Abstract: CdEr2Se4, a spinel, was shown to be the first spin ice in a crystal structure other than the rare earth pyrochlore [1]. Although it has the correct entropy, the exact nature of the spin ice state therein, especially the form of the spin correlation function was not further established. A further particularity was the spin relaxation time, which, at low temperature, was found to display a similar activation energy to that of a canonical spin ice, yet the dynamics are three orders of magnitude faster. Using diffuse neutron scattering, we established that the spin correlations in both CdEr2Se4 and CdEr2S4 are well modeled by the dipolar spin ice Hamiltonian, and used this to parameterize the magnetic Coulomb gas existing in each compound. Both are dilute and non-interacting, as in canonical spin ices, so the monopole population alone cannot account for the enhanced dynamics. By a combination of conventional and high frequency susceptibility measurements, and neutron spin echo spectroscopy, we examine the full temperature dependence of the relaxation time, locating the previously known low temperature thermally activated regime [1], and the uncharacterized intermediate plateau and high temperature thermally activated regime, all as in a canonical spin ice but with much faster timescales. Following the approach of Tomasello et al.,[2], we find that the crystal field Hamiltonian of CdEr2X4, as parameterized by our inelastic neutron scattering experiments, supports the faster monopole dynamics primarily through increased susceptibility to transverse fields. Ultimately CdEr2X4 are dipolar spin ices with dilute magnetic Coulomb gases, in which fast monopole dynamics are produced by an increased hopping rate.
Dipolar spin ice states with fast monopole hopping in the spinels CdEr$_2$X$_4$ ($X=$Se, S)

International Workshop on Quantum Spin Ice, June 2017
Acknowledgements

- **Shang Gao**, Oksana Zaharko, Christian Rüegg
- Samples: V Tsurkan, L Prodan (Augsburg/Moldova); A Loidl (Augsburg); J Lago (Universidad del Pais Vasco)
- High frequency susceptibility: E Riordan, S Giblin (Cardiff); J Blomgren, C Johansson (RISE Aereo AB)
- Susceptibility: M Medarde (PSI)
- Neutron Scattering: B Fåk, A Wildes, M Koza, C Ritter, P Fouquet (ILL); L Keller, E Canevet (PSI)
- Heat capacity: S Vrtnik, J Luzar (Josef Stefan Institute)

**arXiv:1705.10737**

\[ \text{MnSc}_2\text{S}_4: \text{SG et al.}, \text{Nat. Phys. (2016)} \]
PHYSICAL REVIEW B 72, 054411 (2005)

Geometrical magnetic frustration in rare-earth chalcogenide spinels

G. C. Lau, 1 R. S. Freitas, 2 B. G. Ueland, 2 P. Schiffer, 3 and R. J. Cava 1
1Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA
2Department of Physics and Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, USA
(Received 18 April 2005; revised manuscript received 21 June 2005; published 8 August 2005)

