FROM THE EARLY UNIVERSE TO THE HUBBARD HAMILTONIAN IN THE HEXAGONAL MANGANITES.

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presented by

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To my Mum,
Mr. K, and Mr. G
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It is good to have an end to journey toward; but it is the journey that matters, in the end.
– Ernest Hummingbird

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PUBLICATIONS

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– A density functional theory study of FeAs comparing LDA+U, GGA+U and hybrid functionals
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– Manipulation of spontaneous symmetry breaking and topological defect duality
F. Huang, S. M. Griffin, Y. Kumagai, O. Gindele, N. A. Spaldin, S. W. Cheong (under review)

– From multiferroics to cosmology: Scaling behavior and beyond in hexagonal manganites
(with features/mentions in Science et Vie, phys.org, Nature Materials, ETH Life)

– Ab initio investigation of FeAs/GaAs heterostructures for potential spintronic and superconducting applications

– Atomic scale model interfaces between high-k silicates and germanium

IN PREPARATION

– Designer single-band Hubbard materials
S.M. Griffin, P. Starr and N.A. Spaldin

– A simple ab initio marker and search for high-Tc in Fe-pnictide superconductors
S.M. Griffin, P. Canfield and N.A. Spaldin

– Simulated graphene from ab initio
E. Sediva, F. Erni, S. M. Griffin and N. A. Spaldin
ABSTRACT

The hexagonal manganites play host to a range of properties from the technologically relevant – ferroelectricity, frustrated magnetism, magnetoellectric coupling, multiferroism, functional domains and domain walls – to being a model system for testing high- and low-energy theories. Recent experiments using piezoresponse force microscopy (PFM), high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and second harmonic generation (SHG) revealed an intriguing cloverleaf pattern caused by topological defects.

The formation of topological defects is central to understanding both the functional and exotic properties in these materials. The Kibble-Zurek mechanism, which remains an open question in cosmology, predicts a scaling law for the number of defects formed during a phase transition. Herein we pursue a complementary line of questioning by combining symmetry analysis, first-principles calculations, and phenomenological models. We show that hexagonal manganites form one-dimensional topologically-protected vortices. We then apply the Kibble-Zurek theory of topological defect formation to the hexagonal magnanites to quantitatively corroborate our predictions arising from first-principles electronic structure theory with recent literature data. Finally we explore the crossover out of the Kibble-Zurek regime.

We next apply the developed topological description of hexagonal manganites to explain the formation of dual domains and domain walls in \( \text{InMnO}_3 \). Again using a combination of theory and calculations, we give a universal description of topological defects in both ferroelectric and non-polar domains and predict the resulting domain wall structures.

Finally, we propose a new class of materials with the hexagonal manganite structure to test the Hubbard Hamiltonian. We take a top-down approach to design a material \textit{ab initio} with a half-filled non-degenerate band. We then characterize the electronic properties of the candidate materials and demonstrate its Mott-insulating behavior and potential exotic superconductivity.

This thesis demonstrates the simplicity and power of applying a topological description to a multiferroic material. It demonstrates an early-universe theory – the Kibble-Zurek mechanism – for the first time in a crystal. Extending the description to the whole class of hexagonal multiferroics provides a universal description of defects, domains, and domain walls. Finally, using the same crystal structure, we design a material obeying the Hubbard Hamiltonian, which harbors possible exotic superconductivity.
Gli ossidi ternari (h-RMnO$_3$) con struttura esagonale presentano una serie di proprietà tecnologicamente rilevanti – ferroelettricità, frustrazione magnetico, accoppiamento magnetoelectrico, multiferroicità, domain walls funzionali – oltre ad essere un sistema modello per testare le teorie ad alta e bassa energia. Recentì esperienze hanno infatti rivelato un intrinseco struttura a trifoglio causata da difetti topologici usando tecniche quale: la microscopia piezoelettrica (PFM), high angle annular dark field (HAADF), scanning transmission electron microscopy (STEM) and second harmonic generation (SHG).


In aggiunta, utilizziamo la descrizione topologica delle h-RMnO$_3$ per spiegare la presenza di una dualità domini e domain walls in InMnO$_3$. Anche in questo caso utilizzando una combinazione di teoria e calcoli numerici abbiamo dato forniamo una descrizione universale di difetti topologici valido sia per i domini ferroelettrici che per quelli non polari. La nostra descrizione ci permette anche di prevedere le strutture di domini presenti in questi sistemi ma non ancora osservati sperimentalmente.

Infine, proponiamo una nuova classe di materiali con la struttura h-RMnO$_3$ come un banco di prova per la Hamiltoniana di Hubbard. Abbiamo considerato un approccio top-down per la progettazione ab initio di un materiale con una banda non degenere e occupazione $\frac{1}{2}$. Inoltre abbiamo caratterizzato le proprietà elettroniche dei candidati e predetto la presenza di uno stato isolante (di Mott) e di un potenziale stato con superconduttività esotica.

I nostri risultati dimostrano la semplicità e la potenza di applicare una descrizione topologica ed un materiale multiferroico. Dimostriamo per la prima volta che una teoria che descrive i primi istanti dell’universo – il meccanismo Kibble-Zurek – può essere applicata ad un cristallo. Estendiamo la descrizione a tutta la classe di multiferroici h-RMnO$_3$ e forniamo una descrizione universale dei difetti, domini e domain walls in questi materiali. Infine usiamo la stessa struttura cristallina per studiare la fisica delle basse energie di Hamiltoniana di Hubbard.
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Learn from the mistakes of others. You can never live long enough to make them all yourself.
– Groucho Marx

Complex oxides have been the focus for a myriad of breakthroughs in science – from high-temperature superconductivity in the cuprates to giant magnetoresistance and multiferroics. While complex oxides by definition contain more than one cation species, those with interesting properties usually contain strongly-correlated electrons. The typical crystal structures are highly suited to chemical and physical tuning, allowing the manipulation of their physical properties in a systematic manner.

Recently, certain multiferroic complex oxides, the hexagonal manganites, have been shown to host topological defects, that is symmetry-protected structures that set the resulting domains and domain walls. They are both of fundamental interest for verifying early-universe theories of topological defect formation and suggest novel applications in creating and controlling ferroelectric domain walls. In this chapter we give an overview of multiferroics focusing on the hexagonal manganite class. We describe the origins of improper ferroelectricity and magnetism in these materials and describe experimental observations of topological defects, domains and domain walls.
Figure 1.: Three of the possible ferroic orderings arising from polarization, magnetism and lattice distortions. The coexistence of two or more of these results in a multiferroic material, depicted by the areas of overlap in the Venn diagram.

1.1 Multiferroics

1.1.1 General introduction

The progress of science has always been propelled by a simple question: can the fundamental forces of nature be unified in a single theory? A paradigm shift was brought about by James Clerk Maxwell in 1855 in his treatise “On Faraday’s lines of force”\cite{maxwell1855} and later in “On physical lines of force”\cite{maxwell1856} which proposed a set of differential equations linking the two observed forces at the time, electricity and magnetism. The first experimental connection between magnetism and electricity was made by Wilhelm Conrad Röntgen in 1888 when he discovered that moving a dielectric in an electric field caused a magnetization to develop\cite{rontgen1888}. In addition to the continued fundamental scientific interest, today technologies are being explored that build on this fundamental posit in combining electricity and magnetism in a single device.

Multiferroics are materials that combine at least two of ferroelasticity, ferromagnetism or ferroelectricity in the same phase\cite{zhang2009, ribbe2009, bauer2011, battaglia2017}. The formal definition of multiferroic has been extended to include antiferromagnetic interactions in the ‘ferromagnetism’ category. The most sought-after multiferroics are those that combine ferromagnetism and ferroelectricity as they are promising for practical applications but challenging to achieve (see Fig. [1]). A ferroelectric is a material that has a spontaneous polarization that is switchable by an applied electric field. Microscopically it is the result of a cooperative reorientation of atomic displacements. In a similar manner, a ferromagnet exhibits spontaneous magnetization that is switchable by a magnetic field. Here it is important to distinguish between a multiferroic – one with more than one switchable order – and a magnetoelectric, which has coupled magnetic and electrical properties that are not necessarily switchable.

Combining ferromagnetism and ferroelectricity could in principle allow a four-state memory in a single device containing independent
electric and magnetic bits. However, usually there is a coupling between the two and so more exciting potential applications take advantage of this coupling. Indeed the electrical reading and writing of magnetic data bits would be a revolution in data storage since it would circumvent the requirement for large magnetic fields for writing.

There is no doubt that the combination of ferroelectricity and ferromagnetism in one device has huge potential. However the difficulty in combining these in a single chemistry was elucidated by Spaldin in 2000 in terms of the general incompatibility of the chemical conditions for ferroelectricity and magnetism. Today, the relatively limited catalogue of mutually magnetic and ferroelectric materials include the boracites $M_3B_7O_{13}X$ (M=Cr, Mn, Fe Co, Ni, Cu and X=Cl, Br, I), the polar fluorides $BaMF_4$ (M= transition metal), the hexagonal manganites $RMnO_3$ (R=Sc, Y, Dy, Ho, Er, Tm, Yb, Lu, In) and several compounds adopting the perovskite structure, the most well-known being BiFeO$_3$. Others include spin-spiral multiferroics like TbMnO$_3$ and charge-ordered multiferroics such as LuFe$_2$O$_4$.

1.1.2 Classification of multiferroic materials

Ferroelectricity and magnetism: together or apart?

Depending on the microscopic mechanism of the onset of ferroelectricity and ferromagnetism, multiferroics can be classified into two types. The first, Type I, occurs when the ferroelectric and ferromagnetic order parameters arise independently of each other. Typically, the ferroelectric phase transition in a Type I multiferroic occurs at a much higher temperature than the magnetic one. For example, the ferroelectric transition temperature in hexagonal YMnO$_3$ is $\sim 1300K$, while the Néel temperature is $\sim 70K$. In fact all of the hexagonal manganite family fall into this Type I class of multiferroics.

Type II multiferroics have magnetic and ferroelectric order parameters that appear at the same temperature. Typically the magnetism and ferroelectricity are strongly coupled in these materials. An example of such a class are those where the magnetic order breaks the inversion symmetry and induces a ferroelectric order. Usually the magnetic interactions that result in the lifting of inversion symmetry are non-collinear spin structures as found in TbMnO$_3$, MnWO$_4$ and CuFeO$_2$, for example.

Proper and improper ferroelectrics

Multiferroics, and more generally ferroelectrics, are further categorized depending on the nature of ferroelectricity in the material. The absence of inversion symmetry is a necessary but not sufficient condition for the appearance of a spontaneous electric polarization. To be ferroelectric it also must be switchable by an electric field. The various different driving forces for ferroelectricity lead us to classify ferroelectrics as proper and improper: Proper ferroelectrics have the ferroelectric distortion as the primary order parameter whereas im-
proper ferroelectrics form the spontaneous polarization from a secondary effect in the material that couples to the primary order.

$\text{BaTiO}_3$ is an example of a proper ferroelectric. It is a displacive ferroelectric where a shift of one of the ions causes a net polarization. In this case the Ti ion off centers due to a rehybridization between the empty Ti $d$ states and the O $p$ states, directly inducing ferroelectricity.

The search for multiferroics has often focused on improper ferroelectricity since it circumvents the usual incompatibility of ferroelectricity and ferromagnetism[?]. To date three types have been identified: In spin-spiral multiferroics the magnetic ground state removes inversion, however the resulting polarization is typically small. Charge-ordered multiferroics like LuFe$_2$O$_4$ remove inversion by forming a mixed-valence compound[?]. Improper geometric ferroelectricity occurs when a structural phase transition that does not itself have a polarization is coupled to a polar distortion which subsequently induces ferroelectricity. The hexagonal manganites $R$MnO$_3$ belong to this class with a structural transition involving the rearrangement of the Mn-O polyhedra coupled to a polar mode consisting of displacements of the $R$ ions. Fig. 2 divides the typical multiferroics into the aforementioned classes. The absence of Type II multiferroics with proper ferroelectricity is interesting since it would require that magnetism and ferroelectricity serendipitously occur at the same temperature but are not coupled. This almost occurs in FeTe$_2$O$_5$Br where the long-range magnetic order sets in at $11$ K and the polarization appears at $10.5$ K in an independent transition[?].

1.2 Hexagonal Manganites

Since their discovery in 1963 by Bertaut et al.[?], the hexagonal manganites $R$MnO$_3$ ($R = \text{Y, Dy, Ho, Er, Tm, Yb, Lu or Sc}$) have been intensely studied because of their coexisting ferroelectricity with $T_C \sim 1000$ K and magnetism with $T_N \sim 100$ K[?] (the exact temperatures depend on the $R$ ion). They lack the usual $d^0$ or lone pair mechanisms for ferroelectricity making the origin of ferroelectricity a topic of much discussion and debate. In this section we introduce the high- and low-temperature structures of the ferroelectric hexagonal manganites and the mechanism for ferroelectricity. Finally we discuss the unusual topological defects and domain walls these materials possess.
1.2.1 Structure and multiferroism

The hexagonal manganites are layered structures consisting of Mn-O trigonal bipyramids with three oxygens in the plane of Mn, and one above and below. These transition-metal and oxygen layers are separated by large rare-earth ions[1, 2, 3]. They undergo a phase transition between a centrosymmetric $P_{6_3}/mmc$ space group and the ambient ferroelectric $P_{6_3}cm$ at $T_S \sim 1000$ K (see Fig. 3).

Figure 3: Crystal structure of YMnO$_3$ in the ferroelectric $P_{6_3}cm$ space group from (a) side view and (b) top view. The five-coordinated Mn ions form trigonal bipyramids with oxygen, and (b) shows the triangular magnetic sublattice comprised of Mn ions.

The exact onset of ferroelectricity and the sequence of symmetry changes to the ferroelectric ground state were initially unknown. It was initially believed by Bertaut et al.[4] that the ferroelectricity was caused by off centering of the rare-earth ions. Analysis of the possible transition routes between the high-symmetry $P_{6_3}/mmc$ structure and the ferroelectric $P_{6_3}cm$ ground state gave three possible transition paths[5, 6]. Single-crystal synchrotron diffraction experiments suggested the ferroelectric transition occurring 300 K below $T_S$, suggesting a proper ferroelectric transition with an intermediate centrosymmetric $P_{6_3}/mcm$ space group[7]. More recent neutron diffraction data contradicts this however and shows a direct transition between the $P_{6_3}/mmc$ and ferroelectric structure[8]. The signature at 300 K below $T_S$ is now believed to be a gradual emergence of the polarization that is coupled to the primary mode and not a second phase transition.

The improper mechanism of ferroelectricity first proposed by Van Aken et al.[9] that is now believed to be valid throughout the hexagonal manganite series is as follows: Size mismatch between the large rare-earth ions and the small Mn causes a tilting of the MnO$_5$ polyhedra resulting in a unit-cell tripling. This is accompanied by an uncompensated net vertical shift of the Y ions into the space created by these rotations. The net effect of these displacements creates a significant polarization along the $z$-axis as a secondary order parameter of the single phase transition.
The microscopic mechanism was further investigated by a combination of Landau theory and density functional theory analysis for the case of YMnO$_3$[?]. This confirmed the primary order parameter as being the unit-cell tripling polyhedra tilting. The improper nature of the phase transition was shown by the coupling of the polarization to the third power of the trimerization order parameter. It also showed a striking degeneracy of the polyhedral tilt angle prior to the onset of ferroelectricity.

The hexagonal lattice symmetry has a strong influence on magnetism with the Mn spins forming a triangular lattice (Fig. 3(b))[?]. Since the primary interaction between the Mn magnetic moments is antiferromagnetic superexchange, the ground state is highly frustrated. This frustration is resolved by the spins forming a 120° non-collinear arrangement with the spins lying in the plane.

Figure 4.: The two possible spin arrangements between the manganites layers. The two Mn layers are shown in different colours (purple and red) with the spins marked by arrows. (a) In the $\Gamma_3$ representation a pair of subsequent spins are parallel. (b) In the $\Gamma_1$ representation a pair of Mn spins in neighboring layers are antiparallel.

