Meteorites, Refrigerants, and Crystals: A collection of projects investigating Frustrated Magnetic Systems

podtitul:

Studium frustrovaných magnetických systémů – od přípravy po neutronovou difrakci

Topics of student projects in the frame of current research of rare-earth oxides at the Department of Condensed Matter Physics:

Témata studentských projektů v rámci současného studia vzácno-zeminných oxidů na Katedře fyziky kondenzovaných látek:

Geometricky frustrovaná mříž 227 oxidů – analýza experimentálních dat

Testing the adiabatic demagnetisation cooling potential of the spin-liquid pyrochlore iridate $Pr_2Ir_2O_7$

Can kitchen-chemistry help solve a cutting-edge physics problem?

Inspiration from the Heavens: Crystal Growth of Meteorite-identified frustrated magnet $FeAl_{12}O_{19}$

Geometricky frustrovaná mříž 227 oxidů – analýza experimentálních dat

studentský projekt 2022/2023 listopad

Úvod:

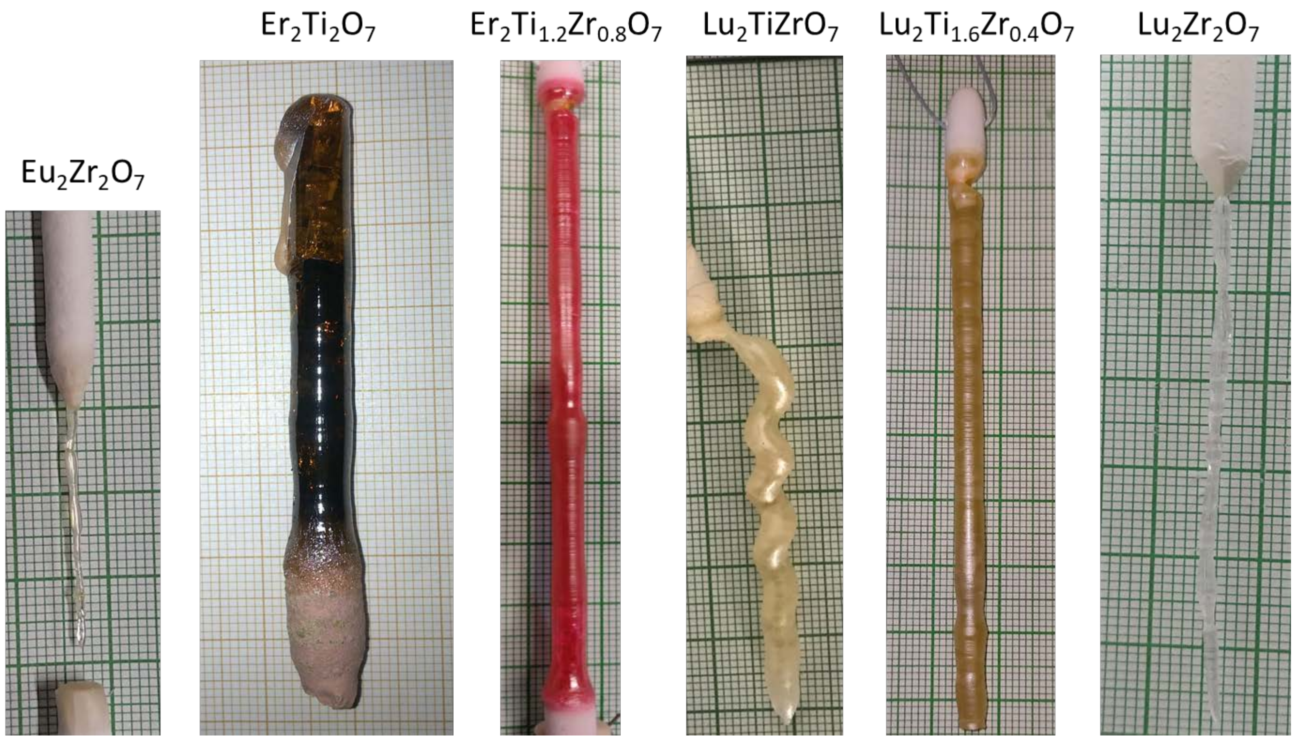
Kubické vzácno-zeminé oxidy $A_2B_2O_7$, kde A značí vzácnou zeminu a B je přechodový kov nebo prvek z hlavní skupiny, jsou systematicky studovány pro jejich často exotické krystalografické a elektronové vlastnosti. V těchto materiálech byly pozorovány rozmanité základní stavy, magnetické structury, a předpovídány elektronové, magnetické a dokonce topologické vlastnosti určené vzájemným působením elektron-elektronových korelací a spin-orbitální interakce. Geometrická frustrace magnetických momentů na krystalografických pozicích A a/nebo B rovněž nabízí široké pole pro vědecká zkoumání těchto oxidů.

