PhD OFFER: : Composite Phases with Translational Disorder

Scientific Context of the Thesis

Although $PbCr_2S_4$ was synthesized as early as the 19th century[1], the group of compounds represented by the general formula MCr_2X_4 (where M includes Pb, Sr, Ba, Eu, Sn, and X includes S, Se) only gained significant interest in the 1970s due to their promising properties for spintronics.[2–6] However, the structural complexity of these phases, which could not be adequately addressed with the tools available at the time, hindered the development of this research field.

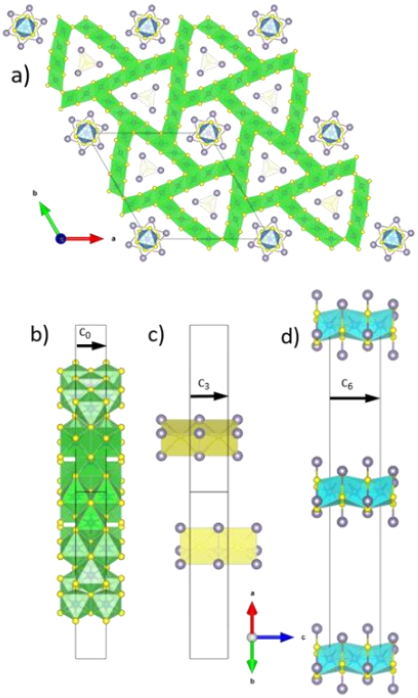

Figure 1 a) structure de $EuCr_2Se_4$ le. Le réseau $Cr_{21}Se_{36}$ est représenté par des octaèdres $CrSe_6$ verts b). (c) Colonnes de prismes trigonaux $SeEu_6$ dans les tunnels triangulaires. (d) Colonnes $Eu_6Cr_2Se_5$ pour les tunnels hexagonaux.

Indeed, MCr_2X_4 compounds adopt an **incommensurable composite channel-type structure**, consisting of multiple sub-units sharing the same periodicity along the ***a*** and ***b*** directions but exhibiting distinct periodicities along the ***c*** direction. As a result, the ratio of these unit cell parameters leads to **irrational values**, preventing strict three-dimensional periodicity. This unique structural characteristic could have a significant impact on their physical and chemical properties, paving the way for new approaches in materials chemistry.[7]

A comparative structural study of $SnCr_2S_4$ and $BaCr_2Se_4$, using **precession electron diffraction** and **X-ray diffraction**, revealed additional complexity in data interpretation. As illustrated in **Figure 2**, the reconstruction of reciprocal space highlights a significant **diffuse scattering contribution** in both samples, indicating structural disorder phenomena. Analysis of cross-sections along the C6 periodicity direction shows that the width of the diffuse scattering is comparable to that of Bragg reflections, suggesting **translational disorder of the C_6 columns along *c***, while maintaining **high periodicity within the tunnel**

Thanks to **recent methodological and technical advances**, these investigations have demonstrated that these two phases not only exhibit a **multidimensional organization** but also present **translational disorder phenomena within the channels**.

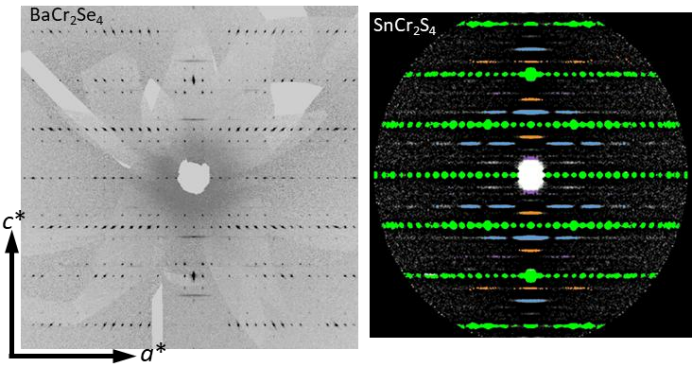

Figure 2 : Coupe (h_0l) du réseau réciproque pour $BaCr_2Se_4$ et $SnCr_2S_4$.

