babkevich et al., 2015; Kraemer et al., 2012). The choice of crystal field parameters does not strongly impact the change in  $H_c$ . Since the nuclear spin locks with the electronic spin, the local  $XY/h_4$  symmetry of the system is unbroken by the disorder and belongs to the category of randommass (also referred to as random- $T_c$ ) disorder (Vojta, 2019). Random field disorder is a stronger form of disorder which breaks the local symmetry. Previous work on LiErF<sub>4</sub> examined the effect of random-field disorder by substituting Er with Ho and found a reentrant glassy state with 6% substitution (Piatek et al., 2013).

#### 3.3 Results

We plot in Fig. 3.3 field sweeps of the ac magnetic susceptibility in the linear and zero-frequency limits along the c-axis on a needle crystal with dimensions  $(0.35x0.35x1.65mm^3)$  at a series of temperatures. Susceptibility measurements were made using a commercial susceptometer (PPMS DR, Quantum Design). Measurements were taken in the linear regime with a drive field of 0.5 Oe and with frequencies of 1 kHz (power law fits) and 10 kHz (phase diagram). No variation in  $H_c$  was observed between these frequencies. We note that our reported critical field,  $H_c(T = 0) = 3645(6)$  Oe, is 10% lower than a reported value of  $H_c(T = 0) = 4000$ Oe (Kraemer et al., 2012). We attribute this discrepancy to demagnetization effects (see material quality/geometry section). At temperatures above 150 mK (Fig. 3.3



Figure 3.2: Single ion calculation of the energy levels of the lowest lying multiplet of erbium-167 in zero field. Energies are calculated by an exact diagonalization of all 128 states. The lowest and highest electronuclear levels are single states (blue); all other states are doubly degenerate (red). Experimental parameters used in the calculation for the crystal field and hyperfine coupling are taken from Ref. (Babkevich et al., 2015) and Ref. (Sattler & Nemarich, 1971), respectively.

top), we observe steadily increasing critical divergence as the temperature drops, corresponding to the diminishing strength of thermal fluctuations. Below 150 mK (Fig. 3.3 middle), the opposite trend is observed: the sharpness of the transition is reduced continuously as the temperature decreases. This evolution in the shape of the divergence can be parameterized by the full width of the peak at 90% of its maximum for each T (Fig. 3.3 bottom). This heuristic metric reinforces the trend apparent in the raw data of two qualitatively distinct regimes separated at T=150 mK. In a conventional description of a QPT, thermal broadening is expected and can be understood as a finite size effect in the imaginary time dimension (Sondhi et al., 1997). The unexpected broadening in the low temperature regime suggests that a new degree of freedom emerges at the lower energy scale.

To elucidate the nature of the  $T \rightarrow 0$  behavior, we measured the specific heat,



Figure 3.3: Ac magnetic susceptibility of  $\text{LiErF}_4$  at 0.5 Oe drive field and 10 kHz frequency vs. c-axis magnetic field at a series of fixed temperatures above (top) and below (middle) T = 150 mK. (bottom) Width of the peak at 90% of its maximum value. Red and blue shading identify the high and low temperature regimes, respectively.

C(T, H), on a single-crystal thin plate (1x1x0.04mm<sup>3</sup>) of LiErF<sub>4</sub> (Fig. 3.4). Data was collected over a temperature range of 0.055 K to 4 K and at fields parallel to c up to 4.25 kOe. These measurements were taken to lower temperatures and higher fields than previously reported (Kraemer et al., 2012; Mennenga et al., 1984), and allow us to fully characterize the specific heat through the QPT. Within this temperature



Figure 3.4: Specific heat vs. temperature for a series of magnetic fields along the c-axis. (inset) Total and purely electronic heat capacities at zero field. Arrow at T = 150 mK marks where the disordered nuclear spin bath couples to the electronic spins.

Measurements were made on a plate sample  $(1x1x0.04\text{mm}^3)$  cut from sample 1 using a commercial sub-Kelvin calorimeter (PPMS DR, Quantum Design) operating in a standard relaxation mode. Away from the phase boundary, data were taken in discrete steps using small thermal pulses ( $\frac{\Delta T}{T} = 0.02$ ) fit to a two-tau model. Near the transition, measurements were made with a large pulse ( $\frac{\Delta T}{T} = 0.15$ ) to obtain higher point density, and the specific heat was extracted by analyzing the evolution of the slope of the T(t) response of the calorimeter (Riegel & Weber, 1986).

The high-T upturn in C(T) is due to the crystal field splitting and is negligible in the temperature range of the magnetic ordering. The peak at the ordering transition is well described by a power law of the form:

$$C(T)=A^{\pm}|\frac{T-T_N}{T_N}|^{-\alpha}+D,$$

where A + and A - are the amplitudes in the paramagnetic and anitiferromagnetic states, respectively, and D is a non-critical background. We find that the specific heat exponent agrees within error of the previously reported value  $\alpha = -0.28(4)$ (Kraemer et al., 2012). As seen in Fig. 3.4, at the lowest temperatures there is an additional upturn in the specific heat, attributable to a Schottky contribution (Mennenga et al., 1984). The Schottky anomaly occurs when the coupling between nuclear and electronic spins begins to dominate over thermal fluctuations. We account for the Schottky contribution by assuming the standard  $T^{-2}$  high-temperature form (Phillips, 1971). This allows us to subtract off the Schottky contribution to the specific heat and isolate the purely electronic contribution (Fig. 3.4 inset). The electronic and total heat capacities begin to separate at 150 mK, coincident with the broadening of the divergence of the magnetic susceptibility, pointing to the naturally occurring isotopic abundance as the relevant source of disorder. Furthermore, an integration of the electronic specific heat gives entropy S=Rln(2) for all fields. The lack of excess entropy rules out a more exotic ground state, such as a quantum spin liquid, as a source of the broadening.