Cíle:

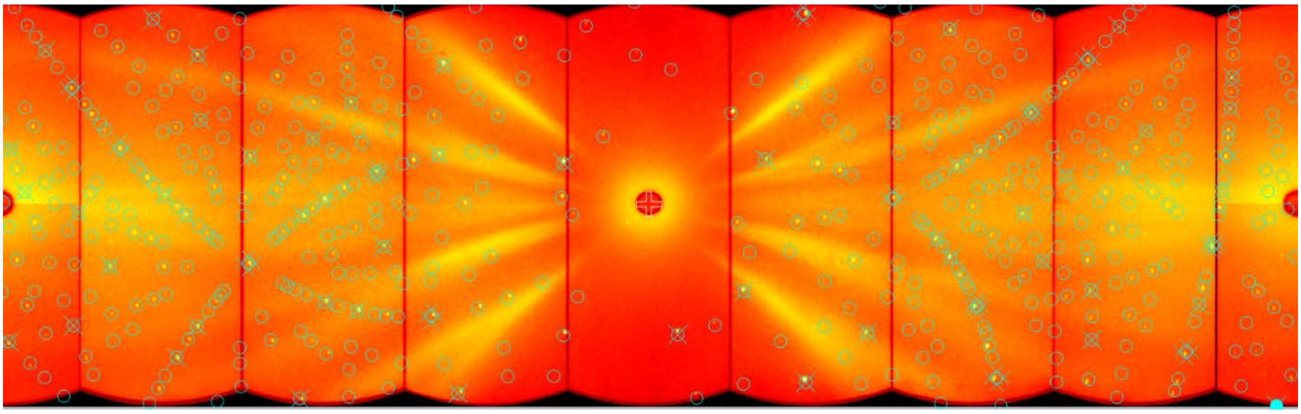
Projekt spočívá v základní **charakterizaci nově připravených polykrystalů a zejména monokrystalů** z rodiny $A_2B_2O_7$ (několik příkladů na Obr.1). Důležitý cíl představuje analýza dat Laueho **neutronového rozptylu** (Obr. 2 a Obr. 3). V případě horší kvality připraveného vzorku bude materiál v rámci SFG syntetizován znovu.

Metodologie:

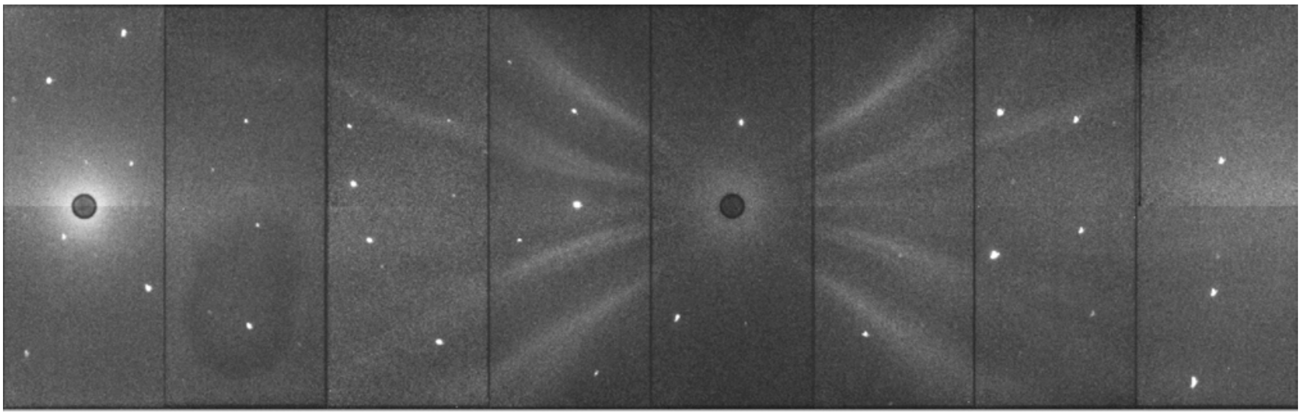
Připravené materiály budou charakterizovány metodami r**entgenové difrakce a skenovací elektronové mikroskopie**. Experimentální data budou analyzována a zpracována v programu FullProf a OrientExpress. Data získáná z experimentu **neutronové difrakce** (Obr. 2 a Obr. 3) budou analyzována programem Esmeralda Laue suite.