PRL 104, 247203 (2010) PHYSICAL REVIEW LETTERS week ending 18 JUNE 2010

CdEr 2 Se 4: A New Erbium Spin Ice System in a Spinel Structure

J. Lago, 1, *I. Živković, 2, 3 B. Z. Malkin, 4 J. Rodriguez Fernandez, 5 P. Ghigna, 6 P. Dalmas de Réotier, 7
A. Yaouanc, 5 and T. Rojo 1, 3
1Departament of Inorganic Chemistry, Univ. del Pas Vasco, 48080 Bilbao, Spain
2Institute of Physics, Post Office Box 304, HR-10 000 Zagreb, Croatia
3Laboratory for Quantum Magnetism, Ecole Polytechnique Federale de Lausanne, CH-1015 Lausanne, Switzerland
4Kazan State University, 420008 Kazan, Russia
5Dipartimento CIT, Fac. Ciencias, Univ. de Cantabria, 39005 Santander, Spain
6Dipartimento di Chimica Fisica M. Rolla, Università di Pavia, V.le Taramelli 16, 1-27100 Pavia, Italy
7Institut Nanosciences et Cryogénie, Commissariat à l’énergie atomique/Direction des sciences de la matière, 38054 Grenoble, France
(Received 4 September 2009; revised manuscript received 19 May 2010; published 15 June 2010)
TABLE I. Structural parameters for CdEr₂S₄ at room temperature. Space group: Fd-3m (227); lattice constant a=11.1178(4) Å; χ²=1.23; R_w=11.25; R_F=8.61.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
<th>R_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>8b</td>
<td>1/8</td>
<td>1/8</td>
<td>1/8</td>
<td>1</td>
<td>1.40(5)</td>
</tr>
<tr>
<td>Er</td>
<td>16c</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1</td>
<td>1.14(4)</td>
</tr>
<tr>
<td>S</td>
<td>32e</td>
<td>0.2541(2)</td>
<td>0.2541(2)</td>
<td>0.2541(2)</td>
<td>1</td>
<td>1.50(6)</td>
</tr>
</tbody>
</table>

Lau et al., PRB (2005)
**Why an erbium spin ice in the spinel structure?**

\[
\text{Er}^{3+}: \quad ^4I_{15/2}
\]

\[
\mathcal{H} = B_0^4 C_0^4 + B_4^4 C_4^4 + B_0^6 C_0^6 + B_4^6 C_4^6
\]

\[
\mathcal{H} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_3^4 - C_{-3}^4) + B_0^6 C_0^6 + B_3^6 (C_3^6 - C_{-3}^6) + B_6^6 (C_6^6 + C_{-6}^6)
\]

2 doublets + 3 quartets \(\rightarrow\) 8 doublets

\(\Gamma_4 (g_{\parallel} \neq 0, g_{\perp} \neq 0), \Gamma_{56} (g_{\parallel} \neq 0, g_{\perp} = 0)\)

---

Lago et al., PRL 2010; Malkin et al., PRB (2004)
Spin ice in CdEr$_2$Se$_4$

- What is the nature of the spin ice state in CdEr$_2$Se$_4$? How about CdEr$_2$S$_4$?
- What are the origins and consequences of the much faster dynamics?

Sample

Big absorbers are very useful in neutron shielding design

e.g. How much Cd is needed to absorb 99.9% of thermal neutrons?

\[ n_s = 0.046 \text{ barn.cm}^{-1}, \sigma_{\text{abs}} = 2520 \text{ b} \]
\[ t = -\ln(T) / n_s \sigma_{\text{abs}} = -\ln(0.001) / 115.9 = 0.6 \text{ mm} \]

But: \( \sigma_{\text{abs}}^{\text{113} \text{Cd}} = 20600 \text{ b}, \sigma_{\text{abs}}^{\text{114} \text{Cd}} = 0.34 \text{ b} \)
Crystal field parameters

![Graph showing intensity vs. energy for CdEr₂Se₄ and CdEr₂S₄]

<table>
<thead>
<tr>
<th></th>
<th>$B_2^0$</th>
<th>$B_4^0$</th>
<th>$B_4^3$</th>
<th>$B_6^0$</th>
<th>$B_6^3$</th>
<th>$B_6^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdEr₂Se₄</td>
<td>-25.70</td>
<td>-107.73</td>
<td>-97.74</td>
<td>25.31</td>
<td>-19.06</td>
<td>9.51</td>
</tr>
<tr>
<td>CdEr₂S₄</td>
<td>-29.18</td>
<td>-122.72</td>
<td>-113.66</td>
<td>25.97</td>
<td>-21.89</td>
<td>14.41</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$J_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdEr₂Se₄</td>
<td>±15/2</td>
</tr>
<tr>
<td>CdEr₂S₄</td>
<td>±9/2</td>
</tr>
</tbody>
</table>