Figure 3.5: Critical behavior of the ac susceptibility of LiErF<sub>4</sub> in the paramagnet (PM) and antiferromagnet (AFM). (top) Susceptibility at T=50 mK (black) and fits to a critical divergence form with Gaussian field broadening (see text for details). Red and blue denote  $H < H_c$  and  $H > H_c$ , respectively. (inset) Susceptibility vs magnetic field at T=50 mK. The scale bar marks absolute units of emu/Oe. The data is well described by a pure power law over 0.8 decades. Near the transition, deviations from linearity occur due to the Gaussian convolution. (bottom) Temperature dependence of the amplitude ratio and critical exponent describing the control parameter susceptibility and a transition between universality classes. Error bars are estimated by refitting with a fit range varied by  $\pm 5\%$  of a decade.

We present in Fig. 3.5 a power law analysis of the susceptibility field sweeps to probe the low-temperature critical behavior. The order parameter of an antiferromagnet is the staggered magnetization, and the critical behavior of the susceptibility along the c-axis does not correspond to a conventional  $\gamma$  exponent. However, it can be understood under the general theory of critical scaling at QPTs developed by Belitz and Kirkpatrick (Kirkpatrick & Belitz, 2015). In this framework, a "control-parameter susceptibility" is defined as

$$\chi_r = -\frac{\partial^2 f}{\partial r^2},$$

where f is the free energy and r is the athermal tuning parameter that induces the QPT. Two critical exponents are defined for this susceptibility: one at zero temperature as a function of field,

$$\chi_r(H, T=0) = B^{\pm} |\frac{H - H_c}{H_c}|^{-\alpha_H} + \chi_0.$$

and the other at H=Hc as a function of temperature,

$$\chi_r(H=H_c,T)=aT^{-\alpha_T},$$

where B+ and B- are the amplitudes in the paramagnetic and anitiferromagnetic states, respectively,  $\chi_0$  is a non-critical background, and a is the amplitude at the critical field. Here the notation  $\alpha$  is used because, in the case of r = T, the control parameter susceptibility is given by C/T. For a QPT induced by a magnetic field along the c-axis,  $\chi_r$  corresponds to  $\chi_c$ , the magnetic susceptibility along the c-axis.

We model a macroscopic distribution of  $H_c$ s with width  $\delta H_c$ , most likely arising from demagnetization fields due to shape effects, by convolving the power law with a Gaussian. The convolution allows us to fit the susceptibility through the transition and improves the fit stability of the amplitude and critical exponent (Wosnitza, 2007). Our fit gives  $\delta H_c \sim 30 \text{Oe} \rightarrow \frac{\delta H_c}{H_c} = 8 \times 10^{-3}$ . The data is well fit by this functional form over a range of reduced fields spanning -0.8 to 0.8 for temperatures up to at least 260 mK. The error in the fit parameters is dominated by the systematic error associated with the fit range. At high temperatures,  $\alpha_H$ increases rapidly as temperature decreases. It begins to saturate at T ~ 150 mK and reaches  $\alpha_H = -0.32(2)$  in the  $T \rightarrow 0$  limit. The amplitude ratio B + /B begins to increase at 150 mK and captures the same behavior as the heuristic width metric in Fig. 3.3. At our base temperature of 50 mK, B + /B has not saturated, but we can establish a lower bound of B + /B - > 5 at T = 0.

#### 3.4 Discussion

The amplitude ratio, B+/B-, typically marks a particular universality class(Pelissetto & Vicari, 2002). The rapid increase in the ratio at low temperatures indicates that the universality class changes as the nuclear and electronic spins lock. Further evidence that the change in amplitude ratio is due to the nuclear spins is seen in a comparison between field sweeps taken on LiErF<sub>4</sub> samples with a natural isotopic abundance and with isotopically pure erbium-168 (Nikseresht Ghanepour, 2012). The isotopically pure sample has a much sharper peak than the natural sample at 35 mK, reaffirming the role of nuclear spins.

The Harris criterion dv > 2 is a necessary condition for a universality class to be unchanged by random mass disorder, where v is the critical exponent of the correlation length(Brooks, 2016; Harris, 1974). The Harris criterion determines if the correlation length grows rapidly enough for the effective strength of disorder to go to zero at the transition. Since only dimensions with random disorder contribute to the Harris criterion, QPTs obey dv > 2 rather than (d + z)v > 2. Hence QPTs require a larger v relative to an analogous classical transition as a manifestation of their sensitivity to disorder (Vojta, 2019).

Given that  $\beta_H$  is far from the mean field value ( $\beta_{MF} = 0.5$ ) and that mean field calculations overestimate  $H_c$ , we assume that the dimensionality of the system is below its upper critical dimension and that a hyperscaling relation is valid. Under this assumption, we can express the Harris criterion in terms of the critical exponents of the control parameter susceptibility using Eqs. 2.23a and 2.23b of Belitz and Kirkpatrick (Kirkpatrick & Belitz, 2015):

$$d\nu = \frac{2\alpha_T - \alpha_H(1 + \alpha_T)}{\alpha_T} > 2.$$

When  $\alpha_T > 0$ , this inequality can be simplified to

$$\alpha_H < 0,$$

which is analogous to the standard form of the Harris criterion expressed in terms of the classical critical exponent,  $\alpha < 0$ . The Harris criterion pertains to the critical exponents of clean systems. Since  $\alpha_T$  remains positive in both the clean and disordered universality classes (Kraemer et al., 2012), we can focus solely on the sign of  $\alpha_H$  in the clean universality class to determine the validity of the Harris criterion in the present measurements. The rapid change of  $\alpha_H$  in the clean regime is cut off by the disorder and prevents us from definitively characterizing  $\alpha_H^{clean}$  in the zero-temperature limit. A linear extrapolation of the clean regime to T=0 finds  $\alpha_H^{clean} = 0.06(10)$ , (see Fig. 3.6) which is consistent within error bars with a specific heat exponent for both the classical 3D Ising ( $\alpha = 0.110(1)$ ) and 3D XY ( $\alpha = -0.015(1)$ ) models. However, a change in universality implies that the Harris criterion was violated,  $\alpha_H^{clean} > 0$  at T=0, and the operative universality class is classical 3D Ising. The critical exponents of all universality classes with a finite effective disorder strength at a phase transition follow the Chayes-Chayes-Fisher-Spencer relation  $dv^{disorder} > 2$  (Chayes et al., 1986). This relation differs from the Harris criterion in that it uses the critical exponents of the disordered universality class. We find that our disordered universality class is consistent with this relation because  $\alpha_H^{disorder} < 0$ .