There are two possible arrangements of spin orientation between the two layers – one has a pair of Mn spins parallel (the $\Gamma_3$ representation) shown in Fig. 4(a), in the other they are antiparallel (the $\Gamma_1$ representation) shown in Fig. 4(b). Further symmetries are possible when the spin tilts away from the crystallographic directions. Because of the large spacing between the Mn planes, these two spin arrangements between the layers are only weakly coupled and these arrangements are close in energy. Powder neutron diffraction first proposed the $\Gamma_3$ spin structure[?]. However, the characterization of complex magnetic orderings in powder neutron scattering is difficult because of the limited resolution in scattering data. However, second-harmonic generation (SHG) has proved a useful probe for uncovering both the ferroelectric and magnetic properties of the hexagonal manganites[?]. In this respect, Fiebig et al. used SHG to identify the magnetic structures of the hexagonal manganite class, concluding that YMnO$_3$ adopts the $\Gamma_3$ representation, for example[?]. The magnetic ordering varies across the series however, with the rare-earth ion also contributing to the magnetism in Er, Yb and Ho.
Below $T_N=100{\text{ K}}$, YMnO$_3$ is multiferroic. An interesting question is then how the ferroelectric ordering and magnetism interact with each other. The noncollinear in-plane magnetism is not allowed to couple linearly to the $z$-axis polarization by symmetry. However, dielectric measurements at $T_N$ showed an anomaly for YMnO$_3$ which was subsequently observed in the other hexagonal manganites.

1.2.2 *Topological defects and domain walls*

The first suggestion of topological defects in the hexagonal manganites was the observation of an intriguing cloverleaf pattern using high-resolution transmission electron microscopy with locked domain walls which prevented a single-phase state even with large poling. Six domains of opposite polarization join at a single point or vortex forming unfavorable head-to-head and tail-to-tail meetings. Moreover the walls between these ferroelectric domains have been shown to be conducting where the electrical conductance depends on domain-wall orientation. The structural vortices result in magnetic vortices with strong magnetoelectric coupling along the domain walls.

1.3 *Thesis Outlook*

Central to understanding the myriad of electronic and magnetic properties in the hexagonal manganites is a full description of the formation of topological defects and domains. From this, the tuning of ferroelectricity, domain wall conductance and multiferroism can then be envisaged. The work we present explains the formation of topological defects in multiferroic hexagonal manganites using a combination of analytical and computational techniques. Using the theoretical toolbox of homotopy theory and topological defects brings a coherence and simplicity to the understanding of defects in these complex systems. While many degrees of freedom are present such as ferroelectricity, magnetism and charged walls, the theoretical framework of topological defects provides a powerful and delightful simplicity which is demonstrated in this work.

We first lay the theoretical foundations for the study of topological defects using the natural mathematical language of homotopy theory. We propose that the hexagonal manganites be studied within this framework to take advantage of the wealth of knowledge currently existing in this area. A key prediction of the theory of topological defect formation is the Kibble-Zurek mechanism – this describes the number of defects formed when a system is quenched through a phase transition. We analyze the suitability of hexagonal manganites for testing this scenario and report the first direct prediction and observation of Kibble-Zurek scaling in a crystal. Dynamics beyond the Kibble-Zurek mechanism are also addressed with reference to recent experiments.

Ferroelectricity in hexagonal InMnO$_3$ has been a matter of contention with different ground states (nonpolar and ferroelectric) reported in experiments. We fully characterize the formation of topo-
logical defects using a combination of density functional theory and Landau theory for both of the possible ground states. This allows us to investigate the domains and domain walls for both scenarios and to compare directly with experimental observations. We uncover a novel duality between domains and domain walls in InMnO$_3$ and identify – for the first time – the third possible phase for the hexagonal manganite family bringing a universality to the description of topological defects, domains and domain walls.

Finally we use the prototypical hexagonal manganite structure to design a material whose Hamiltonian is that of the single-band Hubbard model from first principles. We identify several compounds with the appropriate chemistries which are then screened for the desired electronic structure using density functional theory and dynamical mean-field theory. After finding a candidate material, we discuss the possibility of synthesis and describe the exotic superconductivity that the material should display.
METHODS: DFT, LANDAU THEORY AND DMFT

It’s still tough, complicated, and more than a little messy, with lessons to be learned, mistakes to be made, triumphs and disappointments to be had, and not every day is meant to be a party.
– Alyson Noel

This chapter summarizes the computational and phenomenological methods used in the thesis. Much of condensed matter theory is concerned with finding solutions to the many-body Hamiltonian. The independent-electron approach naturally captures the nonlocal nature of electrons in metals through its use of planewaves. However, in the more localized $d$- and $f$- electron materials, the independent-electron approximation breaks down. Because of the strong spatial confinement of $d$ and $f$ orbitals, the electrons experience strong onsite Coulomb repulsion. Modern pursuits try to explain the physical properties of these strongly-correlated electrons. In this chapter we first introduce density functional theory (DFT), which treats the electrons at a mean-field level and address some of the successes and failures of DFT. We discuss how strong correlations are included beyond the DFT limit using DFT+U and DFT+DMFT approaches.
2.1 DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) is the workhorse of modern computational condensed matter physics and material science[?]. It is routinely applied to a large range of problems in chemistry and physics from binding energies and band structures to more advanced topics such as superconductivity and multiferroic materials. Owing to its diverse applicability and usefulness, its father, physicist Walter Kohn, was awarded the Nobel Prize for Chemistry in 1998[?].

DFT’s power lies in the generality of its fundamental building blocks, and in its versatility for addressing several areas of quantum matter. DFT is build on a rigorous and formally exact framework which will be summarized in this section. We will first discuss the many-body problem and where difficulties arise in solving it. Following this, the fundamental DFT theorems and equations will be introduced; the Hohenberg-Kohn theorems and the Kohn-Sham equations. We will then briefly discuss some issues relating to its technical implementation and some particular aspects of DFT used in this thesis.

2.1.1 The many-body problem

We first recall from elementary quantum mechanics that the wavefunction, $\Psi$, contains all possible information about a system. In the context of electronic structure we will be concerned with the properties of the atoms and electrons in our material. In the non-relativistic limit we calculate the wavefunction $\Psi$ from solving the many-electron Schrödinger Equation. The system’s Hamiltonian consists of several contributions: the nuclear and electronic kinetic energies, the nuclear-nuclear repulsion, the electron-electron repulsion and the nuclear-electron repulsion. We now employ the ‘Born-Oppenheimer approximation’ in which the atomic nuclei are treated as fixed and provide a static potential $V$ which the electrons experience. Our Schrödinger Equation (in Hartree atomic units) can then be written:

$$\hat{H}\Psi = [\hat{T} + \hat{V}_{\text{ext}} + \hat{V}_{\text{int}} + E_H] \Psi$$ (1)

where $\Psi = \Psi(r_1, r_2, ..., r_N)$. In the following the sum of $i$ runs over electrons, and $I$ over nuclei. The first term is the kinetic energy of the electrons:

$$\hat{T} = -\sum_{i} \frac{1}{2} \nabla_i^2,$$ (2)

the second term describes the interaction of the static nuclei with the electrons (the external potential):

$$\hat{V}_{\text{ext}} = -\sum_{i, I} \frac{1}{2} \nabla_i^2,$$ (3)
the next is the electron-electron interaction (the internal potential):

\[ \hat{V}_{\text{int}} = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}, \]  

(4)

and finally the nuclear-nuclear interaction:

\[ E_H = \frac{1}{2} \sum_{i \neq j} \frac{Z_i Z_j e^2}{|R_i - R_j|}, \]  

(5)

where the \( R_I \) are the nuclear positions, the \( r_i \) are the electron positions and the \( Z_I \) are the nuclear charges.

2.1.2 Theorems of DFT

Hohenberg-Kohn theorems

The standard approach to solving Eqn. \([\text{4}]\) is to first specify the system via the \( V_{\text{ext}} \), substitute the potential into the Schrödinger equation, and solve for the unknown wavefunction \( \Psi \). From \( \Psi \), observables such as the energy can be calculated by taking expectation values. One such observable is the charge density \( n(r) \), which is the key variable in DFT:

\[ n(r) = N \int d^3 r_2 \int d^3 r_3 \ldots \int d^3 r_N \Psi^*(r, r_2, \ldots, r_N) \Psi(r_1, r_2, \ldots, r_N). \]  

(6)

The first theorem of DFT proves the corollary of this relation for the ground state (GS) density, \( n_0 \); that is, that the GS wavefunction \( \Psi_0 \) is uniquely determined by \( n_0 \) [7]. Thus any GS expectation value, such as the GS energy for a given potential \( V_{\text{ext}} \):

\[ E_{V,0} = \min_{\Psi \rightarrow n_0} \langle \Psi |\hat{T} + \hat{U} + \hat{V}|\Psi \rangle \]  

(7)

must also be a functional of \( n_0 \) where \( E_{V,0} \) denotes the GS energy for a given potential \( V_{\text{ext}} \).

This brings us to the second theorem of DFT. Given another arbitrary density \( n \) different from the GS density \( n_0 \), the corresponding \( \Psi \) will be different from \( \Psi_0 \), and the resulting energy \( E_V[n] \) will be greater than or equal to the GS energy \( E_{V,0} = E_V[n_0] \). Therefore the energy functional \( E_V[n] \) is minimized by the GS density \( n_0 \). The total energy functional is then

\[ E_V[n] = T[n] + E_{\text{int}}[n] + \int d^3 r V_{\text{ext}}(r)n(r) + E_H \]  

(8)

In principle to calculate all observables one needs to minimize \( E_V[n] \), however there is no prescription for doing this explicitly because all of the terms in Eqn. \([8]\) are not known.
Kohn-Sham equations

The Kohn-Sham (KS) approach is the most widely-used method for practically implementing DFT. Instead of using the many-body density as the fundamental variable, it employs an independent-particle treatment. The resulting KS equations are then formulated in terms of non-interacting particles that give the same ground state density and energy as the interacting system.

We first decompose the kinetic-energy functional \( T[\rho] \) in terms of the kinetic energy of noninteracting particles \( T_S[\rho] \) (the ‘single-particle’ energy) and the remainder \( T_C[\rho] \) (the ‘correlation’ energy)

\[
T[\rho] = T_S[\rho] + T_C[\rho]
\]

Now the exact energy functional can be reformulated as

\[
E_{KS} = T_S[\rho] + \int dr V_{ext}(r)n(r) + E_{Hartree}[\rho] + E_{H} + E_{xc}[\rho]
\]

where we define the exchange-correlation functional \( E_{xc}[\rho] \) as the difference between the kinetic and interaction energies of the full interacting system and the auxiliary single-particle system. \( E_{xc}[\rho] \) can be broken down into \( E_{xc} = E_x + E_c \) where \( E_x \) is the exchange energy due to the Pauli principle, and \( E_c \) is from any remaining electron correlations. No explicit expression for the correlation energy is known – a common treatment is described in Section 2.2. The other four terms in Eqn. involve only independent particles and are therefore solvable.

It thus remains to minimize \( E_{KS} \) which is carried out via the Kohn-Sham equations

\[
\left(-\frac{1}{2}\nabla^2 + V_{KS}(r) - \epsilon_i\right) \psi_i(r) = 0
\]

with the \( V_{KS} \) given by

\[
V_{KS}(r) = V_{ext}(r) + V_{Hartree}(r) + V_{xc}(r).
\]

This replaces the problem of minimizing \( E[\rho] \) to that of self-consistently solving a noninteracting Schrödinger equation.

2.2 DEaling with exchange and correlation

A central approximation in the practical implementation of DFT is the choice of the exchange-correlation functional in Eqn. which contains all of the many-body aspects of the problem. The exchange contribution can be calculated explicitly whereas the correlation energy, while formally exact, needs to be approximated in order to find solutions to the Kohn-Sham equations. The development and choice of exchange-correlation functional to accurately describe chemical and physical systems in computationally-reasonable timeframes remains an active research area – here we describe three of the most widely-used functionals, which will also be employed in this thesis.
2.2 Dealing with Exchange and Correlation

2.2.1 The local-density approximation (LDA)

The local-density approximation (LDA) is one of the simplest approximations for calculating the exchange-correlation energy. It approximates the local density of the fully-interacting system with the corresponding energy of a homogeneous electron gas with the same local density. Explicit calculation of the exchange and correlation energy using the LDA usually comes from Quantum Monte Carlo calculations\[?] which are already calculated and tabulated. The total exchange-correlation energy in the LDA is then given by

\[
E_{xc}[n] = \int d^3 r n(r) \epsilon_{xc}(n(r))
\]

where \( \epsilon_{xc} \) is the energy for the homogeneous electron gas. The LDA splits the inhomogeneous many-body problem into two parts: first by solving the exchange-correlation for a spatially homogeneous system electron gas, and secondly by using this in the solution of the inhomogeneous problem from the Kohn-Sham equations. Perhaps surprisingly for such an ostensibly simple approximation, the LDA has proven remarkably successful in the description of both chemical and physical properties.

2.2.2 The generalized-gradient approximation (GGA)

The LDA assumes homogeneity and regards only the local density of the electron gas, however real physical systems are not homogeneous in this manner. An obvious extension to the homogeneous solution is to account for some degree of spatial variation in the functional. One route is to include the gradient of the density,

\[
E_{xc}^{GGA}[n] = \int d^3 r f(n(r), \nabla n(r)),
\]

in the so-called generalized-gradient approximation (GGA). In fact a straight-forward inclusion of the gradient of the density and higher-order gradients generally never improves the LDA. However taking particular functions of the gradient of the density and comparing to experimental data has been extremely successful. The particular treatment of the function \( f(n(r), \nabla n(r)) \) varies, with one of the most successful being PBE developed by Perdew, Burke and Ernzerhof in 1996[?]. The GGA method has led to excellent results and improvements over the LDA for molecular geometries and ground-state energies.

2.2.3 Plus-U functionals: LDA+U, GGA+U

The LDA and GGA have proved very successful in describing a wide range of systems, however problems arise when systems with strongly-correlated electrons are encountered. Examples of such systems are materials that contain transition metal or rare-earth ions with partially filled \( d \) or \( f \) manifolds in which the electrons are localized and
strongly interacting. For these the LDA and GGA fail because they
do not include orbital dependence in the potentials, underestimating
the electronic localization. A typical failing is the prediction of
transition-metal oxides to be metallic when in reality they are Mott
insulators.

The LDA+U method[?] includes an orbital-dependence by splitting
the electrons into two groups: the delocalized s and p electrons which
are usually described well by the LDA, and the localized d and f elec-
trons. For the latter, a Hubbard repulsive term $\frac{1}{2} U \sum_{i\neq j} l_i l_j$ is added
to treat the Coulomb interaction for the d and f orbitals, labelled $l_i$.
With this treatment the total energy is then given by:

$$E^{LDA+U}[n(r, \{l\})] = E^{LDA}[n(r)] + E^U[\{l\}] - E^{dc}[\{l\}]$$  \hspace{1cm} (15)

where $n(r)$ is the electron density and $\{l\}$ is the density matrix
for the d or f electrons. The first term is the usual LDA energy, $E^U$
is a Hubbard-like term treating the Coulomb electron-electron inter-
action, and the final term accounts for double counting that removes
the pure LDA energy contribution for the d and f electrons from the
total energy.

In DFT calculations, $E^U$ and $E^{dc}$ are reformulated in terms of two
parameters: the Hubbard energy $U$ and Hund’s exchange $J$. These
are then adjusted according to the degree of localization of the d or
f electrons in the material and compared with experimental observa-
tions to choose an appropriate value. There are several prescriptions
in the treatment of the double-counting term, $E^{dc}$.

### 2.2.4 Hybrid functionals

In the quest for more accurate XC functionals, empirically-based ‘hy-
brid functionals’ are gaining in popularity. Typically the LDA overbinds
resulting in gaps that are too small compared with experiment, whereas
the Hartree-Fock method underbinds giving gaps that are too large.
Hybrid functionals average these effects by combining a portion of
exact exchange from Hartree-Fock theory (HF) with exchange and
correlation from either DFT or empirical data is used[?]. Different
hybrid functionals differ in the weighting of the HF and DFT contrib-
utions. In this thesis, the HSE (Heyd-Scuseria-Ernzerhof) functional
is employed which standardly uses 25% exact Hartree-Fock exchange
and 75% GGA[?].

### 2.3 Practical Implementation of DFT

#### 2.3.1 Basis functions

To explicitly calculate solutions to Eqns. 11 12 the Kohn-Sham or-
bitals are expanded in a set of basis functions which are then substi-
tuted back into the auxiliary equations and solved. Several options
for the basis functions exist, the most common in band theory be-
2.3 Practical Implementation of DFT

Figure 5: Typical self-consistent workflow for a DFT calculation.

