Incommensurate Phase Transitions as a Route to Functional Materials Design

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**3rd Supervisor:** Mark Senn (Chemistry, University of Warwick)

**Abstract**

An *incommensurate* phase is one in which the atomic structure possesses a modulation, usually long-ranged, which has a period that is not an integer multiple of that of the basic underlying lattice. Having two distinct periodicities coexisting inside the same crystal structure can lead to local structural distortions that evolve non-periodically as a result of global lowering of the free energy.

The *Frenkel-Kontorova* model is the paradigmatic example of how the rich physics of incommensurate phases can arise from a very simple model Hamiltonian in one-dimension [1]. In real materials, however, it is in general poorly understood why certain types of structure readily support incommensurate modulation while others do not. Since many interesting physical properties are associated incommensurate phases, a detailed understanding of why and when these unusual states of matter occur is needed.

This project will focus a family of materials known as the “<110>-cut” layered perovskites \((\text{AnB}_n\text{X}_{3n+2})\) [2] (Fig. 1), several of which exhibit incommensurate phase transitions. They also have many technologically interesting properties, including ferroelectricity and multiferroicity, and obtaining a detailed predictive understanding of the atomic mechanisms underlying their incommensurate phase transitions constitutes a key step in harnessing their potential functionality. One of the supervisory team (Senn) has recently reinvestigated this family experimentally using high resolution XRD. This project will hence provide an excellent opportunity for direct theory-experiment collaboration.

![Fig. 1. Crystal structures of \(\text{A}_2\text{B}_2\text{X}_8\) (n=2) polymorphs: (a) aristotype, (b) out-of-phase oxygen octahedron tilts, (c) in-phase oxygen octahedron tilts. In certain chemistries, these tilting modes can modulate in magnitude in an incommensurate fashion. Adapted from Ref. 2.](image)


What is the multi-scale nature of the project?
There are three scales associated with the project. At the largest scale, the incommensurate phase transition will be simulated using computationally efficient Monte Carlo or molecular dynamics (MD) with second-principles effective potentials that are able to capture the relevant time and length scales of the transition as well as temperature-dependent effects.

These effective potentials are in turn built from information (including energetics, forces and stresses of MD snapshots) at the atomic and electronic scales from linear-scaling quantum mechanical DFT calculations.

Finally, conventional DFT phonon calculations at the primitive unit cell level will provide insight into the character of the modes that may be involved in the incommensurate phase transition.

How do the expertises of the supervisors complement each other?
AM has extensive expertise of large-scale DFT methods, as one of the main developers of a leading linear scaling DFT code (ONETEP). These methods will enable calculations of the AnBn3n+2 <110>-cut layered perovskite phases, which need to have unit cells of the order of a few hundred atoms to be effective models for the incommensurately modulated phases.

The DFT calculations of the energetics and phonons of various 110-type phases, will feed into effective potentials for even larger length scale Monte Carlo or molecular dynamics calculations at finite Temperature. NCB has been developing and testing these new types of potentials and has already applied them to ferroic perovskites, the end member of the layered family.

The experimental work of MS has inspired this project, and he brings significant experience in layered perovskite systems and performing the detailed crystallographic experiments and analysis required to determine the subtle incommensurate atomic displacements that arise (see for example MS Senn, “To superspace and beyond”, Acta Cryst. A73, 1 (2017)). He has already collected high-resolution single crystal X-ray diffraction temperature dependent data on the most famous example of an incommensurate phase in this class of materials (Ba2Mn2F8) and will be analysing this in parallel with the theoretical study carried out by the student.

Literature Review
Title: The theory of incommensurate phase transitions and their role in functional materials

The student should conduct a general review of incommensurate phases and any relationship that they are known to have with various functional properties, for example, the connection between charge density waves and superconductivity, or incommensurate modulation of a polar mode and (anti)ferroelectricity.

Suggested reading
1. General introduction to the theory of incommensurate phase transitions:
2. The AnBnX3n+2 system:
Simulations of specific incommensurate phases:

- S Arapan et al, “Prediction of incommensurate crystal structure in Ca at high pressure”, *Proc Natl Acad Sci* 105, 20627 (2008)

**MSc Project**

The self-contained 16 week MSc project will initially use density functional perturbation theory (DFPT) to calculate phonon dispersion curves of high symmetry commensurate structures of a non-magnetic <110>-cut layered perovskite, eg, Srₙ(Ti, Nb)ₙ₋₃O₃ₙ₊₂, or the magnetic Ba₂Mn₂F₈. These calculations will be essential to address the fundamental question, “to what extent can the existence of an incommensurate phase be predicted just from static DFT/DFPT calculations?”

Phonon instabilities at low-symmetry q-points will provide an idea of the wavelength of the modulation and the character of the dynamic displacements that are the precursor of the incommensurate phase transition.

This work will provide preliminary insight into the underlying reasons for incommensurate modulations in this family of materials. Furthermore it should also give indication of possible routes to tune the modulation, via strain, chemical composition, external fields, etc..

Finally, time-permitting, large supercell models will be calculated, providing commensurate simulants to the incommensurate phases. This work will set the scene for developing the effective potentials that will be used to simulate the dynamics associated with the incommensurate phase transition in the PhD.

Calculations will be supplemented by group theoretical analysis, and comparison with experiments. This interplay is especially important in these complex systems.