Obr. 1: Připravené ingoty materiálů z rodiny $A_2B_2O_7$.



Obr. 2: Laue neutronová difrakce a simulace reflexí monokrystalu $Er_2Ti_2O_7$, CYCLOPS, ILL, Grenoble, Francie.



Obr. 3: Laue neutronová difrakce na monokrystalu $Yb_2Zr_2O_7$, CYCLOPS, ILL, Grenoble, Francie.

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Testing the adiabatic demagnetisation cooling potential of the spin-liquid pyrochlore iridate $Pr_2Ir_2O_7$

Adiabatic demagnetisation refrigeration is a niche method of cooling to very low temperatures, without the need for complex cryogenic fluid systems. It utilises the entropy increase associated with a magnetic material going from a field-polarised state, to a paramagnetic state, under adiabatic conditions, to drive a temperature decrease.

For a material to have a reasonable cooling power, two things are required:

1. It must have magnetic ions with spins that remain dynamic down to extremely low temperatures (< 0.1 K).
2. It should have a high density of magnetic ions.

Remaining dynamic is unusual, as interactions between spins typically cause the system to order into a static ground-state (e.g. a ferromagnetic or antiferromagnetic state), or freeze into a disordered but static state (a spin-glass) at a temperature similar to the interaction strength. Increasing the density of magnetic ions, pushes the ions closer together which typically increases interaction strengths too.

Current industrially used materials are water containing rare-earth salts, with magnetic ions spaced far apart to reduce the interaction strength. To increase cooling power, a higher density of magnetic ions is needed. *Frustrated magnets* are systems that use the geometry of the magnetic lattice to prevent magnetic order [1]. The pyrochlore iridate $Pr_2Ir_2O_7$ is a frustrated magnet that doesn't magnetically order [2], and this project will test it's potential as an adiabatic demagnetisation refrigerant.

The project will involve:

1. Low-temperature magnetocalorimetry, to characterise the changes in magnetic entropy of $Pr_2Ir_2O_7$ in zero-field, and when field is applied. The expected cooling power will then be calculated (Fig. 1a).
2. Testing the ability to adiabatically cool by demagnetisation (Fig. 1b).
3. [Possible extension as Bachelor project] Synthesis of new $Pr_2Ir_2O_7$ crystals, and other frustrated magnets.

[1] Tokiwa, Y. *et al.* Frustrated magnet for adiabatic demagnetization cooling to milli-Kelvin temperatures. *Commun. Mater.* **2**, 42 (2021).

[2] Nakatsuji, S. *et al.* Metallic spin-liquid behavior of the geometrically frustrated kondo lattice Pr2Ir2O7. *Phys. Rev. Lett.* **96**, 087204 (2006).

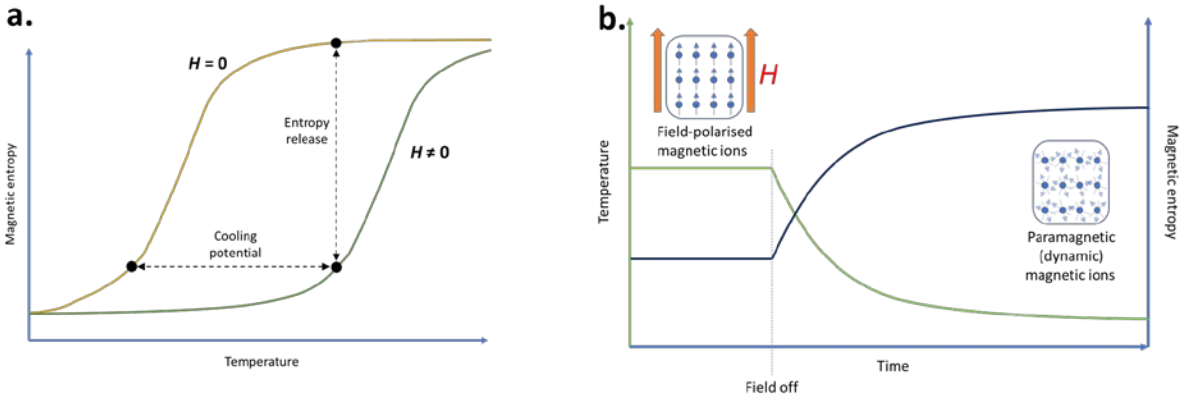

Fig. 1. a. The expected magnetic entropy behaviour of a frustrated magnet, with a shift of the entropy to high temperature when a field is applied. **b.** the possibility to use the entropy change when switching field to adiabatically cool a sample.