...ing a plane-wave basis. These are particularly suited to periodic systems since periodic boundary conditions are straight-forward to implement with plane waves. Further advantages include simple algorithms for computational steps and an unbiased choice of basis vectors. Expanding the Kohn-Sham orbitals in Bloch states we have

$$\psi_{k,j} = e^{i\mathbf{k} \cdot \mathbf{r}} \sum_n c_{n,j}(\mathbf{k}) e^{i\mathbf{G}_n \cdot \mathbf{r}}$$

where \(k\) is the wavevector, \(j\) gives the band index, and \(\mathbf{G}_n\) are the reciprocal lattice vectors. The density is evaluated by taking the square modulus of Eqn. 16. While the sum over \(n\) is exact if evaluated to \(\infty\), in practice it is calculated up to a cut-off value that achieves the required convergence of total energy (or other physical variables such as force). This cut-off is frequently given in terms of the energy corresponding to a particular \(\mathbf{G}_n\) defined by \(E_{cut} = \left(\hbar^2/2m\right)G_{cut}^2\).

2.3.2 The pseudopotential method

A further approximation common in practical DFT is the introduction of pseudopotentials to treat core states in a calculation. The properties of core electrons are essentially independent of their chemical environment, and more importantly, their contribution to the bind-
ing energy in a crystal is negligible. Since the bonding in a crystal is then determined by the valence electrons, an appropriate approximation is to combine the core electrons with the nuclei in the external potential and not treat them explicitly during the DFT calculation. This approximation greatly reduces the computational demands in the calculation since far more planewaves are required to describe the strongly spatially-varying wavefunctions near the core. The core electrons and the nucleus are described by smoothly varying effective pseudopotentials, derived from all-electron calculations. The accuracy of these "pseudopotentials" are typically determined by comparing their scattering properties to those of the atom, as well as comparing pseudopotential calculations for the materials of interest to all-electron calculations.

A generalization of the pseudopotential method is the projector augmented wave method (PAW). Here the all-electron atomic wavefunction is calculated in a spherical region around the nuclei, the ‘augmentation sphere’, which is matched to the smooth wavefunction at the sphere’s surface. The main advantage of the PAW method is its excellent convergence speed in comparison with conventional pseudopotential methods of comparable accuracy.

2.3.3 Workflow for a DFT calculation

The main steps in performing a density functional theory calculations are outlined in Fig. 3. Essentially the Kohn-Sham equations are solved iteratively, using the various approximations mentioned above, until self consistency is achieved within the required accuracy.

2.4 DYNAMICAL MEAN-FIELD THEORY (DMFT)

Both the independent-electron method and the mean-field treatment using DFT capture the itinerant nature of the electrons by a plane-wave treatment, but do not adequately describe localized electrons. Even though LDA+U has been very successful in treating several strongly-correlated d- and f-electron systems, there are several systems where it fails. For example, the correct magnetic order and the Mott metal-insulator transition in vanadium dioxide cannot be reproduced using LDA+U methods.

Dynamical mean-field theory has been successfully applied to a range of strongly-correlated materials. It partitions the strong correlations into two problems, a crystal problem and an impurity problem. The impurity problem maps the many-body electron problem to an electron interacting with an effective bath. In this mean-field approach, the conduction electrons are determined by the crystal problem. Solutions to the crystal problem are found using the self-energy from the impurity problem with a Green’s function approach. Here we summarize the main steps in the DMFT approach with more details given in [...].
2.4 DYNAMICAL MEAN-FIELD THEORY (DMFT)

Figure 6: Scheme of dynamical mean-field theory (DMFT). The purple spheres are atoms with the spin of the electrons represented by arrows. In DMFT a single impurity atom (purple) is coupling to a bath of electrons (red). Here we show the time evolution as an electron hops between sites. This is the essence of the dynamical approach – it captures the dynamics of the electron as it fluctuates between the atomic sites. The hybridization $V_\nu$ describes the amplitude of an electron to flip between two of the configurations shown above.

2.4.1 The elements of DMFT

The first step in the development of DMFT was in 1980 by Metzner and Vollhardt who introduced the idea of infinite lattice coordination to the strongly-correlated electron problem[7]. DMFT maps the many-body lattice to a local problem. This is generally only solvable by making the approximation that the lattice self-energy does not depend on momentum. This momentum-independence is the only approximation in standard DMFT. Metzner showed that in the limit of lattices with infinite coordination this is actually exact. The link to strongly-correlated systems was then made by Georges and Kotliar who mapped the Hubbard model (a lattice problem) to a quantum impurity problem[8] – the Anderson impurity model. Here an impurity (a single site) interacts with a bath of electrons through a hybridization function as illustrated in Fig. 6. The impurity electron can fluctuate among the different sites with the hybridization, $V_\nu$, being the amplitude for how likely a state is to flip between two configurations.

The essential quantity in DMFT is a Green’s function that gives the probability amplitude for an electron to be created with spin $\sigma$ at site $i$ at a time $\tau’$ and be annihilated at the same site at a time $\tau$:

$$G_{i\sigma}(\tau - \tau’) := \langle c_{i\sigma}(\tau’)c_{i\sigma}^+(\tau) \rangle.$$  \hspace{1cm} (17)
The exact local Green’s function can be found by solving the Anderson impurity model

\[ H_{\text{AIM}} = H_{\text{atom}} + \sum_{\nu,\sigma} e^v_{\nu,\sigma} n_{\nu,\sigma} + \sum_{\nu,\sigma} (V_{\nu} c^\dagger_{\nu,\sigma} a^\dagger_{\nu,\sigma} + h.c.) \]  

until the hybridization between the site and the bath, \( V_{\nu} \), achieves self-consistency. Here, \( H_{\text{atom}} \) describes the lattice site’s atomic degrees of freedom, the second term describes the non-correlated electronic levels \( e^v_{\nu} \) of the bath with \( n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma} \) being the density of electrons at site \( i \) with spin \( \sigma \). The final term describes the hybridization between the bath and the impurity through \( V_{\nu} \). In fact, the \( e^v_{\nu} \) and \( V_{\nu} \) are combined in a single expression called the hybridization function:

\[ \Delta(\omega) = \sum_{\nu} \frac{|V_{\nu}|^2}{\omega - e^v_{\nu}} \]  

This is a frequency-dependent parameter making it a dynamic quantity. Self-consistency of the Green’s function is achieved when the impurity Green’s function is equal to the local lattice Green’s function. The remaining task is then to solve the impurity problem using one of the many impurity-solver techniques such as quantum Monte Carlo[?] or continuous-time Monte Carlo[?].

\[ \text{2.4.2 Maximum entropy method} \]

Our goal is to calculate the spectral function, however straightforward DMFT does not calculate this. The impurity solver calculates the Green’s function in imaginary time, \( G(\tau) \), which can be transformed into \( G(i\omega_n) \) where the \( i\omega_n \) are Matsubara frequencies. From this we can calculate the spectral function \( A(\omega) \) using the relation

\[ G(\tau) = \int_{-\infty}^{\infty} e^{-\tau \omega} A(\omega) d\omega \]  

which can be recast in terms of \( G(i\omega_n) \)

\[ G(i\omega) = \int_{-\infty}^{\infty} \frac{A(\omega)}{i\omega_n - \omega} d\omega. \]

However, inverting these equations is very difficult to perform numerically. The Maximum Entropy Method[?] is currently the most successful way of inverting Eqn.20 to find \( A(\omega) \). In essence, it describes how Eqn.20 can be inverted accurately for noisy data. Using statistical arguments, the \( A(\omega) \) can then be taken from those that give the required \( G(\tau) \).
2.5 Landau Theory and Critical Phenomena

2.5.1 Landau theory

Landau was the first to develop a general theory of phase transitions based on an order parameter description. The Landau theory is based on thermodynamic and symmetry arguments, rather than on the particular microscopic characteristics of the system under question. Since the minimum of the free energy defines the equilibrium of a system, and the free energy varies with temperature; we assume the minimum point also changes with temperature. Landau postulated that the free energy should obey two conditions: it obeys the symmetry of the Hamiltonian and it is analytic. From this he postulated that the free energy could be written as a function of the order parameter

\[ F(\Psi) = \alpha + \beta \Psi^2 + \gamma \Psi^4 + \delta \Psi^6 + \ldots \]

(22)

where \( \Psi \) is our order parameter and enters only in even powers of \( \Psi \) because of the condition \( F(-\Psi) = F(\Psi) \).

Despite having some issues, the Ehrenfest categorization is a useful way of dividing phase transitions into distinct groups depending on the values of the derivatives of Eqn. For first-order phase transitions the first derivative is nonzero:

\[ \left. \frac{\partial F}{\partial T} \right|_{T=T_C} \neq 0 \]

(23)

This implies the existence of latent heat at a first-order transition. This latent heat is often seen as the distinguishing characteristic of first-order phase transitions. Experimentally this often manifests as discontinuities in the temperature evolution of lattice parameters in going through a first-order phase transition. Second-order phase transitions have a nonzero second derivative of \( F \):

\[ \left. \frac{\partial^2 F}{\partial T^2} \right|_{T=T_C} \neq 0. \]

(24)

The power of Landau theory lies in its generality and wide applicability to a large range of systems. From it one can examine the temperature dependence of an order parameter and compute thermodynamic properties such as heat capacity.

2.5.2 Critical phenomena

Landau theory treats the phase transition on a mean-field level – to investigate behaviour close to the phase transition when correlations are important we use the theory of critical phenomena. This describes the behaviour near the critical point using a set of indices called critical exponents. Critical exponents are postulated to be universal; they do not depend on the particular physical details of the
system, but rather on its dimension, range of interaction and spin
dimension.

We first define a relative temperature which measures how close
we are to the critical point,

\[ \epsilon(T) := \frac{T-T_C}{T_C} = \frac{T}{T_C} - 1 \]  \hfill (25)

When a phase transition is approached, correlation lengths diverge
throughout the system. Near to \( T_C \) the correlation length \( \xi \) exhibits
power-law behaviour determined by the critical exponent \( \nu \):

\[ \xi(T) \sim \epsilon^{-\nu} = \left( \frac{T-T_C}{T} \right)^{-\nu} \]  \hfill (26)

The system dynamics also slow down as the critical point is reached.
This can be expressed in terms of another power law for the relax-
tation time, \( \tau \), controlled by critical exponent \( \mu \):

\[ \tau(T) \sim \epsilon^{-\mu} = \left( \frac{T-T_C}{T} \right)^{-\mu} \]  \hfill (27)

Power-law behaviour applies to many other static functions near
the phase transition described by \( \alpha, \beta, \gamma, \delta, \eta \), critical exponents. The
critical exponents can often be related by scaling relations, and it can
be shown by splitting the exponents into universality classes, that
there only exist two independent exponents, usually taken as \( \nu \) and
\( \eta \).
Topology in matter has experienced a renaissance of interest with the recent discovery of topological insulators and skyrmionic lattices. Each of these systems possess a property that is ‘protected’ in a symmetry sense, and is defined rigorously using a branch of mathematics known as topology. Indeed, the concept of topology and ‘protected-ness’ is not novel to condensed matter physics; several systems exhibit protected features called topological defects from liquid Helium and superconductors to liquid crystals and – as will be presented in this thesis – multiferroic materials. It is important to distinguish between a topological defect as was originally classified in terms of homotopy theory, and the manner in which the term has been applied to some other systems. Where a defect results from the precise symmetry-breaking conditions as laid out in the Kibble mechanism, we define it as a topological defect. In contrast to this, when features appear because of the particular stacking or structure of the material (topographical features), the term topological defect is not appropriate as it implies the symmetry constraints are applicable. In this chapter the conditions for topological defect formation are described and motivated by simple examples, and finally, put on a firm mathematical grounding.
It was in the context of cosmological phase transitions in the early universe that the concept of topological defects was first given a rigorous definition by Tom Kibble[?]. The Kibble mechanism has two key results: firstly it gives symmetry requirements for when topological defects will form during a phase transition, and secondly it predicts – based on the particular details of the initial and final symmetries – what kinds of defects will form. Below we describe the two requirements of the Kibble mechanism for which systems will form topological defects, and how those defects will manifest. We then give two simple examples of topological defect formation in materials, before giving a more rigorous mathematical treatment of the Kibble conditions in terms of topology.

3.1.1 Spontaneous symmetry breaking

The Kibble mechanism gives two conditions for topological defect formation. The first requires that the phase transition be spontaneously symmetry breaking. As a system undergoes a phase transition its symmetry changes from a higher to a lower symmetry state, which can be described by the onset of an order parameter, often called $\phi$, that contains the relevant variables for the transition. Here we do not consider isomorphic phase transitions, although they are also described by an order parameter. A simple example of this is the paramagnetic to ferromagnetic transition where time-inversion symmetry is lost with the onset of a magnetic order parameter (often taken to be the magnetization). While many phase transitions in physics are caused by changes in temperature, the concept is applicable to changes driven by applied fields or pressure for example. In the case of a magnetic phase transition, the axis of magnetization can be randomly chosen, with each crystallographically-equivalent easy direction being degenerate in energy[^1].

Identifying what the actual order parameter physically corresponds to is not always a trivial task, which is highlighted in the effort it took to prescribe the order parameter for superconductivity and superfluidity to be a complex function $\phi$ representing the condensate wave function. The high symmetry phase (non-superconducting or non-superfluid) conserves particle number, whereas in the broken-symmetry phase the particle number is indeterminate, but the magnitude of $\phi$ remains constant throughout. This gives the order parameter space for superfluids and superconductors to be $S^1$.

When a system has more than one degenerate choice of ground states following a phase transition, it is referred to as ‘spontaneously symmetry breaking’. Buridan’s famous ass, when placed between two identical piles of hay, was unable to choose between them and died of hunger[^2, ?]. How does a physical system, when approaching multiple equivalent states of lower energy, decide which to adopt?

[^1]: In real materials, a spin-orbit coupling term in the Hamiltonian removes the rotational symmetry and causes a preferred easy axis.

[^2]: In real materials, a spin-orbit coupling term in the Hamiltonian removes the rotational symmetry and causes a preferred easy axis.
Figure 7: Buridan’s ass and a Mexican-hat potential displaying the degenerate choice of ground states for spontaneous-symmetry breaking phase transitions.

The canonical example of spontaneous symmetry breaking is the ‘Mexican hat’ or ‘Wine bottle’ potential as shown in Fig. 7, with many applications in cosmology, high-energy physics and condensed matter. Dropping from the high-symmetry peak of the hat corresponds to a particular angle of phase choice, $\theta$. The brim of the hat is an infinite collection of equal-energy ground states with $\theta \in \{0, 2\pi\}$. Once the system falls from the top of the hat, it chooses a particular value of $\theta$, losing its initial U(1) symmetry. Since any choice of $\theta$ is degenerate, there exists a massless Goldstone boson running along the brim of the hat – a signature of the initial higher symmetry of the system.

3.1.2 Using topology to describe defects

Kibble’s second condition is that the symmetry breaking is described by a non-trivial homotopy group. Two topological spaces are homotopic if they can be deformed into each other by twisting and pulling. Take the case of a coffee cup: if we imagine pushing the base of the cup upwards so that it meets the upper rim and then deforming the cup by pulling outwards, it can be transformed into a doughnut. At no point did we need to make a cut or glue two parts together; a continuous deformation leads us from one shape to the other.

Instead consider a bowl and a doughnut and try to carry out the same operation. The only way we can transform the bowl into the doughnut is if we either make a hole in the bowl, or form a long cylinder with the bowl and attach the ends. Both of these involve ‘forbidden’ cutting and gluing operations, and so these two shapes are homotopically distinct. Physically speaking, a non-trivial homotopy group results in a local kink or crease in the order parameter field that can only be removed with a global change in the symmetry. In this case, the global change results in a change in the topological space of the order parameter, whereby the topology of the space allows for a continuous (kink-free) order parameter to be defined.

To exploit the results of homotopy theory, we must map our symmetry groups to topological spaces and use the standard results of homotopy theory to classify the relationship between the two. Two spaces are considered homotopic when they can be continuously de-
formed into one another; when this is not the case we have a non-trivial homotopy mapping. This information is encompassed in a function between the topological spaces known as the homotopy group. The type of defects created depend on the order of the homotopy group and can be examined in detail in homotopy tables.

3.1.3 Classification of topological defects

A powerful feature of homotopy theory is the classification of topological defects once the initial and final symmetries are known[?, ?].

We define our physical space to be a manifold, \( A \), and our space of minima to be \( M \), between which there exists a mapping, \( \phi : A \rightarrow M \). A topological defect occurs when there exists a discontinuity in the mapping, \( \phi \) between \( A \) and \( M \). This can be caused by two effects, one being some pathological behaviour of \( \phi \), and the other being due to symmetry attributes. The former results in an unstable defect, the latter a stable one. It is with stable defects caused by symmetry constraints that we will be concerned.

Let us begin with a model that is invariant under some symmetry group \( G \). If the symmetry group \( G \) is spontaneously broken, then there exists a field which remains a solution to the theory, but that is no longer invariant under \( G \). We identify this field with the order parameter (field). The ordered parameter space of the ordered, low-symmetry system is then defined as \( M = G/H \) where \( H \) describes the symmetry of the order parameter. Our ordered medium is thus described by a mapping \( \phi \) from the real space \( A \) into the order parameter space \( M \).