Figure 3.6: Critical field exponent replotted from Fig. 3.5, showing a linear extrapolation to T=0 of the data in the clean, high-temperature limit (red points). Shaded region shows the  $1\sigma$  error band of the extrapolation.

In conclusion, magnetic susceptibility and specific heat measurements reveal that the QPT in antiferromagnetic  $\text{LiErF}_4$  is affected profoundly by naturally-occurring isotopic disorder. At temperatures below 150 mK, nuclear spins slave to electronic

spins, reducing the effective field and introducing random mass disorder. We identify  $\chi_c$  as a relevant observable to study the critical behavior of a field-induced QPT and relate its critical exponents to the Harris criterion and the Chayes-Chayes-Fisher-Spencer relation. Our data is consistent with a violation of the Harris criterion in the clean high-temperature regime, above the energy scale of the hyperfine coupling, and a change in universality class when disorder becomes manifest at low T. The critical exponents of the disordered universality class obey the Chayes-Chayes-Fisher-Spencer relation.

The unconventional power behavior of the susceptibility in the disordered universality class that characterizes  $\text{LiErF}_4$  may well point to Griffiths physics and motivates further studies of the paramagnetic regime. More generally, nuclear moments present a well-characterized platform to manipulate disorder in situ, with sensitivity to temperature and magnetic field, and potential tunability of the low-T electronuclear spectrum itself.

#### **3.5** Note on effects of material quality and sample geometry

Two parent single crystal samples were obtained from commercial sources.  $T_N$  at zero field was used to determine sample quality. Susceptibility measurements found sample 1 and sample 2 had  $T_N$  's of 361 mK and 333 mK, respectively. Hence sample 1 was used for susceptibility, and heat capacity, while sample 2 was characterized with susceptibility measurements for comparison. Measurements in the needle limit (0.35x0.35x1.65mm<sup>3</sup>) and plate limit (3x3x0.4mm<sup>3</sup>) were made on samples cut from sample 1 to investigate demagnetization effects on  $H_c$  when H||c. At T=50 mK,  $H_c$  was measured as 3560 Oe and 4669 Oe for the needle and plate, respectively. The geometry had no effect on  $T_N$  at zero field. Additionally, measurements were made on a needle (1.25x1.25x6mm<sup>3</sup>) cut from sample 2. An  $H_c$  of 3223 Oe with H||c was measured at T=50 mK, corresponding to a reduction of ~10% in  $H_c$  and  $T_N$  relative to sample 1. Broadening was observed at T=150 mK regardless of geometry or parent sample, substantiating the critical role ascribed to nuclear spin disorder.

#### 3.6 Quantum Phase Transition with H||a

We now turn to an alternative parameter to tune the ordered state to a quantum phase transition. If a sufficiently large magnetic field is applied along the a-axis, it will become energetically favorable for the spins to rotate within the easy plane and align with the magnetic field. A quantum phase transition occurs when all the spins align, and the staggered magnetization goes to zero. The QPT induced by a field applied along the a-axis fundamentally differs from a field applied along the c-axis. When the field is applied along the c-axis, the spins are left fluctuating in the easy plane and retain spin-inversion symmetry. This is not the case for the field applied along the a-axis. This naturally leads to the question of the relevance of disorder in this QPT.

The only previous experimental work on this QPT was a neutron scattering study (Kraemer, 2009; Kraemer et al., 2012). They reported that a field of 300 Oe suppressed domains with spins aligned with the b-axis and formed a mono-domain of spins aligned with the a-axis. They found that the intensity at Q = (0, 0, 3), which tracks the staggered magnetization, is sharply suppressed with field up to H = 2.0(2) kOe and has a long tail which persists to H = 4 kOe. Additionally, they performed inelastic scattering experiments at Q = (0, 0, 2.9) to track the evolution of the soft mode of the quantum phase transition. The gap of the soft mode closes at  $H \sim 900$  Oe, indicating a quantum phase transition. The inconsistency between these field scales could be due to different sample shapes and accordingly different demagnetization fields. A large distribution of demagnetization fields could also explain the long tail in the inelastic scattering experiments. A mean-field calculation of the critical field considering only electronic degrees of freedom found  $H_c = 3.25$  kOe (Kraemer, 2009). The overestimate of  $H_c$  indicates the significance of fluctuations in this QPT as well.

We characterize the QPT by measuring susceptibility along the a-axis, which is its control parameter susceptibility. These measurements were performed using the susceptometer discussed in Chapter 2. The sample was cut from sample 1 and has dimensions of  $(6.12x0.66x0.66mm^3)$  to ensure minimal demagnetization effects. Field sweeps were taken with a drive field of 40 mOe and at a frequency of 40 Hz. A lower drive field must be used in this apparatus because the sample is thermally linked to the copper mount, which can be heated by strong eddy currents. The real and imaginary parts of the susceptibility are shown in Fig. 3.7. In the ordered state, the real susceptibility increases with field up to 200 Oe, and then flattens. This feature corresponds to the previously reported formation of a mono-domain. The peak at  $H_c = 962(1)$  Oe in both the real and imaginary susceptibility corresponds to the phase transition. The behavior of this peak strongly contrasts with that of the QPT with H||c. Both peaks remain sharp at T<150 mK and have no obvious response to the slaving of the nuclear spins to the electronic spins. The full width at



Figure 3.7: Field sweeps along the a-axis of (left) real susceptibility and (right) imaginary susceptibility.

90% maximum of the real susceptibility is shown for both QPTs in Fig 3.8.