Objectives:

This thesis deals with the crystallography of incommensurable phases, where structural complexity goes beyond the conventional framework of three-dimensional periodicity. It combines solid synthesis and crystal growth with structural determination in a multidimensional formalism, enabling the exploration of materials with singular atomic arrangements and remarkable emergent properties. The central objective of this research is to deepen our understanding of the interactions between incommensurability and translational disorder in these materials, with three major thrusts: (i) to elucidate the fundamental mechanisms governing these interactions; (ii) to assess their influence on the physical properties of the materials; (iii) to identify the structural and chemical parameters determining their behavior.

The project is based on an integrated approach combining experimentation and modeling. The study relies primarily on diffraction, while incorporating analysis of transport properties to exhaustively characterize the structural and functional behavior of these complex phases.

Work Environment and Supervision:

This thesis will be conducted within the Crystallography and Physical Measurement team of the CRISMAT laboratory (Crystallography and Materials), under the supervision of Carmelo Prestipino (CNRS Research Scientist) and Olivier Perez (CNRS Research Director). The supervisors possess recognized expertise in the synthesis of chalcogenides and crystallography, particularly in the study of incommensurable phases. This thesis project is part of an internationally renowned team that combines a deep understanding of crystallography with state-of-the-art instrumentation that meets the highest global standards. This synergy ensures a dynamic and innovative scientific environment.

Candidature Profile:

Master's degree in Solid-State Chemistry, Solid-State Physics, Materials Science or Crystallography.
Knowledge in applied crystallography and solid-state synthesis is a plus.

Terms

- Doctoral contract University of Caen, average salary: €1,813 net/month (€2,255 gross/month)
- Provisional dates: October 1, 2025, to September 30, 2028

Application

Send a CV and a cover letter to Carmelo.Prestipino@ensicaen.fr or Olivier.Perez@ensicaen.fr.
References will be requested if you are selected for an interview.

References:

1) Gröger, M. Die Sulfochromite. *Monatshefte Für Chem.* **1881**, *2* (1), 266–275.
2) Omloo, W. P. F. A. M. et al. Lead Chromium Sulfide, $PbCr_2S_4$, and Some Isotypic Compounds. *Recl. Trav. Chim. Pays-Bas* **1968**, *87* (5), 545–548.
3) Omloo, W. P. F. a. M. et al. Europium Chromium Sulfide, $EuCr_2S_4$, and Some Isotypic Compounds. *Phys. Status Solidi A* **1971**, *5* (2), 349–357.
4) Brouwer, R. et al. Intergrowth Structure of $Eu_{1-p}Cr_2Se_{4-p}$ (P= 0·29) and Isotypic Compounds. A Novel Type of Crystal Structure with Three Incommensurate Periodicities in One Direction: X-Ray Study. *J. Chem. Soc. Chem. Commun.* **1977**, No. 23, 879–880.
5) Onoda, M. et al. Diffuse Scattering from the Channel-Type Composite Crystals $Pb_{1-p}Cr_2S_{4-p}$, $Sr_{1-p}Cr_2S_{4-p}$ and $Ba_{1-p}Cr_2Se_{4-p}$(p ~0.3). *Jpn. J. Appl. Phys.* **1993**, *32* (S3), 423.
6) Fukuoka, H. et al. An X-Ray and Electron Diffraction Study of the Channel-Type Composite Crystal $Sn_{1-p}Cr_2S_{4-p}$. *J. Solid State Chem.* **1995**, *115* (1), 7–12.
7) van Smaalen, S. Editorial: Incommensurate Crystallography of Modulated and Composite Crystals. *Z. Für Krist. - Cryst. Mater.* **2009**, *219* (11), 680–680.