Essentially, homotopy theory examines the mapping between a sphere (of any dimension) and the vacuum manifold \( M \). The dimension of the sphere and manifold then determine what type of defect will form. Knowing the symmetry characteristics of the phase transition, we can predict and classify the types of defects that form[?]. The possible defects for various dimensions in condensed-matter systems are given in Table [1].

Domains are formed when \( M \) has disconnected components, which is usually the result of discrete symmetry breaking. If \( M \) is not simply connected, then holes in the manifold can trap loops that surround them. These unshrinkable loops are associated with the formation of strings/vortices like those formed in liquid Helium and superconductors. Likewise, monopoles are formed when \( M \) contains unshrinkable surfaces.

3.1.4 Examples in condensed matter

Next we look at some examples that occur in condensed matter systems to clarify the concept of order parameter and order parameter space in real systems.
Table 1.: Classification of the possible topological defects in condensed-matter systems for $1 \leq d \leq 4$ where $d$ is the dimension of the system.

<table>
<thead>
<tr>
<th>Homotopy Class</th>
<th>$d=1$</th>
<th>$d=2$</th>
<th>$d=3$</th>
<th>$d=4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi_0$</td>
<td>Monopole</td>
<td>Vortex</td>
<td>Surface</td>
<td>Hypersurface</td>
</tr>
<tr>
<td>$\pi_1$</td>
<td>Texture</td>
<td>Monopole</td>
<td>Vortex</td>
<td>Surface</td>
</tr>
<tr>
<td>$\pi_2$</td>
<td>-</td>
<td>Texture</td>
<td>Monopole</td>
<td>Vortex</td>
</tr>
<tr>
<td>$\pi_3$</td>
<td>-</td>
<td>-</td>
<td>Texture</td>
<td>Monopole</td>
</tr>
<tr>
<td>$\pi_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Texture</td>
</tr>
</tbody>
</table>

*Misfit dislocation*

The first example that we discuss is a simple misfit dislocation as shown in Fig. 8. The topological defect is located where the extra row disappears; no local rearrangement of the ions will remove the defect. To examine this from a topological perspective, we first need to identify what the order parameter space is. Since we are dealing with a 2D square lattice, the order parameter space must have two dimensions, but with translational symmetry in both directions. In this case, we find that the order parameter space is defined by a torus since wrapping a 2D plane in the $x$-direction results in a cylinder; and subsequent imposition of boundary conditions in the $y$-direction joins the ends of the cylinder to form a torus.

![Figure 8: Loop surrounding a misfit dislocation. The shaded rectangle marks the extra row. The order parameter space is described by a torus.](image)

Now, to analyse the properties of the defect, we circumnavigate the defect and note the motion of the order parameter on the torus. Going from site $A$ to site $B$, we clearly see the order parameter has an upwards drift with respect to the ideal lattice. As we continue around the defect, we can see that there is a continuous drift of ions with respect to the perfect lattice. Though we are again on an ideal lattice site at $C$, we now have an extra row of ions in the $y$-direction. On the order parameter space, this gives us a loop which is shown as a loop around the torus in Fig. 8. The torus contains one hole which corresponds to one extra row of ions. In order to return to exactly the same point, we need to perform a full displacement of one ion in looping around the defect once, corresponding to a winding number of 1.
1D skyrmion

A 1D skyrmion provides our second example of a topological defect. We consider a 1D lattice composed of magnetic XY spins. In the high-symmetry phase we have a paramagnetic solution where the spins are disordered. At the phase transition in the skyrmion the spins form a spiral as shown in Fig. 9. However, imposing periodicity causes a discontinuity in the order parameter since this would require, for instance, an ‘up’ spin to be located next to a ‘down’ spin, resulting in a highly unfavorable 180° spin rotation. To remedy this, the order parameter space becomes a Möbius strip – that is, it twists once to restore the continuity of the order parameter.

By comparing the properties of a loop with and without a twist, we can determine the topological charge carried by the defect in this 1D case. Fig. 10 summarizes the topological charges of different order parameter spaces with ‘kinks’ as in the 1D example. The \( n \) index refers to the topological charge of the defect which labels topologically distinct states. In our case, we have a single kink which results in a change of \( \pi \) of the order parameter, giving a topological charge of \( n = \frac{1}{2} \). Likewise higher charges can be classified by the number of twists in the space.

Figure 9.: 1D Skyrmion. To restore continuity of the order parameter we introduce a kink in the manifold resulting in a Möbius strip.

Figure 10.: Topological charges corresponding to different numbers of twists in a space.

Ising model

The result of one of the most important PhD theses in science, the Ising model mathematically describes the ferromagnetic phase transition.
Initially proposed by Wilhelm Lenz, it was solved for 1D by his student Ernst Ising in his 1924 thesis where he showed there is no transition at $T \neq 0$ for the 1D model. In the Ising model, we have a straight-forward order parameter in the magnetization, $m$. Above the Curie temperature, the system is invariant under a symmetry group, $G$. However, this is spontaneously broken with the onset of magnetic ordering, described by the order parameter, which is strictly zero above the transition temperature, and non-zero below. In the Ising mode, this order parameter can take two possible values; +1 or -1 at $T = 0$. Thus $\mathbb{Z}^2$ describes the space of minima.

3.2 MATHEMATICAL FORMALISM

Finally we provide a more rigorous mathematical foundation to the use of homotopy theory and the Kibble mechanism for topological defect formation. Now that the mapping between the mathematical formalism of the order parameter space and the physical system has been established, we proceed as follows: the mathematical definition of homotopy is introduced by comparing two loops on the order parameter manifold. The particular relationship between different loops separates them into various classes which distinguish if and what defects are formed. Further details can be found in Ref.\[7\].

3.2.1 Homotopy theory

Figure 11: Two loops $f(t)$ and $g(t)$ parametrized by $t$ that coincide at a point $a$.

Consider a set of loops on $M$ that pass through a point $a$ (Fig. 11). Parameterize the loops in the interval $0 \leq t \leq 1$ by a set of continuous mappings, $f(t)$, so that the beginning and ending of the mapping occur at the same point, $a$:

$$f(0) = a = f(1) \quad (28)$$

Two of these loops are considered homotopic to each other at a point $a$ if one of them can be deformed into the other by stretching, shrinking or ‘jiggling’, while still maintaining contact with $a$.

\footnote{An explanation of the mathematical nomenclature for describing topological spaces is given in Appendix A}
To show that two loops \( f(t) \) and \( g(t) \) are homotopic, a mapping \( h \) between the two loops is constructed, which is called the homotopy mapping. We introduce a variable \( s \) that parametrizes the mapping between \( h(s, t) \) and the loops \( f(t) \) and \( g(t) \). It remains to find a particular \( h(s, t) \) that is continuous for \( 0 \leq s \leq 1, 0 \leq t \leq 1 \). That is, we need to find \( h(s, t) \) such that

\[
\begin{align*}
    h(0, t) &= f(t) \\
    h(1, t) &= g(t)
\end{align*}
\]

We require that the mapping \( h(s, t) \) includes the point \( a \)

\[
h(s, 0) = h(s, 1) = a
\]

### 3.2.2 Homotopy classes

Let \( f(t) \) and \( g(t) \) be homotopic. In order to construct a homotopy, we need to compose a mapping that takes \( f(t) \) back to \( g(t) \). This outlines the symmetric nature of the homotopy mapping. In group theoretical terms homotopy is reflexive, symmetric and transitive, making it an equivalence relation. This outlines a simple manner into which different homotopic mappings can be classified – homotopic functions are thus split into homotopic classes.

The first homotopy group \( \pi_1(M) \) is also called the fundamental group of the manifold \( M \) at \( a \) because all groups \( \pi_1(M, a) \) are identical.

### 3.2.3 Kibble mechanism: Homotopic condition for defect formation

To generalize the first homotopy group to higher homotopies, a fundamental theorem will be stated (without proof) and then applied to a symmetry-breaking process. The upshot is that to determine the homotopy group of a symmetry breaking, we need not know both the high- and low-symmetry groups \( G \) and \( H \). Rather it is sufficient to know the topology of the vacuum manifold.

Let a simply-connected \( G \) be spontaneously broken to a subgroup \( H \). The vacuum manifold \( M \) is then given by the space of cosets \( H \subset G, M = G/H \).

Let the subgroup \( H \) have a component \( H_0 \) connected to the identity. The disconnected components of \( H \) can be labelled by the quotient group \( \pi_0(H) = H/H_0 \). This is isomorphic to the fundamental group of the coset space \( \pi_1(G/H) \), that is

\[
\pi_1(G/H) \cong \pi_0(H)
\]

---

3 The restriction of simply-connected group can be imposed by extending any (compact, Lie) group into a universal covering group.
Thus the condition as to whether or not defects will form is determined by the topology of the vacuum manifold. Consider the order parameter mapping \( \phi : A \to M \). The defect condition is then

\[
\pi_k(M) \neq 1
\]  

(33)

where \( \pi_k(M) \) is the \( k \)-th homotopy group of \( M \) and \( k \in \mathbb{R} \). To find the homotopy group \( \pi_k(M) \), the various classes of homotopy mappings from \( S^k \) to \( M \) are found. If \( M \) is some \( m \)-sphere, the \( \pi_k(S^k) \) is only non-trivial when \( k \geq m > 1 \). Considering the case for \( m = 1 \), the \( k \)-th homotopy \( \pi_k(S^k) \) is only non-trivial when \( k = 1 \). To classify defects, the unbroken symmetry group is all that is necessary, provided we started with a simply-connected group in the beginning. So in order to have a defect, a non-trivial group is needed in the first place.

3.3 SUMMARY

Topological defects are features that result from strict symmetry requirements relating to symmetry-breaking phase transitions. The Kibble mechanism gives the requirements for their formation using the field of homotopy theory. Firstly, it requires that the symmetry is spontaneously broken, that is, that the ground state is degenerate. The second requirement is that the symmetry change corresponds to a non-trivial homotopy group, whose key properties are described above. An advantage of using homotopy theory to study phase transitions is that it predicts, if a topological defect is formed, what the dimension of the resulting defect will be (monopole, vortex or domain wall) once the homotopy group and dimension of the system are known.
In the previous chapter the strict mathematical criteria were laid out for the formation of topological defects; central to these were the concepts of topology and ‘protectedness’. Here a related concept, that of geometric frustration – which leads to so-called geometric defects – is described and compared to topological defect formation. The distinction between the two is elucidated with simple examples and making use of symmetry.
4.1 TOPOLOGICAL DEFECTS AND GEOMETRIC KINKS

Topological defects form when the symmetry-breaking characteristics of the system induce a discontinuity in the ground state of the system. The formation of these defects are laid out by strict symmetry conditions using the Kibble criteria[?].

A somewhat more familiar term in condensed matter physics is geometric frustration. This describes how long range order can be prohibited from forming in some systems because of short-range constraints. The latter are often due to lattice constraints, magnetism, or bonding in a material. The term ‘frustration’ was first published in 1977 by Toulouse[?] and Villain[?], however P. W. Anderson is believed to have invented the term when he wrote “Frustration is the name of the game” on an Aspen blackboard. Examples of geometrical frustration in solid state physics include tiling of a plane with regular pentagons (related to the field of quasicrystals) and antiferromagnetic interactions on a triangular lattice.

An obvious connection exists between topological and geometric phenomena; both have a feature that preclude the system from reaching a homogeneous global minimum. In the case of topological defect formation, the order parameter has a ‘kink’ which can never be ironed-out, whereas geometric frustration also prevents the system from adopting long-range order whereby a ‘kink’ in the short-range order results.

However, these two descriptions are not equivalent; they describe different phenomena that are both caused by symmetry constraints in the phase transition. In both cases, the easiest explanation can be given by using mappings to topological spaces wherein the properties of the ‘kinks’ can be studied in a straightforward manner.

Here we outline a procedure for distinguishing between topological and geometric defects. Throughout the discussion, we will refer to the resulting ‘defects’ and ‘frustrated features’ as ‘kinks’ for simplicity. We first address the notion of topological defects in a condensed-matter system, reviewing the standard classification scheme via the Kibble mechanism and results from homotopy theory. Our discussion will refer to the simple examples in the previous chapter of classifying topological defects and the importance of topological spaces in their understanding. We then discuss geometric frustration by reference to known examples in condensed-matter physics. We review tools for understanding geometric frustration, and again use symmetry spaces to study the geometric kinks. This enables a direct comparison between topological defects and geometric frustration, clarifying the differences and similarities between these two concepts.

4.2 GEOMETRIC DEFECTS

4.2.1 Example: Pentagonal tiling

Firstly, we describe a simple geometric example which is of particular relevance to quasicrystals. We consider the tiling of a 2D plane
4.2 GEOMETRIC DEFECTS

Figure 12.: Pentagons cannot tile a 2D plane. The defects are removed when applied to a higher-dimensional space, forming a dodecahedron.

Figure 13.: Ising spins on a triangular lattice. If the spins have antiferromagnetic coupling, they cannot form a long-range ordering.

with regular polygons. For triangles, squares, hexagons, etc. this is straightforward. However, tiling the plane with regular pentagons is impossible without forming kinks called defects or excesses (Fig. 12). The former are formed when a gap remains between adjacent pentagons and the latter when there is an overlap. These kinks are called geometric defects, and are a result of the incompatibility of the local-ordering rule of regular pentagons with the 2D surface that it is tiling. Because of this frustration, pentagons cannot be used to tile a plane.

The local rule of pentagonal tiling can be used for a global tiling only if we move away from a 2D surface into three dimensions. In this case, the curvature of the space allows the pentagons to fit neatly together avoiding the formation of geometric defects and forming a "football", as shown in Fig. 12. This simple example contains the most relevant characteristics of geometric defects – a local constraint (regular pentagons) prevents long-range ordering from forming with the production of geometric defects. To restore the local order, one must change the global space on which the local ordering is applied, in our case moving from tiling a plane to a sphere.

Another example of geometric defects is the case of Ising spins on a triangular lattice, as depicted in Fig. 13, first studied by Wannier[?]. If each spin is to be antiferromagnetic to its neighbours then a problem arises. The total energy is independent of the orientation of the last spin, which gives rise to frustration, and the formation of a geometric
The antiferromagnetic coupling between the spins causes a $120^\circ$ spin structure to form in triangular lattices.

Indeed such frustration prevents the formation of long-range magnetic order. However, moving away from a simple Ising picture, which only allows for collinear spins, the local ordering can reach a compromise ordering which will remove the frustration and defects. This can occur by forming non-collinear spin structures in a variety of arrangements as shown in Fig. 14, where the interaction between each spin is antiferromagnetic.

**Example: Ising spins on a triangular lattice**

These examples of geometric defects highlight their main feature: a local ordering is incompatible with the global symmetry of the lattice and results in a defect or kink. The only way that the local order can be restored is by changing the global space/lattice, in the pentagon case this involves going from the plane to a sphere, and in the Ising triangle this involves non-collinear spin solutions. However, the new global space has the same topology as the initial space.

**4.3 The Distinction Between Topological and Geometric Defects**

Geometric defects are a more familiar concept and can be understood without resorting to mathematical tools like homotopy theory. However, to fully understand the divergence between topological defects and geometric defects, I will make use of the notion of symmetry spaces.

In the case of topological defects, it is the incompatibility of the initial symmetry group and the final symmetry group in a topological sense that results in the formation of defects. A discontinuity in the order parameter can only be removed by changing the topology of the underlying space (by the introduction of more holes, or twists), and not just the global space. Knowing both of these groups, one can predict precisely what types of defects will form (monopoles, vortices, etc.).

However, for geometric defects, the frustration resulting from the incompatibility of the local ordering rules with the lattice or global
symmetry in which it sits causes defects. To restore local order, the
global symmetry is changed to that of a higher symmetry group.