\[ \mathcal{H} = B_0^2 C_0^2 + B_0^4 C_0^4 + B_3^4 (C_3^4 - C_{3-3}^4) + B_0^6 C_0^6 + B_3^6 (C_3^6 - C_{3-3}^6) + B_6^6 (C_6^6 + C_{6-6}^6) \]
Diffuse neutron scattering and DSM (I)

\[ \mathcal{H} = J_1 \sum_{\langle ij \rangle} \sigma_i \sigma_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \sigma_i \sigma_j \\
+ D r_0^3 \sum_{ij} \left[ \frac{\hat{n}_i \cdot \hat{n}_j}{|r_{ij}|^3} - \frac{3(\hat{n}_i \cdot \hat{r}_{ij})(\hat{n}_j \cdot \hat{r}_{ij})}{|r_{ij}|^5} \right] \sigma_i \sigma_j \]

\[ D = \mu_0 (\langle J_z \rangle g \mu_B)^2 / (4\pi r_0^3) = 0.616 \text{ K} \]

\[ J_{\text{eff}} = J_1 + 5D/3 = 1 \text{ K}, \quad J_1 = -0.027 \text{ K} \]

\[ J_2 = 0.042 \text{ K} \]
Coulomb gas parameterization

$$Q_m = 2\langle J_z \rangle g \mu_B \sqrt{3/2} r_0 \quad \nu_0 = 2J_1 + (8/3)(1 + \sqrt{2/3})D$$

<table>
<thead>
<tr>
<th>Material</th>
<th>$Q_m$ ($\mu_B/\text{Å}$)</th>
<th>$a$ (Å)</th>
<th>$\nu_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdEr$_2$Se$_4$</td>
<td>3.28</td>
<td>5.03</td>
<td>2.93</td>
</tr>
<tr>
<td>CdEr$_2$S$_4$</td>
<td>3.42</td>
<td>4.83</td>
<td>3.84</td>
</tr>
<tr>
<td>Dy$_2$Ti$_2$O$_7$</td>
<td>4.53</td>
<td>4.38</td>
<td>4.35</td>
</tr>
<tr>
<td>Dy$_2$Ge$_2$O$_7$</td>
<td>4.6</td>
<td>4.3</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Overview of dynamics

Dynamical processes: moderate-low temperature

\[ \tau_0 (s) \quad \Delta (K) \]

- CdEr\(_2\)Se\(_4\) \(6.37 \times 10^{-10}\) \(10.07\)
- CdEr\(_2\)S\(_4\) \(1.84 \times 10^{-9}\) \(10.17\)
- Dy\(_2\)Ti\(_2\)O\(_7\) \(1.93 \times 10^{-6}\) \(9.93\)
\[ \Gamma(T) = \sum_j B_j n_j \]
\[ n = 1/(\exp(\Delta/k_B T) - 1) \]
\[ B_j \propto \zeta_{\mu(u,v)} Z_{\mu(D_j)} \]

\[ \Delta_{\text{Se}} = 75.3 \text{ K}; \quad \Delta_{\text{S}} = 96.3 \text{ K} \]

Ruminy, TF et al., PRB (2017)
Dynamical processes: moderate-low temperature

In Debye-Hückel theory $f \propto u \rho$

$\tau_0$ (s) $\quad \Delta$ (K)

- CdEr$_2$Se$_4$ $\quad 6.37 \times 10^{-10} \quad 10.07$
- CdEr$_2$S$_4$ $\quad 1.84 \times 10^{-9} \quad 10.17$
- Dy$_2$Ti$_2$O$_7$ $\quad 1.93 \times 10^{-6} \quad 9.93$
Origin of the fast dynamics

In Debye-Hückel theory $f \propto u\rho$

Tomasello et al., PRB (2015)
CdEr$_2$X$_4$ (X=Se,S) are dipolar spin ices with fast dynamics.

... The parameters of the dipolar spin ice states point to weakly correlated Coulomb gases of classical monopoles. ... The fast dynamics are due to a much greater monopole hopping rate.