Integrated approach for Quantum Materials

New materials, synthesis and advanced characterization

ABSTRACT

MRS

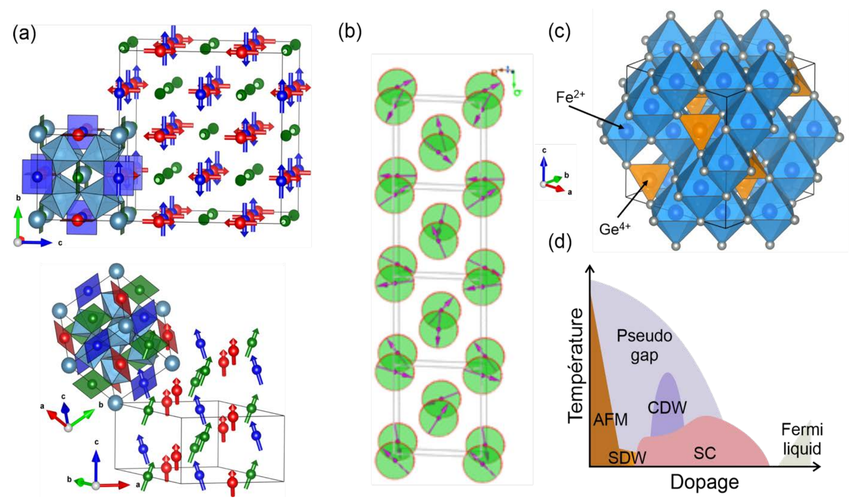
The interplay between **spin, charge, lattice, and orbital** degrees of freedom drives remarkable phenomena in strongly correlated materials. In **frustrated magnets**, lattice geometry and magnetic exchange interactions lead to exotic states such as **non-trivial order**, **metamagnetism**, and **spin liquids**.

Our research focuses on **multiferroics** — materials combining magnetic and electric orders through **magnetoelectric coupling**. This effect enables control of **polarization** by a magnetic field and **magnetization** by an electric field, offering exciting prospects for new technologies.

We also explore **emergent quantum states** tuned by **non-thermal parameters** such as pressure, magnetic field, or chemical composition. Close to these phase transitions, **critical fluctuations** give rise to unconventional superconductivity and exotic magnetism.

Our target materials include **cation-ordered perovskites**, **spinels**, **pyroxenes**, **layered systems**, and **mixed-anion compounds**.

We follow an **integrated approach** combining synthesis, structural and magnetoelectric characterization, and advanced experiments using **neutron** and **X-ray scattering** at large-scale facilities.



Targeted materials: a) cation-ordered perovskite, b) pyroxene c) spinel and d) phase diagram of cuprate superconductors

Charge density wave in superconducting oxychlorides

The high energy-resolution Resonant inelastic X-ray scattering (RIXS) technique has been used to study the charge density waves (CDW) and its excitations in one particular superconducting cuprate belonging to the oxychloride family.

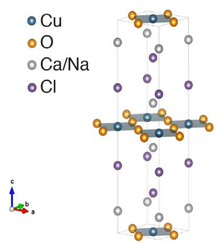
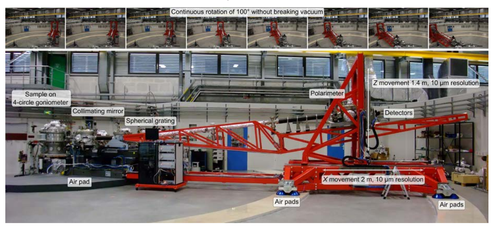


Figure: Crystal structure of Na-COOC, highlighting the CuO_2 planes

RIXS endstation at ID32, ESRF



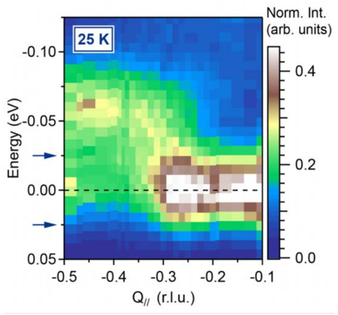


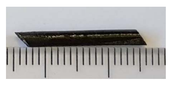
Figure: RIXS intensity map recorded on Na-CCOC and at 25 K, evidencing the CDW peak.