4.4 SUMMARY

Here we have summarized the concepts of topological defects and
geometric defects with simple examples illustrating their properties
and occurrence. Topological defects result from a change in the cor-
responding topology of symmetry groups as we go through a phase
transition. The incompatibility of the initial and final topological
spaces results in kinks or topological defects that cannot be removed.
However, geometric defects are caused by a mismatch between local
ordering rules following a phase transition and the space or lattice
in which it is defined. To restore the local ordering, a higher dimen-
sional symmetry must be used which removes the geometric defects.
Global symmetry changes can remove geometric defects, which is
not the case for those of a topological nature.
Jumping from the expanse of galactic scales to land in the laboratory might seem a gargantuan task. Common to both, however, is the concept of symmetry breaking and in particular the formation of topological defects. Here we discuss the formation of topological defects in multiferroic YMnO$_3$ whose ferroelectric behavior enables the direct imaging of these defects. We also show how this material can be used to study the Kibble-Zurek model of topological defect formation in the early universe and give quantitative insights on the number of domains formed during the spontaneous symmetry breaking phase transition. We provide the first confirmation of Kibble-Zurek scaling in a homogenous quench in a crystal, and also uncover a surprising ‘beyond Kibble-Zurek’ behaviour, and discuss this in the context of the material’s properties.
5.1 BACKGROUND OF THE KIBBLE-ZUREK MECHANISM

5.1.1 Introduction

As described in Chapter 3, topological defects result from a phase transition that causes spontaneous symmetry breaking with a non-trivial homotopy group. In real physical systems, the phase transition proceeds at a finite rate, requiring a study of the dynamics of the system to put a quantitative estimate on the number of defects that form. In the early universe, or indeed in condensed-matter experiments, traversing a spontaneous-symmetry-breaking phase transition results in a random choice of the possible available ground states. For slower cooling across the transition, the system has more time to propagate its choice of ground state causing large regions with the same choice and a large separation between defects connecting different choices. This is the essence of the Kibble-Zurek mechanism (KZM): the number of defects formed during such a phase transition will depend on the quench rate through the transition.

5.1.2 Derivation of the Kibble-Zurek equations

To put the number of topological defects formed on a quantitative footing we use Zurek’s approach which relies on the notion of competing timescales: The first relevant timescale is the time it takes for one region of the system to communicate its choice of vacuum state with another. The second is the quench time $\tau_q$ that the system spends cooling through the phase transition. This time becomes divergently long towards the critical temperature, a phenomenon termed “critical slowing down”.

The size of the domains is set at the temperature $T_C + \Delta T_f$ where the communication distance across which information can be transferred during the progressing phase transition becomes equal to the correlation length $\xi(T)$ (Fig. 3). While the correlation length $\xi(T)$ continues to diverge as the temperature further approaches $T_C$, the communication distance set by the speed of light/sound remains unchanged, and the system is unable to adapt to its increase. As a consequence a “freeze-out” occurs in the temperature interval between $T_C + \Delta T_f$ and $T_C - \Delta T_f$: The size of the correlated regions is unable to increase and so the domain size is fixed at the value $\xi(T_C + \Delta T_f)$ (Fig. 15). For fast cooling through the transition, the distance over which information can be transferred during the transition is small, and becomes equal to the correlation length at small values of $\xi(T)$. Therefore freeze-out occurs when the domain size is small, and consequently the number of topological defects is large. In contrast, for slow cooling, the distance for information transfer is large, and does not become equal to $\xi(T)$ until close to the phase transition temperature, where $\xi(T)$ is large. In this case large domains, with fewer topological defects, form.

Here we summarize the derivation of the density of topological defects as a function of quench rate through the phase transition within the Kibble-Zurek mechanism. For a detailed derivation we
Figure 15: Domain formation in the Kibble-Zurek scenario. Above \( T_C \) fluctuating regions of lateral extension \( d \) with uniform orientation of the emerging order parameter occur (fuzzy patches). At high temperature \( (T_\gamma > T_C + \Delta T_f) \) the size of the correlated regions is determined by the correlation length (purple curve). At temperature \( T = T_C + \Delta T_f \) a freeze-out of the lateral extension \( d \) begins. Below the freeze-out temperature, fluctuations occur but the lateral extension of the fluctuating regions can no longer follow the diverging correlation length while the system continues to cool. The size of the fluctuation regions in this range, for example at \( T_\gamma \) remains set by the correlation length at the freeze-out temperature, \( \xi(T_C + \Delta T_f) \), and corresponds to the “communication length” which is the distance that information can propagate during the time in which the system cools from \( T_C + \Delta T_f \) to \( T_C - \Delta T_f \). Below \( T_C - \Delta T_f \) stable domains of the lateral extension \( \xi(T_C + \Delta T_f) \) form (areas confined by black lines). From Griffin et al.\cite{Griffin}. Copyright (2012) by the American Physical Society. Reproduced with permission.
recommend particularly Ref.[?]. First, we use critical scaling: As the system approaches $T_C$, the correlation length, $\xi$, and relaxation time, $\tau$, diverge as

$$\xi(T) = \xi_0 \left| 1 - \frac{T}{T_C} \right|^{-\nu}$$

$$\tau(T) = \tau_0 \left| 1 - \frac{T}{T_C} \right|^{-\mu}$$

where $\xi_0$ is the zero-temperature correlation length and $\tau_0$ is the zero-temperature time, which is equal to $\xi_0$ divided by the speed of information transfer in the system. Both $\xi_0$ and $\tau_0$ are system-dependent quantities. $\nu$ and $\mu$ are critical exponents that are determined by the universality class of the phase transition, that is its general behaviour as determined by the symmetry properties of the phase transition, irrespective of the material properties of the specific system.

Assuming that the temperature varies linearly with time near the phase transition, and taking $t = 0$ at $T = T_C$, it is clear that $T = T_C + t \times r_q$, where $r_q$ is the cooling rate. Rearranging this expression yields

$$\left| 1 - \frac{T}{T_C} \right| = \frac{r_q}{T_C} t = \frac{t}{\tau_q}$$

where $\tau_q = \frac{T_C}{r_q}$ is called the “quench time”.

The speed at which information is transferred in the material is then given by the characteristic velocity,

$$c(T) = \frac{\xi(T)}{\tau(T)} = \frac{\xi_0}{\tau_0} \left| 1 - \frac{T}{T_C} \right|^{\mu - \nu}$$

and the corresponding distance over which information can propagate in time $t$ is

$$\int_0^t c \left( T \left( t' \right) \right) dt' = \frac{\xi_0}{\tau_0} \int_0^t \left( \frac{t'}{\tau_q} \right)^{\mu - \nu} dt'$$

$$= \frac{1}{1 + \mu - \nu} \frac{\xi_0}{\tau_0} \tau_q \left| 1 - \frac{T}{T_C} \right|^{1 + \mu - \nu}$$

where in the last step we have substituted $t = \left| 1 - \frac{T}{T_C} \right| \tau_q$.

Equating the distance over which information can propagate to the correlation length yields an expression for the freeze-in temperature, $T_f$:

$$\frac{1}{1 + \mu - \nu} \frac{\xi_0}{\tau_0} \tau_q \left| 1 - \frac{T_f}{T_C} \right|^{1 + \mu - \nu} = \xi_0 \left| 1 - \frac{T_f}{T_C} \right|^{-\nu}$$

5.1 BACKGROUND OF THE KIBBLE-ZUREK MECHANISM
so
\[ 1 - \frac{T_f}{T_C} = \left( 1 + \mu - \nu \right)^\frac{1}{\tau q}. \] (39)

At temperature $T_f$, the domain sizes are frozen in with a characteristic length scale given by the information propagation distance (which is equal to the correlation length) at the freeze-in temperature:
\[ \xi_f = \xi_0 \left( 1 + \mu - \nu \right)^\frac{\nu}{\tau q}. \] (40)

Formally, this corresponds to the length-scale of the vortex “strings” or intersections, that is the three-dimensional continuation of the vortex cores through the bulk of the sample. The number of vortex intersections per unit area, $n$, is then approximately equal to the length of vortices per unit volume, $\frac{1}{\xi_f^2}$, giving
\[ n \approx \frac{1}{\xi_f^2} \left( \frac{\tau_0}{\tau q} \right)^\frac{2\nu}{\tau q}. \] (41)

Because the phase transition occurs at a finite rate, the system is forced to make a choice of ground state resulting in different regions having different ground states. Up until the point at which this choice is made – at the freeze-out temperature $T_F$ – the system evolves adiabatically and obeys critical scaling. However, the KZM postulates that the non-equilibrium dynamics, that is, those below $T_F$, are governed by the equilibrium-scaling behavior of the system. This is known as the ‘adiabatic-impulse approximation’. It should be noted, however, that it does not suggest that the system ceases to evolve at $T_F$; rather that the order parameter will no longer be able to assume its equilibrium value as it is ‘frozen’ into the value at which the system ceased to evolve adiabatically.

5.1.3 Summary of recent experiments

Verification of the KZM in the laboratory requires two observations: firstly that topological defects form during a quench, and secondly, that the non-equilibrium behaviour is determined by the equilibrium scaling dynamics of Eqn. [41]. The latter is often difficult to verify experimentally since the scaling exponent is usually very small requiring a large range of quenches to properly investigate the scaling. Furthermore, the rapid quenches required for such a large range often induce thermal inhomogeneities in the samples, substantially complicating the interpretation of results.

Attempts to demonstrate Kibble-Zurek scaling in condensed-matter systems to date have proved challenging, and the “ideal Kibble-Zurek system” has remained elusive. Zurek’s original paper[?] discussed the analogue between cosmic strings and the vortex cores formed in a quench-induced phase transition from normal-state to superfluid $^4$He. However the corresponding experiment[?, ?] yielded large de-
5.1 Background of the Kibble-Zurek Mechanism

Figure 16.: An annulus contains a superfluid with an average domain size, $\xi$, much less than the circumference of the container $C = 2\pi R$. This will result in $N \sim \frac{C}{\xi}$ domains with a different value of phase.

viations from the predicted behavior, probably because of thermal effects[?]. In $^3$He the symmetry breaking is closer to that postulated for the early universe[? , ?], but the density of topological defects can only be inferred indirectly and many assumptions must be made to compare with predictions. No flux-line formation at all was observed in experiments on high-$T_C$ superconducting thin films[?]. Perhaps the most promising candidates to date are liquid crystals, in which successful studies of defect dynamics have been performed[?]. In addition, the diffraction pattern formation in nonlinear-optic experiments was shown to exhibit a scaling law [?], but strong interactions between the defects continue to cause difficulties. In the following we give a short survey of the most recent and conclusive KZM experiments with several thorough reviews on the multitude of KZM experiments given in [? , ? , ?]. We omit discussion of the substantial literature on numerical studies of the KZM [? , ? , ?].

Random phase walks in annular superfluid containers

These experiments were based on Zurek’s original suggestion of topological trapping of nontrivial solutions in superfluids[?]. Consider an annulus containing a substance which undergoes a phase transition to a superfluid under some external influence (temperature or applied field for example). The experimental setup is such that the circumference of the annulus, $C$, is greater than the average-domain size, $\xi$, and the annular width is negligible so we can treat the loop as being one-dimensional as shown in Fig.16. When the substance undergoes the phase transition to the superfluid state, different regions around the circumference of the annulus will assume different values of the superfluid wavefunction’s phase, $\theta$. This will result in

$$N \sim \frac{C}{\xi}$$

(42)
regions with different choice of \( \theta \). Because of the resulting mismatch between the phase as the loop is circumnavigated, we find an average net winding number of

\[
W \simeq \frac{\theta}{2\pi} \simeq \frac{\sqrt{N}}{2\pi} \simeq \sqrt{\frac{C}{2\pi \xi}}.
\] (43)

This random phase assignment resulting from the causal disconnection between different areas around the loop was tested in a superconducting ring comprising several superconducting ‘weak links’. These were then recombined after the phase transition to form a complete superconducting loop. The experiment confirmed the first aspect of the KZM: several flux quanta were trapped circumnavigating the loop verifying the formation of topologically-protected features due to communication bounds. However, due to the nature of the experiment, the quenching and thus the scaling law behavior cannot be tested since the size of the domains was fixed by the distance between the weak links. Hence, the domain size was constant and did not depend on the quench rate.

**Superconducting loops**

Building on a similar idea, experiments were proposed for annular-shaped superconductors in which, in contrast to the case of superfluids, \( C \ll \xi \). In the limit \( C \ll \xi \), winding numbers other than \(-1, 0, 1\) are not expected, invalidating the random phase summation given by Eqn. 43. A modification to the scaling law was proposed for this scenario with the scaling exponent \( \sigma \sim 0.25 \).

Monaco et al.[?] performed a quench of composite Josephson tunnel junctions comprising of Nb-Al/Al\(_{23}\)/Nb. A scaling relation was found between the probability to trap a single fluxon during the phase transition and the quench time, with \( \sigma \sim 0.5 \). This value is twice the theoretically-predicted exponent. Additional experiments on superconducting loops gave \( \sigma = 0.62 \pm 0.15 \)[?], also significantly different from the theoretical prediction.

Two resolutions have been proposed to account for the factor of \( \simeq 2 \) between the theoretical scaling and that obtained in experiment. The first attributes the divergence to extrinsic factors such as the proximity effect in superconductors and fabrication. More recently, a second proposal by Zurek[?] reevaluates the derivation of the scaling law, and in particular the distribution of winding numbers obtained in the small circumference limit, \( C \ll \xi \)[?]. It remains to be determined which of these, if either, account for the observed discrepancy between theory and experiment in annular geometries.

**Bose-Einstein condensates**

Recent experiments using Bose-Einstein condensation (BEC) validated Kibble-Zurek scaling for quenching of ultracold sodium atoms. The possible low-temperature choices for the condensate wavefunction
lie on a circle in the complex plane. Upon undergoing the phase transition, different areas of the system acquire a different condensate phase. As two of these regions merge, a defect – in the form of a soliton – is formed. In these experiments extremely accurate control of temperature and cooling rate could be achieved and the number of solitons created was found to follow the expected scaling law for BEC.

A crucial difference exists between these experiments and the formulation of the KZM. Here the BEC solitons are not topologically protected, and can in fact disappear with an unwinding of the condensate wavefunction. In fact, the observed longevity of the quench-created solitons was a surprising finding as the majority were expected to decay before detection. Regardless, this experiment provides clear validation of the second prediction of the KZM: equilibrium scaling can predict the number of defects formed in systems undergoing non-equilibrium dynamics.

5.2 Symmetry and Physical Properties of Hexagonal Manganites

We now propose a class of systems – multiferroic hexagonal manganites – as the ideal testbed for both aspects of the KZM. We will theoretically describe the formation of topologically-protected vortices that can be directly imaged experimentally. We will then derive the appropriate scaling laws for these systems and perform a thorough comparison with experiments. Much of this work is described in Ref. [?].

First we describe the properties of RMnO$_3$ that are relevant for testing the Kibble-Zurek mechanism, particularly the symmetry properties of the phase transition. The structure of RMnO$_3$ consists of planes of MnO$_5$ trigonal bipyramids separated by planes of $R$ ions which form a hexagonal mesh (Fig. 17(a))[?]. In the high-temperature paraelectric phase, the space group is centrosymmetric $P6_3/mmc$. At $T_C \sim 1400$ K (the exact value depends on the $R$ ion) a spontaneous symmetry breaking occurs, with the condensation of primarily two phonon modes with distinct irreducible representations of the high-symmetry structure[?, ?].

First, a mode of $K_3$ symmetry condenses, which involves a trimerizing tilt of the trigonal bipyramids and is the primary order parameter (Fig. 17(b)). Three choices of the $K_3$ orientation yield minimum energy states, and the tilt can be in the “in” or “out” direction, so six trimerization domains are formed; these have been shown using dark field transmission electron microscopy to meet at vortex cores[?]. Importantly (and unusually), while this mode lowers the symmetry to that of a polar space group, it carries no net polarization, as any net local polarity vanishes macroscopically due to the non-zero mode wave vector.

A secondary mode of $\Gamma_-$ symmetry (referring to the parent space group), which does not further lower the symmetry, provides the ferroelectric polarization (Fig. 17(c)). The orientation of this secondary ferroelectric polarization is set by the in- or out- tilt of the $K_3$ mode and so it does not result in additional domains, however it is essential
Figure 17: (a) High-symmetry $P6_3/mmc$ structure of $R\text{MnO}_3$ before the onset of trimerization. (b) Action of the $K_3$ trimerization mode on the $R$ ions and $\text{MnO}_5$ trigonal bipyramids. The insets below the main structure are to emphasize that outward trimerization results in a downward shift of the corresponding $R$ ion, whereas inward trimerization results in an upward shift. (c) The subsequent additional displacements of the $R$ ions (blue arrows) in the $\Gamma_2^-$ mode provide the ferroelectricity. Note that once the orientation of the trimerization mode is set, the spontaneous polarization can emerge in only one direction. (d) Typical domain structure measured using piezoforce microscopy. The black and white regions correspond to opposite orientations of the ferroelectric polarization along the $z$ axis. Note that the domain structure is isotropic, in spite of the layered crystal structure. From Griffin et al.[?]. Copyright (2012) by the American Physical Society. Reproduced with permission.
for our experiments as it allows the straightforward imaging of the domain structure using piezoresponse force microscopy (PFM). Indeed PFM measurements reveal that domains of alternating polarization are locked to the trimerization domains around vortex cores[17, 18] yielding appealing six-fold patterns (Fig. 7(d)). Electric-field poling experiments have shown that the vortex cores are protected in the sense that they cannot be annihilated or driven out of the system by an electric field[17, 18]. Surprisingly, the domain structure and density of these topological defects when viewed from the side of the sample is similar to that viewed from the top in spite of the layered crystal structure and uniaxial ferroelectricity[17] (Fig. 7(d)). This absence of anisotropy in the domain structure allows for straightforward determination of the defect densities from two-dimensional top-view scans of their areal density, rather than requiring a complex three-dimensional analysis.