Figure 3.8: Full width at 90% maximum of the QPTs induced by H||a and H||c. (right) The data points mark the measured phase diagram as a function of temperature and a-axis magnetic field (filled circles). Imagemap shows the real susceptibility data from Fig. 3.7.

We consider two potential explanations for the apparent insensitivity to nuclear disorder: (1) The hyperfine coupling does not affect the effective field along the a-axis and thus does not act as random mass disorder. While the hyperfine coupling is isotropic within the full LiErF<sub>4</sub> Hamiltonian, in the truncated subspace, its anisotropy is proportional to the electronic anisotropy  $\frac{A_{\perp}}{A_{||}} = \frac{g_{\perp}}{g_{||}} = 3.7$ . Accordingly,

we may expect a lower temperature scale, T = ~41 mK, for the dirty regime in this QPT. As seen in Fig. 3.8, we take field sweeps down to T=12 mK and still see no broadening, discounting this hypothesis. (2) The universality class of the QPT satisfies the Harris criterion, meaning no changes are expected. A test of this potential explanation requires a power law analysis of the control parameter susceptibility. If  $\alpha_H > 0$ , the Harris criterion is valid, and the disorder is not expected to affect criticality. We were unable to fit a power law to our present data over sufficiently large field range to confidently claim a value for the critical exponent  $\alpha_H$ . A power law analysis may be possible for measurements with a higher field resolution and using a multi-axis magnet to null out any field along the c-axis due to sample misalignment.

#### Chapter 4

#### QUANTUM RELAXATION IN A SPIN GLASS

#### 4.1 Introduction

Spin glasses are a long-standing problem in condensed matter physics, with applications to computation, economics, engineering, and neuroscience, among other areas of inquiry. Disorder and frustration cause spins to freeze into a nonergodic state and accordingly, have very slow magnetic relaxation(Mydosh, 1993). This is challenging problem theoretically because the usual approaches of statistical mechanics do not apply. Systems with quenched disorder require sophisticated techniques to solve analytically (Mezard et al., 2004) or numerically (Zhang et al., 2021) The problem is also difficult experimentally because relaxation times are long on a laboratory timescale and highly specific experimental procedures must be used to acquire reproducible results (Vincent et al., 1997). While great strides have been made in understanding classical spin glasses, there has been limited progress in the understanding of quantum spin glasses (QSG) (Mydosh, 2015). In a QSG, quantum fluctuations are introduced by a non-thermal tuning parameter which cause relaxation via tunneling rather than thermal relaxation. Previous work on quantum spin glasses has focused on equilibrium properties (Schechter & Stamp, 2005; Tabei et al., 2006; Wu et al., 1991, 1993). The dynamic behavior of classical spin glasses has produced unexpected results and informative insights. In this work, we extend the investigation of spin glass dynamics to the quantum regime.

Phenomena in classical glasses are typically understood within the theoretical framework of a hierarchical free energy landscape of metastable states. This theoretical picture was developed from the mean field solution of the infinite-range Sherrington-Kirkpatrick model; however, it is more broadly used to form an intuitive understanding of glassy physics. Furthermore, various phenomenological models have been inspired from this theory (Zhang et al., 2021). In this picture, an effective free energy landscape is defined as a function of temperature. At each temperature, the free energy landscape is defined by the set of accessible free energy valleys. As the temperature decreases, each valley subdivides into new valleys. Valleys and their sub-valleys form a branching tree hierarchy where sub-valleys form a lower level of the tree. Two key dynamic properties which are explained by this model are rejuvenation and memory. Rejuvenation occurs when a small decrease in temperature restarts the relaxation process. When temperature decreases and the system forms new sub-valleys, the process of finding a minimum in this new set of valleys is described as rejuvenation. Memory occurs when a system relaxes at a constant temperature for a time. Lowering the temperature and later returning it to the original value causes the system to resume relaxation from its previous state. Within the hierarchy picture, this results from the sub-valleys reverting to their parent valleys and relaxation resuming in this original valley.

This theoretical framework is not appropriate for QSGs. In analogous quantum experiments, a non-thermal tuning parameter changes instead of temperature. This alters the true energy levels of the system rather than an effective free energy landscape. Instead, we use a more fundamental description of resonant interactions between two-level systems to describe relaxation. This process is governed by an equation of motion where spins have some bias energy,  $\xi = E_{\uparrow} - E_{\downarrow}$ , and are coupled to a bath (Prokof'ev & Stamp, 1996, 1998). This relation is given by

$$\frac{P_{\alpha}(\xi,r)}{dt} = -\Lambda(\xi) [P_{\alpha}(\xi,r) - P_{-\alpha}(\xi,r)] - \sum_{\alpha'} \int dr' \int d\xi' \Lambda(\xi') \times [P_{\alpha\alpha'}^{(2)}(\xi,\xi',r,r') - P_{\alpha\alpha'}^{(2)}(\xi - V_D(r-r'),\xi',r,r')].$$

Here,  $\Lambda(\xi)$  is the transition matrix element whose form is dependent on the nature of the coupled bath.  $P_{\alpha}(\xi, r)$  is a one spin probability distribution function for a spin in state  $|\alpha\rangle$  at position r with bias energy  $\xi$ . This distribution governs local spin flip events.  $V_D$  is the spin-spin interaction energy.  $P_{\alpha\alpha'}^{(2)}$  is a two-spin distribution function for spins at site r and r' and states  $|\alpha\rangle$  and  $|\alpha'\rangle$ . This distribution governs co-flipping events between spins which are brought into resonance by a pairwise interaction  $V_D$ . It is important to note that this theory truncates higher order spin correlations, and a more accurate, but considerably more complex extension could be developed to include them.