- Sample: $Ca_{2-x}Na_xCuO_2Cl_2$ (Na-CCOC) with x = 0.10 doping
- Methods: High energy resolution RIXS measurements at the Cu L_3-edge at the ID32 beamline at the ESRF
- Key results:
  - Incommensurate short-range CDW
  - Anomalies of the bond-stretching phonon in the vicinity of the CDW.
  - Evidence of electron-phonon coupling anomalies arising in the presence of dispersive charge excitations that emanate from the CDW and interact with the bond-stretching phonon.
- Impact: First observation of a bulk CDW in this compound. Confirmation of the observation of a new kind of charge excitations dispersing from the CDW in another cuprate family than Bi2212, extending their observations to different compounds.
- Collaboration: MRS and MAGSUP (Institut Néel) with Brookhaven National Laboratory and ID32 beamline at ESRF.

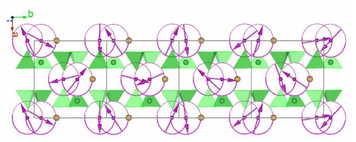
Further reading: Bulk charge density wave and electron-phonon coupling in superconducting copper oxychlorides L. Chaix, B. Lebert, H. Miao, A. Nicolaou, F. Yakhou, H. Cercellier, S. Grenier, N. B. Brookes, A. Sulpice, S. Tsutsui, A. Bosak, L. Paolasini, D. Santos-Cottin, H. Yamamoto, I. Yamada, M. Azuma, T. Nishikubo, T. Yamamoto, M. Katsumata, M. P. M. Dean, M. d'Astuto. PHYSICAL REVIEW RESEARCH 4, 033004 (2022)

Low dimensionality and frustration promote multiferroicity

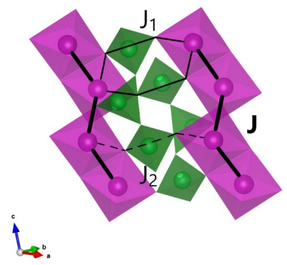
Magneto-electric coupling with both fundamental and applied interest. Pyroxenes host frustrated quasi-1D spin chains, favoring incommensurate orders and multiferroicity.



Single crystal of $SrMnGe_2O_6$ grown by floating zone method



Polar elliptical cycloidal spin structure.



The MnO_6 zigzag chains connected through GeO_4 tetrahedra in $SrMnGe_2O_6$. The bold solid, thin solid and dotted lines correspond to exchange paths J, J_1 and J_2.

- Sample: Large $SrMnGe_2O_6$ single crystals grown by optical floating-zone, following multiferroicity identified in polycrystals.
- Methods: Magnetization, heat capacity, pyroelectric current; elastic/inelastic neutron scattering; magnetic phase-diagram calculations and spin-wave simulations.
- Key results:
  - Two incommensurate magnetic transitions: at 4.36 K, non-polar collinear sinusoid; below 4.05 K, polar elliptical cycloid.
  - Spontaneous polarization confirmed at the second transition via pyroelectric current.
  - Spin-wave spectra quantitatively reproduced by a minimal model.
- Minimal model: Three antiferromagnetic isotropic exchanges (J dominant along chains; J1, J2 frustrated interchain) + weak single-ion anisotropy. An extended Dzyaloshinskii–Moriya mechanism accounts for the emergence and direction of polarization.
- Impact: $SrMnGe_2O_6$ is a benchmark where a simple J–J1–J2 scheme with weak anisotropy captures structure, dynamics, and multiferroicity.
- Collaboration: MRS and MAGSUP with support from Cristaux Massifs and Auto-Caractérisation (Institut Néel).