First-principles calculations[17] and Landau Theory analysis[18] have shown that for small magnitudes of the trimerizing $K_3$ mode, the polar mode appears only as a third-order term, and so the magnitude of the ferroelectric polarization just below $T_C$ is vanishingly small. This is important for our discussion for two reasons: First, the formation of the domain structure at $T_C$ is not influenced by the system’s attempts to minimize the depolarizing field from the ferroelectric polarization. Strong evidence for this is given by the large numbers of electrostatically unfavorable head-to-head and tail-to-tail domain walls that form in RMnO$_3$, but rarely occur in conventional ferroelectrics[17]. Second, first-principles calculations show that the energy lowering provided by the condensation of the $K_3$ mode is independent of the angle of the tilt until the polar mode subsequently develops[17]. This means that the potential below the phase transition temperature is given by the continuous “Mexican hat” form (Fig. 13). The discrete nature of the lattice does not manifest until lower temperatures when the domain structure is already determined. As a result we can use the mathematics of continuous symmetries which are usually assumed in the Kibble-Zurek mechanism. In this language, the full rotational symmetry is broken when the polyhedra tilt in the $2\pi$ range of angles, resulting in a $U(1)$ vacuum. We note also that the Landau free energy derived in Ref. [17] has a branch cut in the trimerization angle that gives a signature of topological protection if the angle rotates through the branch cut when traced round the vortex core.

For larger magnitudes of the $K_3$ mode, obtained upon temperature decrease, a cross-over to linear coupling with the polar $\Gamma_2^-$ mode occurs and the polarization becomes measurably large. This lifts the degeneracy with angle of the $K_3$ mode and fixes the polyhedra into discrete tilt angles of $0, 2\pi/3$ or $4\pi/3$, described by $Z_3$ symmetry. The additional degeneracy provided by the direction (“in” or “out”) of the polyhedral tilting gives an additional $Z_2$ symmetry reduction, resulting in $Z_2 \times Z_3 \cong Z_6$. It is an open experimental question whether the onset of the $\Gamma_2^-$ mode, which is observed $\sim 300$ K below $T_C$ is an “emergence” or an additional isosymmetric phase transition[17, 18].

5.2 SYMMETRY AND PHYSICAL PROPERTIES OF HEXAGONAL MANGANITES
Figure 18.: Mexican-hat potential energy surface of the hexagonal manganites. At high energy (the peak of the hat) the energy is independent of the angle of trimerization, and the system has $U(1)$ symmetry. At lower energy (in the brim of the hat), six of the trimerization angles become favorable (white circles), and the symmetry reduces to the six-fold discrete symmetry described by $\mathbb{Z}_6$. From Griffin et al. [?]. Copyright (2012) by the American Physical Society. Reproduced with permission.

5.3 Kibble-Zurek Mechanism for the Hexagonal Manganites

In this section we first show that the symmetry of $R\text{MnO}_3$ results in topologically protected vortex cores as described by the Kibble mechanism. We then analyze the vortex cores using the Zurek scenario to determine the density of topological defects that should be produced as a function of the cooling rate through the phase transition. We use first-principles density-functional theory to evaluate the relevant parameters, and show that our predictions are in agreement with literature data.

5.3.1 Kibble mechanism and the formation of topological defects.

The requirements for the formation of topological defects at a phase transition within the Kibble mechanism as laid out in Chapter 3 are (i) a spontaneous symmetry breaking and (ii) a change in symmetry across the phase transition that corresponds to a non-trivial homotopy group. The trimerization transition in $R\text{MnO}_3$ clearly fulfills the first condition; next we show that it also fulfills the second.

As discussed earlier, in the temperature range just below the phase transition, $R\text{MnO}_3$ exhibits a continuous symmetry; this allows us to use the methods and results of homotopy theory – which are developed for continuous symmetry groups – to assess the topology of $R\text{MnO}_3$. It is established within homotopy theory that the symmetry characteristics of the order parameter, in our case $U(1)$, can be used to assess the topological characteristics of a phase transition. To make the assessment, the order parameter symmetry is first mapped onto an $n$-dimensional sphere. In the case of the $U(1)$ sym-
metry, this is a one-dimensional circle, \( S^1 \). Next a function called the homotopy group, \( \pi_k \), which describes the topological nature of the order parameter symmetry is defined. If \( \pi_k \) differs from the identity, then it is non-trivial and topological defects are formed. It has been known since the 1960’s[?] that \( \pi_1(S^1) \) is indeed non-trivial and in fact produces one-dimensional topological singularities, called strings or vortex cores[?]. Therefore the vortex cores in \( \text{RMnO}_3 \) are mathematically topologically protected, in concordance with their physical topological protection – their resistance to annihilation by an electric field – that we discussed earlier[?]. We note also that within the Kibble mechanism the topological defects are remnants of the parent phase trapped within the lower symmetry phase. For \( \text{RMnO}_3 \) this implies that the high-symmetry paraelectric phase is preserved at the meeting point of the six domains defining a vortex core.

5.3.2  \textit{Zurek scenario for RMnO}_3

Within the Zurek scenario, the density of topological defects formed during a spontaneous symmetry breaking phase transition described by the Kibble mechanism follows a power-law dependence on the rate at which the transition is crossed[?]. In this section we first relate the material properties of \( \text{RMnO}_3 \) to the parameters in the Zurek scenario. We then evaluate their magnitudes to calculate quantitatively the temperature dependence of the defect formation within the Kibble-Zurek mechanism.

To apply the linear Zurek scaling law given in Eq. (41) to the hexagonal manganites we next identify the relevant time- and length-scales in the system, and evaluate their magnitudes. Our electronic structure calculations were performed using density functional theory within the local density plus Hubbard-\( U \) approximation following the Liechtenstein approach[?], with the double-counting corrections treated in the fully localized limit. Following previous literature studies[?], we set the LDA+\( U \) parameters on the Mn \( 3d \) orbitals to \( U = 8 \) and \( J = 0.88 \) eV respectively and enforced an A-type antiferromagnetic ordering. We used the projector-augmented wave method for core-valence partitioning[?], which significantly reduces the required plane-wave energy cutoff, and carefully tested the convergence of plane-wave cutoff and k-point sampling.

The zero-temperature correlation length, \( \xi_0 \), is usually equated with the zero-temperature domain wall width in ferroelectrics. In order to extract this value we performed density functional calculations within the LDA+\( U \) method using the VASP code [?, ?]. We constructed supercells containing two 180° domain walls and in turn 120, 180, 240 and 300 atoms. We fixed the lattice constants of the supercells to those of the corresponding relaxed single-domain supercells, and then optimized the internal positions until the forces acting on all atoms converged to less than 0.01 eV/Å respectively. We initialized a different trimerization phase and ferroelectric orientation within adjacent domains, and subsequently performed full relaxations on the structures; in all cases the system remained in the metastable multi-domain state. For all supercell sizes, we found that the struc-
tural phase defined by either the tilt of the MnO bipyramids or the direction of off-centering of the Y ions changes abruptly at the domain walls, indicating an effective domain wall width close to zero. This is consistent with a recent experimental electron microscopy study[?], and sets an upper limit on $\xi_0$ of $\sim 1$ Å.

To calculate the characteristic timescale of the system, $\tau_0 = \frac{\xi_0}{s}$, we require $s$, which is the speed at which the system communicates the lattice distortion as it passes through the phase transition. For solid-state systems, $s$ is given by the speed of sound. To calculate the speed of sound at zero Kelvin we used the ABINIT[?] software package[?, ?] to optimize the structure of a 10-atom unit cell, then calculated the full phonon band structure using frozen-phonon techniques. A supercell was constructed with doubling and trebling in each of the directions required to sample the first Brillouin zone, then symmetry-distinct displacements were made to construct the full matrix of interatomic force constants. The dynamical matrix was diagonalized along each of the high symmetry lines shown in the phonon band structure using Fourier interpolation[?, ?]. The speed of sound was then extracted from the calculated phonon band structure by fitting the acoustic branch with a polynomial, then evaluating the group velocity 

$$v_g = \frac{\partial \omega}{\partial k} \bigg|_{k=0} .$$

The relevant velocity for our Kibble-Zurek fit is the doubly degenerate branch with the atoms displacing in plane and the wavevector propagating in plane. For this branch we obtained $v_g = 640$ m.s$^{-1}$.

For comparison with quenching experiments we also need the Curie temperature, $T_C$, which relates $\tau_q$ to the cooling rate, $r_q$ through $r_q = \frac{T_C}{\tau_Q}$. This is known experimentally to be $\sim 1400$ K, with the exact number depending on the $R$ ion.

Finally, we extracted the critical exponents by identifying that, as in the case of the superfluid transition in $^4$He, the $RMnO_3$ transition belongs to the universality class denoted as the 3D XY model. The values of the critical exponents for this universality class have been calculated using Monte Carlo simulations[?] to be $\nu = 0.6717$ and $\mu = 1.3132$, giving a Kibble-Zurek scaling exponent of $\frac{2\nu}{1+\mu} \approx 0.29$. Taking the values introduced so far, with our upper limit for $\xi_0$, we find that domains of 5$\mu$m width should be formed for a quench time of $\tau_q \sim 40$ min (corresponding to a cooling rate of $\sim 0.5$ K/s), and domains of 40 $\mu$m with a quench time of around one month (cooling rate $\sim 1.5$ K/hour). These rates are calculated allowing for the 10 K window around the phase transition. These are readily experimentally accessible cooling rates.

In Fig. 5(d) we compare our calculated scaling behavior with recently reported vortex densities measured as a function of cooling rate in ErMnO$_3$ (red circles)[?]. We obtain the best match with a value of zero-temperature correlation length of 0.06 Å (red line), consistent with the approximately zero domain wall width obtained in our density functional calculations. The agreement in scaling behav-
Figure 19: (a) to (c) Distribution of ferroelectric domains in \( z \)-oriented YMnO\(_3\) samples after annealing cycles at different cooling rates. The images are obtained using PFM on an area of \( 30 \times 30 \ \mu m^2 \) and reveal a striking "anti-Kibble-Zurek" behavior with higher cooling rates leading to larger domains. (d) Areal vortex core density as a function of cooling rate for slow cooling (red triangles, Ref.[?]) and fast cooling (blue circles, Ref.[?]). Note the turnover in the cooling-rate dependence of the vortex-core density occurring between rates of 0.3 and 3 K/min. The red solid line is the result of our \textit{ab initio} application of the Kibble-Zurek scenario with parameters from first-principles calculations. From Griffin \textit{et al.}[^?]. Copyright (2012) by the American Physical Society. Reproduced with permission.
ior between the experiment and the Kibble-Zurek prediction is clear, with the scaling exponent in particular matching well the theoretical prediction.

We thus find a unique situation in RMnO$_3$. Topologically, it is a model system for the experimental verification of the Kibble-Zurek mechanism. In the temperature range where the Kibble-Zurek mechanism is expected to govern the formation of domains and the distribution of vortex-core singularities, the unwanted ferroelectric polarization which could influence domain formation is effectively absent. However, at room temperature the coupling of the distortive order parameter to the now finite ferroelectric polarization allows straightforward imaging of the topology and vortices via spatially resolved measurements of the ferroelectric domain structure. And finally, a distinguishable range of domain sizes and hence defect densities is obtained for an experimentally accessible range of cooling rates through the primary distortive phase transition at $T_C$.

### 5.4 BEYOND THE KIBBLE-ZUREK LIMIT

The Kibble-Zurek mechanism applies only to the regime in which the system has time to respond adiabatically to the cooling until the freeze-out temperature, $T_C + \Delta T_f$ is reached. For faster quenching, it is expected that the Kibble-Zurek mechanism should break down and be replaced by a dynamics that is largely unknown. [? , ? , ? , ?] Therefore in the final part of this work, quenching experiments were performed by Martin Lilienblum (ETH) and Prof. Manfred Fiebig (ETH) at rates more rapid than those explored in Ref. [?] to investigate whether Kibble-Zurek behavior continues, or whether an evolution out of the Kibble-Zurek regime occurs.

#### 5.4.1 Experiments by Lilienblum et al.

For the experiment YMnO$_3$ was chosen rather than the ErMnO$_3$ that was used in Ref. [?] because of the greater thickness of the YMnO$_3$ samples at hand. Since the domain formation at the surface may be different from the bulk or affected by surface effects during the annealing, special care was taken to image the true bulk domain structure in the subsequent PFM measurements. Therefore the samples were thinned down by 5-10 $\mu$m using Al$_2$O$_3$ and polished chemically-mechanically. In the last step the ferroelectric domain structure was imaged using PFM [? , ?]. The area density of vortices was extracted from the PFM images by an unfortunate graduate student.

First the samples were cooled at rates matching the fastest quenches of Ref. [?] – 0.3 and 3 K/min – to verify that we obtain a comparable density of defects in these experiments. The domain structure resulting from quenching with 3 K/min is shown in Fig. 19(a). Including an additional quenching of the same sample with 3 K/min an averaged vortex density of $0.60 \pm 0.23 \mu m^{-2}$ was obtained which matches remarkably well with the data of Ref. [?] and lies on our predicted Kibble-Zurek scaling curve (two left-most blue points of Fig. 19(d)). This agreement between the vortex densities formed in
ErMnO$_3$ and YMnO$_3$ when quenched at the same rates confirms the independence of the vortex core density to the choice of $R$. Subsequently the same samples were quenched at higher cooling rates of 195 and 1360 K/min resulting in the domain structures shown in Fig. 19b) and (c), respectively. The slower cooling rate was achieved by temperature control in a furnace, the latter by removing the sample from a high-temperature furnace and allowing it to cool to room temperature. Surprisingly an increase in the cooling rate leads to a lowering of the density of vortex cores and thus to larger domains. For the fastest quenching the vortex density is one order of magnitude smaller than for quenching at 3 K/min (Fig 19d). This behavior in the fast-cooling regime may be denoted as “anti-Kibble-Zurek” behavior, since it is opposite to the prediction of the standard Kibble-Zurek mechanism present in the slow cooling regime. The connection between these two regimes is given by a crossover transition at \(\sim 1\) K/min. This crossover point corresponds to a correlation length (and hence a crossover domain size) of \(\sim 2.2\ \mu m\), and a relaxation time of \(\sim 4.1 \times 10^{-4}\) s, with a characteristic information transfer velocity of \(\sim 5.4 \times 10^{-3}\) m/s, considerably reduced from the speed of sound by the critical slowing down.

We emphasize that the observed behaviour is highly reproducible: the measurements were repeated on YMnO$_3$ samples grown in different batches, and it was verified that there are no cumulative effects in consecutive annealing cycles. We therefore conclude that these results suggest an evolution out of the Kibble-Zurek regime at a cooling rate of \(\sim 1\) K/min in the hexagonal manganites.

5.4.2 Possible origins of the Kibble-Zurek/“Anti-Kibble-Zurek” crossover

A number of possible deviations from Kibble-Zurek behavior have been discussed in the literature, but none of them are consistent with our measurements. Here we outline the most likely scenarios with reference to the experimental results.

**Vortex-antivortex annihilation**

Zurek\cite{Zurek1993} showed that vortex–anti-vortex annihilation becomes significant at fast quench rates where domains are smaller and topological defects are closer together. Such vortex–anti-vortex annihilation causes a leveling off of the rate at which the density of vortex cores increases with cooling rate, but not the decrease in density that we observe.

**Kosterlitz-Thouless transition**

In Ref.[?] it was suggested that the observed production of defect–anti-defect pairs could be the result of a Kosterlitz-Thouless transition\cite{Kosterlitz1973}, in which vortex–anti-vortex pairs are formed above the transition temperature and annihilate as the system is cooled. As a result, more vortex cores survive during a fast quench when the pairs do not
have time to annihilate. This is the opposite of our observed fast-quenching behavior. A rigorous theoretical treatment of defect formation in a Kosterlitz-Thouless transition reveals a critical slowing down that is described, not by a simple scaling critical exponent, but rather by a more complex function of the reduced temperature. The result of this would be a much more complicated dependence of the number of defects on the quench time. In addition, a Kosterlitz-Thouless system would show a dramatic change in the density of vortices after repeated annealing cycles as well as a dependence on the temperature at which the quench begins, neither of which we observe.