Many experimental procedures have been used to study dynamic behavior in classical spin glasses with variants that monitor magnetic relaxation via the magnetization (Refregier et al., 1987) or a.c. susceptibility (Dupuis et al., 2001). Here, we focus on a.c. susceptibility variants of the memory dip procedure. This is a standard procedure that has been fruitful in uncovering the properties of rejuvenation and memory. In the memory dip procedure, the sample begins at a temperature well above its freezing temperature,  $T_f$ . The sample is cooled at a slow rate to some

temperature,  $T_w$ , where  $T_w < T_f$ . The sample relaxes at  $T_w$  for a set time and is then cooled to base temperature,  $T_{base}$ . A separate reference measurement is performed without the relaxation step. The susceptibility peaks at  $T_f$ , and then decreases monotonically with temperature until the relaxation step. During relaxation, the susceptibility continues to decrease with time. When temperature is decreased after the relaxation step, the standard response is that the susceptibility rapidly increases until it merges with the reference curve, and then begins to decrease with temperature. This rapid increase in susceptibility is interpretated as rejuvenation. After reaching  $T_{base}$ , a common extension to this procedure is to slowly increase temperature above  $T_g$ . The susceptibility of both the reference and relaxation procedure increase with temperature; however, the susceptibility of the relaxation procedure will temporarily remain constant or decrease with temperature at  $T_w$ . This is an example of memory. In this work, we develop an analogous procedure for a quantum memory dip experiment where transverse field is used to introduce quantum fluctuations that suppress the spin glass state.

We use the  $LiHo_xY_{1-x}F_4$  material system as an experimental platform for this study. Substitution of Ho with non-magnetic Y introduces disorder and frustration into the system. The system orders as a spin glass in the concentration range of x < 0.25 (Quilliam et al., 2012). In this work, we investigate a concentration of x = 0.20, which has a  $T_g = 0.145$  K (Ancona-Torres et al., 2008). Application of a transverse field introduces quantum fluctuations that suppress the spin glass phase to T=0 at  $H_g = 5$  kOe. At this concentration, the average dipolar coupling strength is comparable to the hyperfine coupling, and fully hybridized electronuclear states must be considered. The longitudinal component of the hyperfine coupling,  $A_{hf} J_z I_z$ , splits each electronic state into a multiplet of 8 states with a separation ~ 205 mK (Giraud et al., 2001). The electronuclear doublet ground state is  $|m_J = \pm 1/2, m_I = \pm 7/2\rangle$ . The transverse field no longer directly mixes the doublet state, and tunneling occurs via the transverse component of the hyperfine coupling,  $A_{hf}(J_+I_- + J_-I_+)/2$ (Schechter & Stamp, 2005). In this manifold, each electronuclear doublet will have its own tunneling amplitude where  $|m_J = +1/2, m_I = -7/2, -5/2, -3/2, -1/2 \rangle \leftrightarrow$  $|m_J = -1/2, m_I = +7/2, +5/2, +3/2, +1/2\rangle$  corresponds to  $\Delta_{7/2}, \Delta_{5/2}, \Delta_{3/2}, \Delta_{3/2}$ , respectively (Schechter & Stamp, 2008). We take temperature effects into account by taking a Boltzmann average over all tunneling matrix elements in this manifold to calculate an effective tunneling matrix element,  $\Delta^{eff}(T, H_T)$ . This nuclear blocking process results in significant reduction in tunneling amplitude relative to a purely electronic system where  $\Delta \approx 2.7 \text{ mK} (B/kG)^2$ .



Figure 4.1: (left) Tunneling matrix element between electronuclear states in the lowest energy manifold. (right) Boltzmann average of the tunneling matrix element at several representative temperatures.

#### 4.2 Memory Dip

As seen in Fig. 4.2, we employ the classical thermal memory dip procedure on our system to provide a baseline for the quantum memory dip behavior. We start at  $T_{initial}$ =250 mK and decrease the temperature at a rate of 0.5 mK/min to  $T_w$  (blue trace). We wait eight hours to ensure that the system fully relaxes (green trace), and then cool to base temperature  $T_{base} = 35$  mK (blue trace). The temperature is then returned to  $T_{initial}$  (red trace). A reference curve was taken with the same  $T_{initial}$ ,  $T_{base}$ , and rate (black trace). Two striking features are the lack of increase in susceptibility after relaxing at  $T_w$ , and the lack of any anomaly at  $T_w$  in the warming trace. This system shows no apparent rejuvenation or memory effects in the thermal memory dip procedure. The time dependence of susceptibility during the relaxation stage is well described by an exponential.

In the quantum memory dip procedure, the transverse field is ramped to  $H_{initial}$ =12 kOe, and then cooled to  $T_{base}$ . The field is decreased to the waiting field,  $H_w$ , at a rate of 16 Oe/min. The system relaxes for ten hours and then the field is decreased to zero. A reference curve is taken using the same procedure with the omission of the relaxation stage. Again, the time dependence of susceptibility during the relaxation stage is well described by an exponential. Unlike the thermal memory dip experiment, the susceptibility strongly increases after the relaxation stage. Moreover, it cuts through the reference curve.

A key aspect to understand this behavior is the non-trivial random fields produced



Figure 4.2: (left) Thermal memory dip procedure. (right) Quantum memory dip procedure. Both plots have four separate memory dip runs plotted that differ by  $T_w$  and  $H_w$  and have a shared reference curve. Susceptibility measurements are performed on a sample with dimensions (0.76x1.78x5.11mm<sup>3</sup>) at a frequency of 5 Hz with an a.c. drive field of 40 mOe.

when diluting a dipolar-coupled system. The dipolar interaction is given by

$$H_{dipolar} = \sum_{i,j,\alpha,\beta} V_{i,j}^{\alpha,\beta} J_i^{\alpha} J_j^{\beta}.$$