Further reading: Incommensurate spin ordering and excitations in multiferroic $SrMnGe_2O_6$, Claire V. Colin, Lei Ding, Eric Ressouche, Julien Robert, Noriki Terada, Frederic Gay, Pascal Lejay, Virginie Simonet, Céline Darie, Pierre Bordet, and Sylvain Petit. PHYSICAL REVIEW B 101, 235109 (2020)

Exploiting structural instabilities in order to prepare new structure types: Ca_2MnO_3X (X = Cl, Br)

Figure 1: Layered structures of selected mixed anion materials.

A mixed anion compound is a solid material containing more than one type of anion in a single phase, such as oxyfluorides (oxide and fluoride anions) or oxyhydrides (oxide and hydride). These materials offer the possibility for novel functionality due to the possibility of forming heteroleptic coordination polyhedra, and the possibility of leveraging the differing charge, polarizability, radii, or electronegativity of the various anions.

Oxyhalide materials, containing oxide and halide (F^-, Cl^-, Br^-, I^-) anions, have attracted attention as battery materials, ionic conductors, phosphors, magnetic materials, and catalysts. A particular synthetic challenge of such materials is that a large difference in ionic radii between different ions results in the occupation of different crystallographic sites, and these materials therefore typically adopt layered crystal structures such as those shown in Figure 1. The emergent properties of these materials tend to be closer to that of the parent monoanionic materials with the added disadvantage of lowered dimensionality. For example, the magnetic ordering in $A_2M^{3+}O_3Cl$ (A = Sr, Ca; M = transition metal) are dominated by M-O-M 180° superexchange interactions and these materials are generally antiferromagnetic insulators with low ordering temperatures.

As we demonstrate, this tendency to layered order can be overcome by exploiting structural instabilities. In Ca_2MnO_3X (X = Cl, Br), the small ionic radius of Ca^{2+} and the Jahn-Teller distortion of Mn^{3+} prevent the adoption of the structure type shown in Figure 1 for the other members of the $A_2M^{3+}O_3Cl$ family of phases. Transmission Electron Microscopy, carried out in collaboration with Christophe Lepoittevin and Stephanie Kodjikian (Néel), was used to solve the crystal structure, revealing 1-dimensional chains of square-planar coordinated Mn^{3+} cations (Figure 2). In this compound, the halide ions play a pivotal role in the long-range magnetic ordering behavior, resulting in tunable low-temperature metamagnetic order.

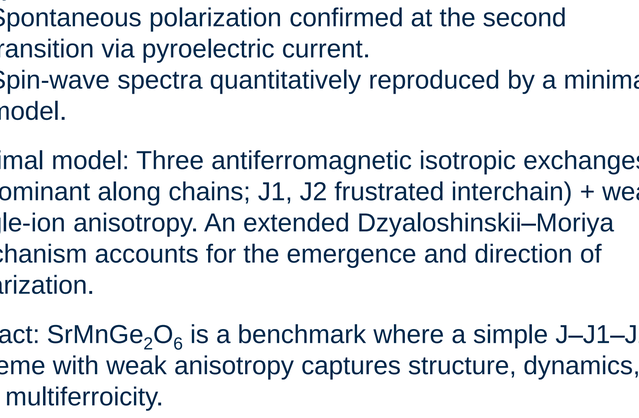


Figure 2: (a) and (b) The crystal structure of Ca_2MnO_3Cl. (c-e) STEM-HAADF images of Ca_2MnO_3Cl

Further reading:
Ca_2MnO_3X(X= Cl, Br) Oxyhalides with 1-Dimensional Ferromagnetic Chains of Square-Planar S= 2 Mn^{3+}
Fabio Denis Romero, Christophe Lepoittevin, Stéphanie Kodjikian, Claire V. Colin, and Michael A. Hayward *Journal of the American Chemical Society* 2023, 145, 23346−23351