Nonlinear quench

One possibility for the deviation from ideal Kibble-Zurek behaviour is that, at fast quenching rates, our quenching is non-linear, rather than following the linear form assumed in the Kibble-Zurek model. The theoretical effect of nonlinearity in the quench rate on the density of defects has been calculated to yield a modified scaling law:

\[
\frac{T - T_C}{T_C} = \left( \frac{t}{t_q} \right)^\alpha
\]

(\(\alpha > 0\)). This yields a new, \(\alpha\)-dependent scaling law. In our quenching experiment we have exponential cooling, but since the correction to the linear temperature decrease across the phase transition is \(\leq 2.5\%\) the deviation of \(\alpha\) from 1 is negligible and cannot explain our observed anti-Kibble-Zurek behaviour.

Extrinsic effects

A possible extrinsic influence on the domain structure could be differences in chemical-defect concentration caused by the different cooling rates, such as off-stoichiometry, anti-site formation, or charge screening at the domain walls. To test for this possibility, the samples were heated to within 2% of the the transition temperature, and annealed at this temperature for six hours under the conditions described above. No changes in the domain structure were observed on heating until 1270 K (just below \(T_C\)), at which point minor isolated domain wall movements, and, once, the formation of a vortex–anti-vortex pair were observed. On heating to 1320 K (just above \(T_C\)), a completely new, but statistically identical domain pattern was obtained. These data and the aforementioned reproducibility of our data points in Fig. 19 show that chemical drift effects do not play a role.

Beyond-equilibrium dynamics

We conclude therefore, that the most likely origin of the transition out of the Kibble-Zurek regime in RMnO$_3$ is the breakdown of the assumption that the system is able to respond adiabatically to the cooling at high temperatures, above the freeze-out temperature \(T_C +\)
\(\Delta T_f\). Our observed behavior in the fast-cooling regime – slower cooling leading to a larger number of smaller domains – is of course reminiscent of nucleation-dominated behavior, with an activation energy for formation of the low symmetry phase from the high symmetry phase. Nucleation-dominated phase transitions show characteristic first-order behavior, and a longer time spent at the transition allows a larger number of smaller domains to nucleate. We note that at the freeze-out temperature corresponding to the crossover quench rate, the order parameter for the trimerization, \(\eta = \left(\frac{T - T_c}{T_c}\right)^\beta\), has already reached 0.5% of its saturation value, taking the experimental value of \(\beta = 0.29\)?. It is possible that this provides a sufficient discontinuity from the zero value to induce a first-order response. An alternative scenario is the fluctuation-induced first-order behaviour proposed for prototypical second-order phase transitions such as the normal-to-superconducting transition and for the nematic-smectic transition in liquid crystals?, both of which belong to the same universality class – the 3D XY model – as the hexagonal manganites. Such an induced-first-order transition could also explain the current controversy regarding the order of the trimerization transition in the hexagonal manganites, with most experiments showing second-order behavior, but occasional reports of first-order characteristics.

5.5 SUMMARY AND OPEN QUESTIONS

In summary, we have shown that the multiferroic hexagonal manganites, RMnO\(_3\), are model systems for testing the Kibble-Zurek scenario. Mathematically, they fulfil the symmetry requirements for the formation of topological defects, and practically, the defects are readily detectable, the quench rate can be varied over a wide range of relevant timescales, and extrinsic factors that might influence the phase transition behavior are absent. Our quantitative calculations of topological defect density as a function of cooling rate using the conventional Kibble-Zurek model and parameters obtained using density functional theory, agree with literature data in the slow cooling limit where the conventional Kibble-Zurek mechanism is applicable. Our measurements of defect density at fast cooling rates, however, reveal a surprising, apparently ”anti-Kibble-Zurek” behavior in which faster cooling yields lower defect densities, reminiscent of a nucleation-dominated phase transition.
Spontaneous symmetry breaking is ubiquitous in physics; from mass generation via the Higgs mechanism in the Standard Model to phase choice of the condensate wavefunction in superconductivity. In this chapter we describe and explain the first chemical manipulation of spontaneous symmetry breaking which occurs in the hexagonal manganite InMnO$_3$. The potential landscape reveals both topological defects and dual ground states: for a ferroelectric ground state we find nonpolar domain walls, and for a nonpolar ground state we find ferroelectric domain walls. Connectivity rules for domains and domain walls within these two ground states are proposed, and we finally identify a previously-unobserved but symmetry-predicted third state in InMnO$_3$. This work provides a universal description of topological defects, domains and domain-wall formation for the class of hexagonal-manganite multiferroics.
6.1 BACKGROUND

The physical properties of InMnO$_3$ have been controversial. The detailed characterization of the crystal structure, specifically whether or not the compound is ferroelectric, has been debated. Two competing structures have been reported and proposed to be the ground state: ferroelectric (FE) structure with space group $P6_3cm$ and a nonpolar (NP) structure with space group $P\bar{3}c$ as shown in Fig. 20.

This work was motivated by recent experimental findings by our collaborators, the group of Sang Wook Cheong in Rutgers.

6.1.1 Crystal structures

The reported $P6_3cm$ structure is that adopted by other h-RMnO$_3$ materials and should therefore have a similar domain structure. This has been verified in high-resolution transmission TEM by Choi et al.[?] who observe a typical vortex-antivortex pair in the domain structure interpreted as six domains ($\alpha^+, \beta^-, \gamma^+, \alpha^-, \beta^+, \gamma^-$ or vice versa) of alternating polarization and phase around each vortex core. The nature and origin of the domain structure is now well understood, as described in the previous chapter for the case of YMnO$_3$: Domains of opposite electric polarization (+, -) interlock with three structural antiphase domains ($\alpha$, $\beta$, $\gamma$) in a so-called $Z_2 \times Z_3$ pattern around a vortex core. The primary order parameter for the symmetry-lowering phase transition from the high symmetry $P6_3/mmc$ phase is a $K_3$ mode consisting of trimerizing tilts of the MnO$_5$ trigonal bipyramids (Fig. 20(c), (d), orange arrows) at angles of $30^\circ n$ ($n$ even), and nonpolar displacements of the R ions in an up-up-down (for $n = 0, 4, 8$) or down-down-up (for $n = 2, 6, 10$) pattern. This is accompanied by a secondary $\Gamma_{-2}$ mode consisting of displacements of the R ions either up (for $n = 0, 4, 8$) or down (for $n = 2, 6, 10$) which gives rise to the ferroelectric polarization.

InMnO$_3$ has also been reported in a non-ferroelectric phase with $P\bar{3}c$ symmetry. The $P\bar{3}c$ structure is reached from the high-symmetry $P6_3/mmc$ prototype by tilting of the MnO$_5$ bipyramids at intermediate angles of $30^\circ n$ ($n$ odd), and an up-down-none pattern of In displacements (Fig. 20(b), orange arrows) resulting in six possible domains ($\tau, \nu, \mu, \tau^*, \nu^*, \mu^*$). This NP phase is of substantially higher energy than the FE phase in the rare-earth and Y h-RMnO$_3$. In InMnO$_3$, however, the NP and FE phases have been shown using first-principles calculations to be almost degenerate by Kumagai et al.[?].

6.1.2 Controversy over ground state

Initially, InMnO$_3$ was expected to be ferroelectric like other hexagonal manganite materials and so much theory and experiment started with this assumption. Evidence for ferroelectricity included polarization-electric field hysteresis loops below 500 K[?]. However, later experiments by Belik et al. failed to observe spontaneous polarization, and pointed to the difficulty in distinguishing between the cen-
Figure 20.: (a) High-symmetry $P6_3/mmc$ structure of InMnO$_3$ before the onset of trimerization. (b) Non-polar $P\bar{3}c$ structure of InMnO$_3$. The action of the $K_3$ mode for $30^\circ n$ ($n$ even) is shown in the lower panel. (c) Ferroelectric $P6_3cm$ structure of InMnO$_3$. The action of the $K_3$ mode for $30^\circ n$ ($n$ odd) is shown in the lower panel. (d) Depiction of the $K_3$ trimerization mode on the R ions and MnO$_5$ trigonal bipyramids in the $P6_3cm$ structure.
trosymmetric and non-centrosymmetric space groups in powder x-ray diffraction[?, ?].

In the sample of Belik et al. a combination of second harmonic generation (SHG) and piezoresponse force microscopy (PFM) did not detect ferroelectricity down to low temperatures[?]. Subsequently Huang et al. stabilized the ferroelectric phase for slowly-cooled samples, suggesting FE as the ground state, while fast cooling in a furnace resulted in the NP phase using transmission electron microscopy and high-angle annular dark-field scanning TEM[?].

The nature of the topological defects in these materials is an intricate question given the subtle balance between the FE and NP ground states. In this chapter we examine the influence of these competing ground states on the topological defect formation, along with resulting domain and domain wall configurations. We investigate both the behaviour of isolated FE and NP domains, and the interaction between them.

6.2 SYMMETRY ANALYSIS

In this section we give a detailed symmetry analysis of the possible structures of hexagonal InMnO₃. We first identify the most-likely low-temperature structures using symmetry constraints and the key experimental observation of unit-cell tripling. We then proceed to investigate the phase transition routes from the high-temperature \( P6_3/mmc \) to the ferroelectric and non-polar structure by performing symmetry mode analysis. We identify the associated primary and secondary order parameters for use in the Landau Theory of Section 6.3.

6.2.1 What are the options for the symmetry breaking?

We first consider the symmetry-allowed subgroups of the \( P6_3/mmc \) parent structure that would result in the experimentally-observed unit-cell tripling. The graph relating the parent structure to the three possible subgroups is shown in Fig. 21 The analysis becomes more transparent if we analyze the generators of these three subgroups of \( P6_3/mmc \). The full table of generators for these selected subgroups is given in the Appendix B. The lowest symmetry group is \( P3c1 \), corresponding in the hexagonal manganites to an arbitrary trimerization angle. Two special cases of this are for \( \phi = 30^\circ + n^\circ 60^\circ, 60^\circ + n^\circ 60^\circ \) which correspond to \( P3c \) and \( P6_3cm \) respectively. These particular choices of rotation tilt induce additional symmetries, which are listed in the table of generators. Of particular note are the following:

- For \( \phi = 30^\circ \), we recover inversion: \( \bar{1} \), resulting in a non-polar space group. For the other two cases, we have a polar space group.

- Both the 6-fold generators and the mirrors are absent from the \( P3c1 \) space group.
Figure 21: Graph of possible subgroups of the parent $P6_3/mmc$ symmetry, consistent with experimentally-observed cell tripling.

The FE $P6_3cm$ structure results from polyhedra tilting along the In-In axis, as described in Section 6.1 and shown in the lower part of Fig. 20(c). This allows tilting angles of $30^\circ\times n$ for $n$ even. In contrast to this, the NP $P3c$ structure corresponds to intermediate polyhedra tilts exactly halfway between the In-In axis (see lower part of Fig. 20(b)). In our notation the allowed tilting angles are then $30^\circ\times n$ for $n$ odd. In both of these cases the angle of tilt of the Mn-O polyhedra sets the resulting space group symmetry. However a further subgroup – which is also a subgroup of the both NP and FE phases – exists with a similar trigonal-bipyramid tilting scheme. This $P3c1$ structure corresponds to an arbitrary tilt angle of the Mn-O polyhedra, with having any value except $\phi = 30^\circ + n^\circ60^\circ$, $60^\circ + n^\circ60^\circ$. In each case, the index of the group-subgroup relationship is $C$, indicating the formation of six inequivalent domain states.

6.2.2 How we get there: Mode decomposition

Ferroelectric ground state, $P6_3cm$

We now present the mode decomposition in going from the parent $P6_3/mmc$ to the FE ground state to ascertain the most-likely microscopic mechanism for the FE phase transition. The decomposition was performed using the AMPLIMODES software[7] provided by the Bilbao Crystallographic Server. The graph of the maximal subgroups relating the high-symmetry and FE structures is shown in Fig. 22. From these symmetry-allowed phase transition routes, we can deduce two possible paths for the phase transition. The first, as is the case in YMnO$_3$, is that the primary order parameter is the condensation of the $K_3$ mode, with the $\Gamma_2$ and $K_1$ entering as secondary modes[7]. However a more complicated scenario is also possible whereby the $\Gamma_2^-$ and $K_1$ are in fact the primary modes which condense separately resulting in two phase transitions (and en route displaying the $P6_3mc$ or $P6_3/mcm$ symmetries).

Regardless of the particular path, we now consider the decomposition of the four modes of the calculated parent phase that recover the calculated FE structure: the unit-cell tripling $K_3$ mode with
Figure 22.: Group-subgroup tree for the symmetry-allowed paths between the high-temperature $P6_3/mmc$ and a low-temperature $P6_3cm$. Each transition is characterized by the irreducible representation that results in the particular change of symmetry.

Table 2.: Mode decomposition with respect to its $P6_3/mmc$ parent structure of the ferroelectric $P6_3mc$ structure of InMnO$_3$.

<table>
<thead>
<tr>
<th>K-vector</th>
<th>Irrep</th>
<th>Subgroup</th>
<th>Amplitude (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(o, o, o)</td>
<td>$\Gamma_1^+$</td>
<td>$P6_3/mmc$</td>
<td>0.0047</td>
</tr>
<tr>
<td>(o, o, o)</td>
<td>$\Gamma_2^-$</td>
<td>$P6_3mc$</td>
<td>0.0583</td>
</tr>
<tr>
<td>(1/3, 1/3, o)</td>
<td>$K_1$</td>
<td>$P6_3/mcm$</td>
<td>0.0300</td>
</tr>
<tr>
<td>(1/3, 1/3, o)</td>
<td>$K_3$</td>
<td>$P6_3cm$</td>
<td>0.8309</td>
</tr>
</tbody>
</table>

$q = (1/3, 1/3, 0)$, the unit-cell tripling $K_1$ with $q = (1/3, 1/3, 0)$, the polar zone-centered $\Gamma_2^-$, and the identity $\Gamma_1^+$. We show in Table 2 the relative strength of each mode in the decomposition in terms of their amplitude in Å. There is much larger contribution of the $K_3$ distortion to the final FE structure than the $\Gamma_2^-$ mode. In fact, in Section 6.4.2 we show that the $\Gamma_2^-$ is not energy-lowering until the $K_3$ mode has been established. This leads us to conclude that the ferroelectric phase transition in InMnO$_3$ is improper, as was shown in the case of YMnO$_3$. Further evidence to the secondary nature of the polar mode will be presented in Section 6.4 using first-principles calculations.

Non-polar ground state, $P\bar{5}c$

We again used AMPLIMODES to analyze the mode decomposition, this time going from the parent $P6_3/mmc$ to the NP ground state. In Fig. 23 we show the maximal subgroups relating these two structures. Like the previous case, there are two possible symmetry-allowed transition routes. The $K_3$ mode can be considered to be the primary order parameter with the $\Gamma_1^+$ and $K_1$ coming in as secondary considerations. Conversely, the transition could proceed via a two-step process with
the primary order parameters being either \( \Gamma_1^+ \) and \( K_1 \) which is followed by a secondary \( K_3 \) mode.

Table 3.: Mode decomposition with respect to its \( P6_3/mmc \) parent structure of the nonpolar \( P3c \) structure of InMnO\(_3\).

<table>
<thead>
<tr>
<th>K-vector</th>
<th>Irrep</th>
<th>Subgroup</th>
<th>Amplitude (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0, 0, 0)</td>
<td>( \Gamma_1^+ )</td>
<td>( P6_3/mmc )</td>
<td>0.0016</td>
</tr>
<tr>
<td>(1/3, 1/3, 0)</td>
<td>( K_1 )</td>
<td>( P6_3/mcm )</td>
<td>0.0355</td>
</tr>
<tr>
<td>(1/3, 1/3, 0)</td>
<td>( K_3 )</td>
<td>( P3c )</td>
<td>0.7993</td>
</tr>
</tbody>
</table>

To distinguish between these routes, we analyzed the relative amplitudes of each symmetry-adapted mode in the final NP structure as displayed in Table 3. For this case we considered three modes of the calculated parent phase that bring us to the calculated NP ground state: the unit-cell tripling \( K_3 \) mode with \( q = (\frac{1}{3}, \frac{1}{3}, 0) \), the unit-cell tripling \( K_1 \) with \( q = (\frac{1}{3}, \frac{1}{3}, 0) \), and the identity \( \Gamma_1^+ \). Note the absence of the polar \( \Gamma_2^- \) which is consistent with the absence of ferroelectricity in this crystal structure. Here again the largest mode weighting comes from \( K_3 \), with over 95% of the final structure comprised of \( K_3 \)-mode condensation. The contribution of the other two modes is negligible compared to this strong zone-boundary mode.