Here  $V_{i,j}^{\alpha,\beta}$  is the dipolar interaction between sites i j.  $\alpha$  and  $\beta$  are the axes on sites i and j, respectively. When a neighboring spin is replaced by non-magnetic Y, the transverse component of the dipolar field will no longer cancel due to symmetry. The transverse field at Ho site i is then dependent on the configuration of Ho and Y atoms and is given by

$$H^i_\perp = H^0_\perp + \widetilde{H}^i_\perp$$

Here  $H^i_{\perp}$  is the transverse field at site i,  $H^0_{\perp}$  is the applied field, and  $\tilde{H}^i_{\perp}$  is the transverse field due to off-diagonal terms at site i (Schechter & Stamp, 2008).  $\tilde{H}^i_{\perp}$ 

will follow a probability distribution centered around zero field. As a first-order approximation, we assume it takes a Gaussian form. The standard deviation of this distribution,  $\sigma(\tilde{H}_{\perp}^{i})$ , is non-trivial to calculate. We make a rough estimate by considering a reported calculation of the phase diagram of LiHo<sub>x</sub>Y<sub>1-x</sub>F<sub>4</sub> with concentration x=0.17(Schechter & Stamp, 2005). This mean-field calculation assumes the effect of the random transverse field is equivalent to a uniform  $\tilde{H}_{\perp}^{i}$  across all sites.  $\tilde{H}_{\perp}^{i}$  is used as a free parameter to match the calculated phase diagram with experimental results. The best agreement is found with  $\tilde{H}_{\perp}^{i}$ =0.65 T. Since disorder is stronger for a concentration of x=0.2, we expect an even larger field. There also will be a random longitudinal field simply because the spins are not aligned in the glass phase. Furthermore, the application of a transverse field will result in a finite magnetization along the transverse axis (i.e.  $J^{x} \neq 0$ ), which will scale linearly with  $H_{\perp}^{0}$ . The off diagonal dipolar terms will then give an additional contribution to the random longitudinal field. When  $SH_{\perp}^{0} \ll \Omega_{0}$ , the random field is well approximated by

$$\widetilde{H}^i_{||} = \frac{2SH^0_{\perp}}{\Omega_0} \sum_j V^{zx}_{ij}.$$

Here S is the effective magnitude of the Ho spin , and  $\Omega_0$  is the energy of the first excited electronic state (Schechter & Stamp, 2008). The distribution of the random longitudinal field will broaden linearly with  $H^0_{\perp}$ . As seen in Fig. 4.3, we use these relations to model the evolution of the random transverse field distribution and the random longitudinal field distribution with applied transverse field.

We employ the equations of motion previously discussed to describe the memory dip experiments with the assumption of coupling to a nuclear spin bath. In this treatment, we assume that the dipolar and hyperfine fields are quasi-static except for a rapidly fluctuating hyperfine component. Then relaxation by a nuclear spin bath follows:

$$\Lambda_{SB}(\Delta,\xi) = T_2 \Delta^2 exp(-\xi/\xi_0),$$

where  $T_2$  is the spin-spin relaxation time,  $\Delta$  is the tunneling matrix element, and  $\xi_0$  is the energy scale of the hyperfine bias field (i.e.  $\xi_0 \sim T_2^{-1}$ )(Prokof'ev & Stamp, 1998). Since there is a distribution of longitudinal and transverse fields for our system and thereby a distribution of bias energies and tunneling matrix elements, the equations of motion must be generalized to average over these distributions. The distribution of tunneling matrix elements follows from the transverse field distribution and the relation between  $H^0_{\perp}$  and  $\Delta$ ,

$$f_{\Delta}(\Delta) = P(|H_T|)(dH_{\perp}^0/d\Delta^{eff}(T,H_T)).$$

In this case, we have chosen T = 35 mK to match with our experimental conditions. The longitudinal field distribution is converted to a bias energy distribution by the relationship  $\xi = 2g_{||}\mu_B S H^i_{||}$ . The final averaged rate that should be compared to our experimentally observed rates is

$$\overline{\Lambda} = \int_{-\infty}^{\infty} \int_{0}^{\infty} P(\xi) f_{\Delta}(\Delta) \Lambda(\Delta, \xi) d\Delta d\xi.$$

For the case of a coupling to a spin bath with a normally distributed longitudinal field distribution, the expression can be evaluated analytically as

$$\overline{\Lambda} = exp(\frac{\sigma(\widetilde{H}_{||})^2}{2\xi_0^2})erfc(\frac{\sigma(\widetilde{H}_{||})}{\sqrt{2}\xi_0})\int_0^\infty \Delta^2 f_{\Delta}(\Delta)d\Delta.$$

We note that this formalism predicts a square root time dependence (Prokof'ev and Stamp 1998). However, this assumes a single value for  $\Delta$ . We attribute our observed exponential time dependence to the widely distributed  $\Delta^{eff}$  for a thermodynamic concentration of spins.

We first focus our discussion on the simpler case of the quantum memory dip experiment. As seen in Fig. 4.3, the relaxation rate decreases as  $H^0_{\perp}$  increases. This behavior is very non-intuitive. One would naively expect an increase in the average tunneling matrix element to increase the relaxation rate. The decrease follows from the transverse field dependence of the random longitudinal and transverse fields. While increasing  $H^0_{\perp}$  rapidly increases  $\Delta^{eff}$  at low fields, at  $H^0_{\perp}$ >12 kOe the rate is substantially reduced. If we assume a transverse field distribution with  $\sigma(\tilde{H}_{\perp}) \sim 12$  kOe, as suggested by mean field calculations, the average  $\Delta^{eff}$  will not vary significantly over experimentally relevant fields. Furthermore, the broadening of the longitudinal field distribution will reduce the fraction of spins which are near resonance and can relax through quantum tunneling. At small  $H^0_{\perp}$ , the effect from random longitudinal fields dominates over random transverse fields and the relaxation rate decreases. As seen in Fig. 4.3, a calculation of the relaxation rate with parameters that characterize the field distributions and their transverse field dependence demonstrates this effect. Both the sign and functional dependence of the relaxation is well-captured by the theory, and opposite to the effects seen classically. However, we note that the calculated rates are a factor of  $10^{10}$  greater than our experimentally observed rates. We propose that this discrepancy results from failing to consider the cluster nature of the glass. The larger length scale of spin clusters will result in a many order of magnitude longer time scale.