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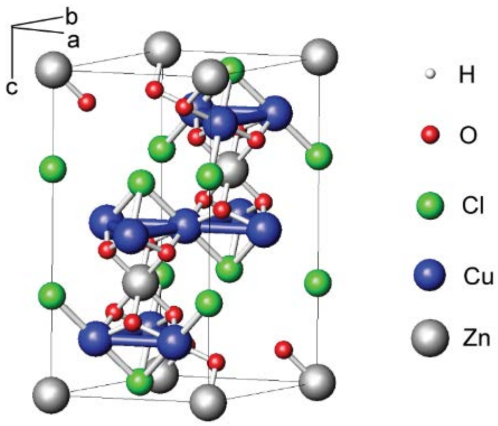
Can kitchen-chemistry help solve a cutting-edge physics problem?

Supervisor: Ross H. Colman

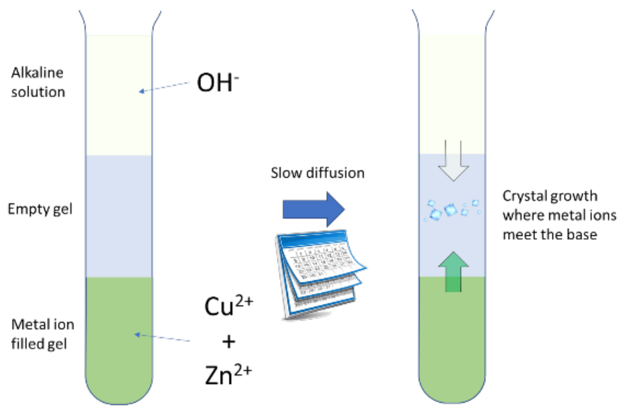
Magnetic materials are a nice playground for testing our understanding of physics, as relatively simple interactions build up to complex magnetic properties, depending on how the magnetic atoms are arranged in the material's crystalline lattice. If we arrange the magnetic atoms such that the overall interaction is frustrated, where pair-wise interactions can't all be satisfied at the same time, we often get unexpected ground-state properties.



One of these unusual magnetic ground-states, is a quantum-spin-liquid. The quantum spin-liquid state is predicted for a Kagome lattice of antiferromagnetically coupled low spin-state ions, but the exact properties are notoriously difficult to predict as they are strongly dependent on the method used for the theoretical calculations.

One material, that has the right arrangement of ions to test the model in real-life is the mineral Herbertsmithite, γ-$Cu_3Zn(OH)_6Cl_2$. It can be synthesised as a single crystal by high-temperature hydrothermal recrystallisation, and has been extensively studied since it was first prepared in 2006.

Despite 18 years of intensive study and more than 136 papers written about Herbertsmithite, the ground-state still remains a contentious issue because of a small complication with the way the crystal samples are grown. During the crystallisation process, the formation of defects is inevitable (e.g. Zn^{2+} and Cu^{2+} swapping positions every now and again) [1,2]. These defects create a big problem in magnetic property measurements, because at very low temperatures they dominate the observed signals – masking the true physics of the Kagome lattice frustration and the properties of the quantum spin liquid ground-state. Defects form in higher concentrations when the material is crystallised at high temperatures, happening about once every 17 unit cells at the temperatures of the current crystal synthesis route. If the crystals can instead be grown at room temperature, the defect concentration is expected to be more than an order of magnitude smaller.



An old, and rarely used crystal growth technique – using slow diffusion through gels [3,4]– may be a solution to this problem. Initial tests using silicate gels hasn't worked due to sensitivity of the gel to the pH level needed for the crystallisation. Instead, this project will attempt to use gelatin based gels (identical to that use in food preparation) to achieve crystal growth. An unrelated study has found that food gelatine may be just right for growing the material we want [5]. The project will involve setting up an extensive series of tests using varying gel thickness and solution concentrations. The tests will be monitored to identify the setup that leads to the best crystals, and then will be used to prepare crystals with different Cu:Zn ratios.

The Cu:Zn ratio will be determined using crystallography and spectroscopic techniques, and defect concentrations will be determined using temperature dependent magnetometry.

References:

[1] A. Olariu, P. Mendels, F. Bert, et al., Phys. Rev. Lett. **100**, 087202 (2008).