Figure 4.3: (left top, left bottom) Transverse and longitudinal field distribution used to calculate relaxation rates at several representative fields. (center) Experimentally measured relaxation rates. (right) Spin-spin relaxation rates calculated by averaging over random transverse and longitudinal field distributions. The parameters used in this calculation are  $\sigma(\tilde{H}_{\perp}) = 12$  kOe,  $T_2 = 10^{-6}$  s,  $\sigma(\tilde{H}_{\parallel}) = 500$  Oe  $+0.1H_{\perp}^0$ . Thermal relaxation rates (red) increase with temperature, while quantum relaxation rates (blue) decrease with transverse field.

The strong rejuvenation seen in the quantum memory dip procedure also can be understood through the field dependence of the random longitudinal field. When waiting at  $H_w$ , there are an initial set of spins that are nearly in resonance and can relax via quantum tunneling. However, when  $H^0_{\perp}$  is reduced and the longitudinal field distribution is reduced, new spins are brought into resonance and the relaxation process restarts.

In the thermal memory dip experiment, quantum fluctuations are still expected to have a large affect because a significant fraction of spins will have a large enough random transverse field to cause appreciable tunneling. This relaxation will occur in combination with any possible purely thermal relaxation process. Furthermore, we expect temperature dependence in the resonant tunneling process through  $\Delta^{eff}(T)$ as seen in Fig. 4.1. We again calculate the relaxation rate using the same parameters used in the quantum memory dip calculations (see Fig. 4.2), but now vary  $\Delta^{eff}(T)$ . We find the relative change in rate to qualitatively agree with experimental results, which suggests the dominant relaxation channel is quantum tunneling. The lack of rejuvenation or memory in the thermal memory dip experiment further points to the limited predictive power of the hierarchy landscape picture for QSGs. Strong rejuvenation is not expected from the quantum resonant tunneling process because the longitudinal field distribution will not vary rapidly with temperature, and no additional spins will be brought into resonance.

#### 4.3 Negative Field Cycle

We now turn our attention to another commonly used experimental procedure, the "negative temperature cycle". The goal of this procedure is to achieve a more quantitative understanding of memory in the glass at the cost of a more complicated procedure. The classical procedure is to quench to some temperature,  $T_{w1}$ , and wait time  $t_1$  and then decrease the temperature to,  $T_{w2}$ , and wait time  $t_2$ . Finally, the temperature is returned to  $T_{w1}$  and relaxes for time  $t_3$ . An additional reference curve is taken where the system is quenched to  $T_{w1}$  and relaxes for time  $t_1 + t_2 + t_3$ . In the case of perfect memory, the third relaxation stage should evolve as is if the relaxation period at  $T_{w2}$  did not occur. The data is analyzed by shifting the third relaxation stage in time by  $\Delta t$  to match the reference curve. Perfect memory would then correspond to  $\Delta t = -t_2$ . An effective wait time is defined as  $t_{eff} = t_2 + \Delta t$ , and should be thought of as the relaxation time at the second stage which contributes to relaxation during the third stage. Typically, perfect memory occurs (i.e.  $t_{eff} = 0$ ) when  $\Delta T = T_{w1} - T_{w2}$  is sufficiently large (Dupuis et al., 2001).

In this work, we employ a negative field cycle experiment using an analogous procedure where temperature variation is replaced by transverse field variation. The transverse field is ramped to  $H_T = 12$  kOe, well above  $H_g$ . The sample is cooled to  $T_{base}=35$  mK. The transverse field is ramped to  $H_{w1} = 5$  kOe and relaxes for  $t_1=1800$  s. The field is ramped to  $H_{w2}$  and relaxes for  $t_2=1800$  s. Finally, the field is returned to  $H_{w1}$  and relaxes for  $t_3=8$  hours. This procedure was done for several  $H_{w2}$ , as seen in Fig. 4.4. The insets show the third relaxation stage shifted in time to agree with the reference curve. This analysis shows a negative  $t_{eff}$  for all  $\Delta H_T$  which grows more negative with increasing  $\Delta H$ . This surprising result is not seen in classical negative temperature cycle experiments. The negative effective time implies memory of relaxation from the first stage is lost.

This unusual behavior again can be understood within the framework of resonant tunneling. When the system relaxes during its first stage, spins in resonance at the



Figure 4.4: Negative field cycle experiments at various fields. Colored curves are susceptibility from the field cycle procedure and the black curved is a reference with the second stage of relaxation omitted. The insets show the third stage of relaxation shifted in time to agree with the reference curved, including a small offset.

initial longitudinal field distribution relax. When the system relaxes at the second stage with a narrower field distribution, new spins are in resonance. The co-flipping events that occur during the second stage of relaxation act to randomize the spin orientations of spins which are not in resonance. During the third stage of relaxation, this randomization removes the memory of relaxation during the first stage. Larger  $\Delta H_T$  results in more memory loss because the fraction of spins in resonance at both  $H_{w1}$  and  $H_{w2}$  fields is reduced.

We have for the first time investigated the dynamic response of quantum spin glass. This was the accomplished by the development of quantum analogues of standard experiments used investigate rejuvenation and memory. In doing so, we have found behavior that fundamentally differs from a classical spin glass and cannot be explained by a hierarchical free energy landscape. We develop a framework centered on quantum resonant tunneling as an appropriate theoretical picture to describe the data.

#### CONCLUSION

#### 5.1 Summary

We study the effects of disorder on quantum phase transitions and quantum dynamics. We use the LiReF<sub>4</sub> material family as a platform for this study. Since a deep understanding of its Hamiltonian has been developed, it is a model system to study the effects of quantum fluctuations on magnetism. Because its spins are dipolar coupled, the energy scale of the ordering is  $\sim 1$  K. It is possible to produce magnetic fields in a laboratory setting that are of a comparable energy scale which can induce QPTs and profoundly alter the systems dynamics. The internal crystal field splitting induces strong anisotropy which provides a platform to study spins with Ising and XY symmetry for Re=Ho and Re=Er, respectively. The existence of isotopes with non-zero nuclear spins provides the opportunity to study the effect of hyperfine coupling on criticality. Disorder can be introduced into the system by using a selection of isotopes, some with and some without hyperfine coupling. Disorder also can be introduced into the system by substituting the Re ion with a non-magnetic Y ion. We study both cases.

LiErF<sub>4</sub> hosts an antiferromagnetic state at zero field. Its thermal phase transition to a paramagnetic state belongs to the 2D  $XY/h_4$  universality class. This state can be tuned to a quantum critical point by applying a magnetic field either along the crystallographic a-axis or c-axis. When H||c, the critical exponents of the QPT agree with a 3D Ising or 3D XY universality class. Er-167 is erbium's only stable isotope with a non-zero nuclear spin and has an antiferromagnetic hyperfine coupling. At temperatures low enough for the nuclear spins to slave to the electronic spins, the hyperfine coupling is known to reduce the effective field felt by the electronic spins.

We investigate LiErF<sub>4</sub> with a natural abundance of Er isotopes and, for the first time, consider the isotopic variation in hyperfine coupling as a source of disorder in the system. We use heat capacity measurements to determine the temperature scale at which the nuclear spins slave to the electronic spins as T=150 mK. In the clean regime above this temperature, the isotopic variation does not disorder the system. In the dirty regime below this temperature, the isotopic variation acts as a source of random mass disorder. We characterize the electronic response to this

disorder by measuring the "control parameter" susceptibility which is analogous to the heat capacity of a thermal phase transition. For the QPT induced by H||c, we find that the peak in the susceptibility corresponding to the phase transition strongly broadens upon entering the dirty regime. A power law analysis of the control parameter susceptibility is consistent with a violation of the Harris criterion in the clean regime, and a change in universality class upon entering the dirty regime. For the QPT induced by H||a, we do not observe any difference between the clean and dirty regimes in the control parameter susceptibility. We posit this QPT belongs to a different universality class which obeys the Harris criterion. Accordingly, the critical behavior would be unaffected by random mass disorder.

When enough disorder is introduced into LiHoF<sub>4</sub> via the substitution of Ho with Y, the ground state of the system transitions from a ferromagnet to a spin glass. The spin glass state has a complex free energy landscape with very slow magnetic relaxation. We characterize the dynamics of the spin glass state of LiHo<sub>0.2</sub>Y<sub>0.8</sub>F<sub>4</sub> by performing a thermal memory dip experiment. The dynamic response shows no apparent memory or rejuvenation, which are standard spin glass phenomena, but can be difficult to observe at milliKelvin temperatures when thermal equilibration times are long. The relaxation rate decreased as the waiting temperature decreased as expected. We performed a quantum memory dip experiment by an analogous procedure in which the transverse field was varied rather than temperature and saw strong rejuvenation. The relaxation rate decreased as the waiting transverse field increased.

These observations were explained within a newly-developed theoretical framework of quantum resonant tunneling which describes the time evolution of spins with a given bias energy that are coupled to a spin bath. This tunneling process is affected both by the introduction of quantum fluctuations and by altering the bias energy. The transverse field not only affects the strength of the quantum fluctuations, but also the bias energy through its coupling to the random longitudinal field via the off-diagonal dipolar coupling. These effects compete with each other, and at low fields, result in a decrease in the relaxation rate with transverse field. The change in the random longitudinal field also brings new spins into resonance and produces the rejuvenation effect. Changing the temperature alters only the strength of quantum fluctuations via the thermal population of the electronuclear levels. Accordingly, the relaxation rate decreases with temperature and shows no rejuvenation effect. Finally, we performed a "negative field cycle" procedure and observed erasure of memory. This behavior was attributed to the randomization that occurs to spins which are not in resonance via co-flipping events.

#### **5.2 Future Directions for** LiErF<sub>4</sub>

The most straightforward extension of this work is to study samples with isotopically pure erbium. Er-166 with no-nuclear spin would provide a platform to study a disorder free, purely electronic QCP. When H||c, we expect  $\alpha_H < 0$  in the low temperature limit, consistent with a violation of the Harris criterion and no change in critical behavior at T=150 mK. These results would categorically demonstrate hyperfine coupling as the cause of the low temperature behavior described in this thesis. Furthermore, the absence of the Schottky contribution would make it possible to study the electronic critical behavior of the heat capacity. The validity of the Harris criterion alternatively can be determined by the heat capacity's critical exponents and their associated scaling relations. A comparison would provide a self-consistency check on the validity of the scaling relations of Kirkpatrick and Belitz.

In addition to altering the universality class of a phase transition, disorder can also induce Griffiths physics. Near the QPT, rare spatial regions with a low concentration of disorder favor ordering locally. Whether these regions contribute to the bulk thermodynamics of the system is dependent on  $d_{RR}$ , the dimensionality of correlation in the disorder, and  $d_{c-}$ , the lower critical dimension of the spin symmetry. In the case of an Ising QPT with random disorder,  $d_{RR}=1$ , and  $d_{c-}=1$  because disorder is correlated in the imaginary time dimension. This equality corresponds to an infinite-randomness quantum critical point (Vojta, 2010). This QPT is predicted to have a non-universal  $\alpha_T$  that varies with the tuning parameter and approaches 1 at the QPT. This has been observed experimentally in some materials (Ubaid-Kassis et al., 2010); however, in many cases an exponent less than one is observed at the QPT (Stewart, 2001). We suggest Griffiths physics as a possible explanation to the unconventional exponent,  $\alpha_T=0.70$ , reported for LiErF<sub>4</sub>. A measurement of the evolution of  $\alpha_T$  with H||c would determine the relevance of Griffiths physics.

#### **5.3 Future Directions for** $LiHo_xY_{1-x}F_4$

A better understanding of the relaxation in the spin glass state could be found be repeating the experiments presented in this thesis on  $LiHo_{0.17}Y_{0.83}F_4$ . This material is known to have a smaller variance in its random longitudinal field distribution and random transverse field distribution. Within our theoretical framework, the

reduction in random field strength would cause the relaxation rate to increase with transverse field at a much lower field scale. We also expect that the system would exhibit weaker rejuvenation and memory erasure in the quantum memory dip and negative field cycle experiments, respectively.

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