[2] D. E. Freedman, T. H. Han, A. Prodi, et al., J. Am. Chem. Soc. **132**, 16185 (2010).

[3] A. R. Patel and A. Venkateswara Rao, Bull. Mater. Sci. **4**, 527 (1982).

[4] L. Dong, T. Besara, A. Henderson, et al., Cryst. Growth Des. **17**, 5170 (2017).

[5] C. J. S. Ibsen, B. F. Mikladal, U. B. Jensen, et al., Chem. - A Eur. J. **20**, 16112 (2014).

Inspiration from the Heavens:

Crystal Growth of Meteorite-identified frustrated magnet $FeAl_{12}O_{19}$

Supervisors: Ross H. Colman and Gaël Bastien

Inspiration for interesting materials to study often comes from nature, where the planet has had millions of years and a near limitless range of environments to prepare the vast catalogue of solid state compounds that we call minerals. To go to an even greater extreme, new minerals can even be formed off-world and identified in fallen meteorites. One such compound, Hibonite-(Fe) or Chihuahuaite $FeAl_{12}O_{19}$, was discovered in the Allende meteorite (Chihuahua, Mexico) [1] and has some potentially interesting magnetic properties – so the goal of this project is to prepare a synthetic analogue of $FeAl_{12}O_{19}$ by solid state reaction and/or by floating zone crystal growth.

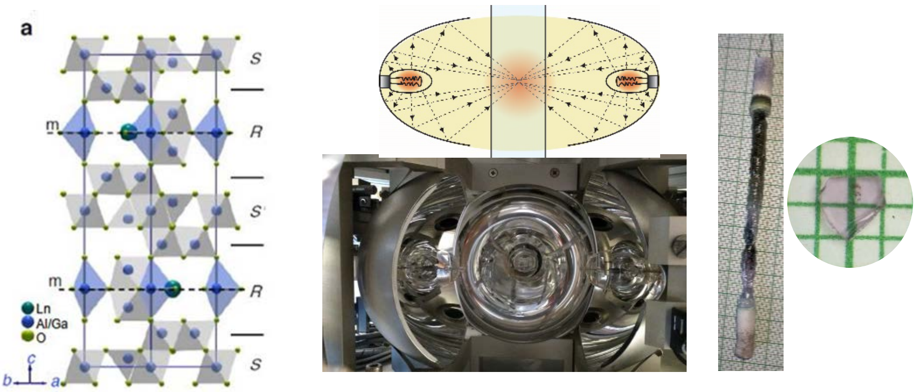


Figure 1 : (a) Crystal structure of the hexaaluminates (adapted from Reference [2]).

(b) Schematic view and photo of our floating zone furnace setup.

(c) Example of a prepared crystal ($CeMgAl_{11}O_{19}$), and crystal fragment ($NdMgAl_{11}O_{19}$).

Frustrated magnets are magnetic materials where all the magnetic interactions cannot be simultaneously satisfied and thus compete with each other. In these materials a large variety of magnetically ordered states and disorder states are possible, often with very small energy differences between them. Interacting electric dipolar moments may also lead to similar frustration in compounds with the magnetoplumbite crystal structure [2] and our recent work has revealed this phenomena in the compound $EuAl_{12}O_{19}$. The new compound $FeAl_{12}O_{19}$ is expected to combine both a frustrated lattice of electric dipoles and a frustrated lattice of magnetic dipoles and we expect both problems to be related via a magnetoelectric coupling offering us the possible realization of exotic magnetoelectric phases.

Investigating the ground-state properties of these materials is best performed using single-crystals. The work will consist of growth attempts of single crystal $FeAl_{12}O_{19}$ by the floating zone technique [3]. Either using optical heating through focusing of IR light using parabolic mirrors, or by laser heating. The total synthesis involves several preparative steps to first pre-synthesise polycrystalline material through solid-state reactions of the oxides; prepare precursor rods through cold pressing; sinter the precursor rods to increase density whilst also increasing structural strength; and finally shape them for mounting within the floating zone furnace.

After the growth, the crystals will be characterized by x-ray diffraction and composition analysis to confirm crystal quality, before characterisation of the magnetic and electric properties are undertaken.

References:

[1] Ma, C. H. I. *Am. Mineral.* 2010, **95**, 188.

[2] S.-P. Shen, et al., *Nature Communications* 2016, **7**.

[3] Alemayehu S. Admasu and Durga Sankar Vavilapa, https://arxiv.org/abs/2103.05587.