6.3 Landau Theory

In the previous section we identified the likely primary order parameter for the FE and NP ground states to be the condensation of a \( K_3 \) mode. Depending on the angle of trimerization (\( \phi = 30^\circ, 60^\circ \)) of this \( K_3 \) mode we recover the NP and FE structures respectively. To establish how the polar mode becomes unstable we calculated the en-
energy landscape as a function of both $K_3$ and $\Gamma_{2}^-$. Since $K_1$ and $\Gamma_{1}^+$ had such small contributions to the final structure we disregard them to simplify our parameter space. We used the amplitude, $Q$ and phase, $\phi$ of $K_3$ and the amplitude, $P$ of $\Gamma_{2}^-$ as the expansion parameters in the Landau theory.

The energy expansion is written in terms of $Q$, $\phi$ and $P$ derived in Artyukhin et al.[?4] from the generators of the $P6_3/mmc$ space group:

$$f = \frac{a}{2}Q^2 + \frac{b}{4}Q^4 + \frac{c}{6}Q^6 + \frac{d}{6}Q^6\cos6\phi - \frac{g}{2}Q^3P\cos3\phi + \frac{h}{2}Q^2P^2 + \frac{ap^2}{2}(45)$$

We then parametrized this energy expansion using first-principles methods as described in the next section.

6.4 ab initio parameterization

We calculated the numerical values of the expansion parameters $a$, $b$, etc. using first-principles methods to explore the energy landscape of the $Q - \phi - P$-parameter space. We constructed supercells with distorted periodic structures commensurate with the required wavevectors. We then extracted the expansion coefficients by fitting Eqn. 45 to the calculated energies as a function of various distortions.

6.4.1 Calculation details

Our spin-polarized density functional calculations were performed using the projector augmented-wave (PAW) method[?] as implemented in VASP with valence manifolds including In $5s$ and $5p$ electrons, Mn $3d$ and $4s$ electrons and O $2s$ and $2p$ electrons. We expanded the wave functions using plane waves with an energy cut off of 550 eV, and used a k-point sampling mesh of $12 \times 12 \times 4$ for 10-atom calculations, $6 \times 6 \times 4$ for 30-atom calculations and $4 \times 4 \times 4$ for 90-atom (tripled unit-cell) calculations. To stabilize the FE state, we used the generalized gradient approximation plus Hubbard correction (GGA+U) method with $U=5$eV and $J=0.88$eV on the Mn-d states following the Lichtenstein approach[?], while for the NP state we used the GGA. We enforce collinear frustrated AFM for all calculations. We performed a full relaxation of the lattice constants and internal coordinates of the structure until the forces were converged to 0.01 eV/Å. The phonon calculations and modulations of phonon modes were performed using the frozen-phonon method as implemented in the PHONOPY software.

6.4.2 Ferroelectric ground state

The calculated parameters of Eqn. 45 which give the FE ground state are given in Table 4. These are obtained by fitting to various mode variations with total energy, as shown in Fig. 25. It is apparent from Fig. 25 (a) that for the $K_3$ mode, the energy depends only weakly on the angle of condensation. Since the angular dependence of the
Figure 24.: (a) Energy landscape of the FE phase as a function of $Q$ and $\phi$. (b) Assignment of domain and domain wall structures for the FE ground state structure. The domains are FE and alternate in polarization circumnavigating the vortex core. These domains are separated by NP domain walls.

energy manifests as the sixth-order term in the Landau expansion and the corresponding parameter $d$ is small, we expect an almost rotationally-invariant landscape for the trimerization angle.
Table A.: Landau coefficients for Eqn. calculated from \textit{ab initio} from fits shown in Fig. and Fig. 26.

<table>
<thead>
<tr>
<th></th>
<th>a (eV/Å²)</th>
<th>b (eV/Å⁴)</th>
<th>c (eV/Å⁶)</th>
<th>d (eV/Å⁶)</th>
<th>g (eV/Å⁴)</th>
<th>h (eV/Å⁴)</th>
<th>a_p (eV/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA (NP ground state)</td>
<td>-0.0107</td>
<td>-0.0007</td>
<td>0.0058</td>
<td>0.0003</td>
<td>0.0561</td>
<td>0.0024</td>
<td>0.2011</td>
</tr>
<tr>
<td>GGA+U (FE ground state)</td>
<td>-0.0436</td>
<td>0.0084</td>
<td>0.0029</td>
<td>0.0003</td>
<td>0.1048</td>
<td>0.1619</td>
<td>0.1231</td>
</tr>
</tbody>
</table>

Table 4.: Landau coefficients for Eqn. calculated from \textit{ab initio} from fits shown in Fig. and Fig. 26.
However, we must also consider the influence of the $\Gamma_2^-$ mode which couples to the $K_3$ for $30^\circ n$ ($n$ even). To see the full energy landscape including the effect of the $\Gamma_2^-$ mode, we minimize Eqn. [45] with respect to $P$, with the resulting energy surface shown in Fig. [24]. We see that the energy surface has a similar "Mexican hat" form as shown previously for YMnO$_3$, with quasi-U(i) symmetry at the peak indicating the angle independence of the $K_3$ mode condensation, and lower energy "valleys" developing as the secondary $\Gamma_2^-$ mode emerges. The presence of this additional $\Gamma_2^-$ distortion induces a stronger angular dependence of the energy. In the brim of the hat there are six minima corresponding to the six ferroelectric ground states. In contrast to the case of the robustly $P6_3cm$ YMnO$_3$, where the barriers between the minima are 25 meV, however, in this case the barriers between the minima are tiny at 4 meV. These small energy barriers are as expected, as they have tilt angles of $30^\circ n$ ($n$ odd) and correspond to the structure of the almost-degenerate NP phase.

Indeed, because of its intermediate nature, the NP phase was suggested previously as a possible candidate for the domain wall structure in the ferroelectric $h$-RMnO$_3$ compounds. Type (I) walls exhibit an abrupt transition between domains of opposite polarization; the type (II) wall, in contrast, is slightly wider with a smooth transition from one ferroelectric domain to another via a layer of the intermediate NP structure. Our collaborators Huang et al.[?] observed NP domain walls (Type II) using HAADF-STEM[?] although only at the surface of samples. These were shown using first principles calculations to be higher energy than an abrupt domain wall with a discontinuous jump from one domain structure to the next (Type I). In the case of FE InMnO$_3$, however, we anticipate that, because of the very small energy barriers, domain walls of NP structure should be energetically favourable. In fact this is found to be the case from HAADF-STEM images[?] of the two types of domain walls that we find commonly in FE InMnO$_3$. In contrast to the case of YMnO$_3$, the type (II) walls are common in FE InMnO$_3$, and in fact we find that the two wall types tend to alternate around each FE vortex core.

### 6.4.3 Non-polar ground state

Next we turn our attention to the NP $P\bar{3}c$ phase, which we stabilize computationally by using the PBE generalized gradient approximation (GGA). Again we evaluate the Landau expansion coefficients by systematically varying the mode amplitudes (Fig. [26]) with the values given in Table [4].

Our calculated potential energy landscape is shown in Fig. [27]. Again, we find a "Mexican hat" form with quasi-U(i) symmetry at its peak and six minima in the brim although this time the minima are at angles of $30^\circ n$, with $n$ odd, exactly intermediate between those of the FE case. Another striking difference compared with the FE case is the depth of the minima. Here the minima are barely visible, with barriers between them of only 0.4 meV, and the symmetry remains close to U(i) even in the brim of the hat. We expect, therefore, negligible energy penalty for forming wide domain walls in NP InMnO$_3$. Inter-
Figure 25: Model parameters extracted from ab initio calculations for the FE ground state of InMnO$_3$. (a) Variation of total energy for the $K_3$ mode with two different trimerization angles, $\phi = 0^\circ$ and $\phi = 30^\circ$. From these the $K_3$-dependent parameters $a$, $b$, $c$ and $d$ were extracted. (b) Variation of the total energy for the $\Gamma_2$ polar mode with no trimerization present. Note that here the polar mode is stable. (c) Variation of total energy for different $K_3$ ($\phi = 0^\circ$ and $\phi = 30^\circ$) as a function of $\Gamma_2^-$. For the optimal value of the $K_3$ mode polar mode is energy lowering. From these the couplings $g$ and $h$ between the $K_3$ and $\Gamma_2^-$ mode were calculated.
Figure 26: Model parameters extracted from *ab initio* calculations for the NP ground state of InMnO$_3$. (a) Variation of total energy for the $K_3$ mode with two different trimerization angles, $\phi = 0^\circ$ and $\phi = 30^\circ$. From these the $K_3$-dependent parameters $a$, $b$, $c$ and $d$ were extracted. (b) Variation of the total energy for the $\Gamma_2^-$ polar mode with no trimerization present. Note that here the polar mode is stable. (c) Variation of total energy for different $K_3$ ($\phi = 0^\circ$ and $\phi = 30^\circ$) as a function of $\Gamma_2^-$. For the optimal value of the $K_3$ mode polar mode is slightly energy lowering. From these the couplings $g$ and $h$ between the $K_3$ and $\Gamma_2^-$ mode were calculated.
Figure 27.: (a) NP energy landscape of the uniformly-trimerized states as a function of $Q$ and $\phi$. (b) Assignment of domain and domain wall structures for the NP ground state structure. The domains are NP. These domains are separated by FE domain walls which alternate in polarization going around the vortex core.

Interestingly, the tilt angles of the maxima are those of the FE $P6_3cm$ structure and therefore they support the emergence of a polarization. Since the phase of the maxima, and hence of the domain walls, changes by $60^\circ$ as one moves around the vortex, any polarization associated with domain walls must alternate in sign.

6.5 NEW HIDDEN PHASE IN HEXAGONAL MANGANITES

By symmetry, condensation of the $K_3$ mode into the high temperature $P6_3/mmc$ phase allows three possible space groups: $P3c$, $P6_3cm$ and $P3c1$, as outlined in Section 6.2. $P6_3cm$ and $P3c$ are direct subgroups of $P6_3/mmc$ and as already discussed manifest in the FE ($\phi = 30^\circ n$ with $n$ even) and NP ($\phi = 30^\circ n$ with $n$ odd) structures (Fig. 20). By symmetry, the $P3c1$ structure must have a phase $\phi$ which is a non-integer multiple of $30^\circ$ for the MnO$_5$-bipyramid tilting angle, which is associated with the true U(i) symmetry. From HAADF-TEM images from Cheong et al. we find this is indeed the case for the wide wall regions in the NP phase, which we therefore assign to the $P3c1$ space group. We note that since $P3c1$ is a subgroup of both $P3c$ and $P6_3cm$ it is allowed by symmetry to form as the DW between these two phases. It has never been observed in the $h$-RMnO$_3$ series because of the high energy barriers between the FE domains and the resulting narrow DWs in those systems.

6.6 DUALITY OF DOMAINS AND DOMAIN WALLS

We find a duality between the vortices in the NP and FE phases: In the NP phase the non-polar domains are separated by polar domain walls of alternating polarity, whereas in the FE phase, the alternating polar domains are separated by non-polar walls which can have the
NP structure (Fig. [28]). The widths of the walls differ in the two cases, with the larger energy barrier between domains in the FE phase leading to narrow walls, and the negligible barrier in the NP phase allowing for walls which are seen experimentally up to around 12 unit cells wide. The broad DWs show a progressive evolution of the In displacements and polyhedral tilt angles corresponding to a new phase of \( P3c1 \) symmetry, which completes the set of symmetry-allowed structures for the hexagonal manganites. Our results indicate and explain the duality between the vortices in FE and NP hexagonal manganites, and provide a unified picture of the symmetry by identifying for the first time the \( P3c1 \) phase.

6.7 UNIVERSALITY OF CONNECTIVITY OF DOMAINS AND DOMAIN WALLS

Given the 6-fold symmetry of the FE and NP domains, an obvious question is how these domains meet and order themselves in the crystal given their meeting points are constrained by a topological defect. Here we revisit the connection rules for FE and NP vortices, and generalize them for the \( \text{InMnO}_3 \) case in which a combination of FE and NP domains have been found in the same sample.

Soon after the first imaging of the FE vortices in YMnO\(_3\), it was observed that vortices could only be connected to anti-vortices because of the required domain sequences. Fig. [29] shows a schematic of a FE vortex and anti-vortex pair. We associate a chirality to the vortex such that circumnavigating the vortex in the direction \( \alpha^+ \rightarrow \beta^- \rightarrow \gamma^+ \rightarrow \alpha^- \rightarrow \beta^+ \rightarrow \gamma^- \) is given a + convection, and a - for the opposite direction. From this convention then, a FE vortex must neighbour a FE anti-vortex, that is, vortices of opposite chirality are always found next to each other.
Since the NP ground state of InMnO$_3$ has a comparable 6-fold structure, it is not surprising that the same connectivity rule holds for the meeting of NP vortices. Here again we find that a NP vortex must join a NP anti-vortex. We assign the same convention to the NP vortices, ensuring that the chirality of the domain walls is consistent with that defined for the FE case (Fig. 30).

The situation becomes interesting when we have FE and NP coinciding in the same sample. If we consider the formation of a NP vortex, will FE vortices or FE anti-vortices neighbour it? This is the scenario depicted in Fig. 31. Moving outwards from the centre of the NP vortex, and reducing the domains to domain walls (as is the case for the dual nature of the FE ground state), we find that there is no choice in the chirality of a neighbour FE state. An NP vortex must be connected to two FE anti-vortices and vice versa.

The connectivity rules suggest that we will find regions of FE-vortices/NP-anti-vortices and regions of FE-anti-vortices/NP-vortices. Given this constraint, an interesting question remains as to the extent of these chiral patches; that is if there are extended regions connected at the boundaries with the usual same-type vortex-antivortex rules or whether there is in fact a homogeneous mixing of all states throughout the sample.
Figure 31.: A more complicated scenario arises when we have NP and FE domains merging. Here we consider an NP vortex in the centre with counter-clockwise chirality. This must necessarily be connected to two FE vortices.

6.8 Summary

We have classified and described the existence of topological defects in both the ferroelectric $P6_3cm$ and non-polar $P3c$ phases of InMnO$_3$, and shown for the FE case we have an improper ferroelectric as in the case of YMnO$_3$. We find a universal description of the vortices in the hexagonal manganites – a remarkable duality exists between the domains and domain walls in these two phases. For the NP ground state we find polar domain walls of alternating polarity, whereas in the FE ground state we find domains of alternating polarity separated by domain walls of the NP structure. In collaboration with experimentalists we identify a new phase of $P3c1$ symmetry, which completes the set of symmetry-allowed structures for the hexagonal manganites. Finally we propose connectivity rules for the case when both FE and NP domains are found in the same sample – these rules are set by the formation of topological defects in the system.
Design is a plan for arranging elements in such a way as best to accomplish a particular purpose.
– Charles Eames (on designing chairs)

The ‘standard model’ of condensed matter physics is widely regarded to be the Hubbard Model. It augments independent-electron band theory through a single parameter to account for electron-electron correlations and has been remarkably successful at addressing a range of correlation effects in transition-metal materials. However, beyond one dimension the problem is intractable and so much current research aims at finding appropriate approximations for obtaining the Hubbard model phase diagram. Here we take a new approach – we use ab initio methods to design a material whose Hamiltonian is exactly that of the Hubbard model so that its solution can be found by measuring the material properties. After identifying a crystal class and several appropriate chemistries, we use density functional theory to screen for the desired electronic band structure, and dynamical mean-field theory to study the Mott transition. Following this, we take the most promising candidate and address its structural stability, possibilities for doping and exotic superconductivity, and its similarity with the cuprate high-temperature superconductors.
7.1 Background on the Hubbard Model

7.1.1 The Hubbard Model

Band theory is among the simplest, yet successful methods of solving the problem of electrons in solids. In the band theory picture, electrons are treated as independent where they are allowed to ‘hop’ between lattice sites acting independently of each other. Each of these hops costs the same amount of kinetic energy, \( t \). However, this picture, and hence band theory, breaks down in the study of strongly-correlated materials, wherein the electron-electron correlation effects dictate the physics.

The Hubbard model is one of the most straightforward yet prevalent equations in solid-state physics. Its initial conception in 1963 was to treat itinerant magnetism in transition metals. Soon after it was used to successfully describe transition-metal oxides. Standard theoretical methods at the time predicted them to be metallic when in fact they are antiferromagnetic insulators.

The first hints of the model can be found in quantum chemistry in the 1950s[? , ? , ?], with P. W. Anderson also suggesting an early variation. It was introduced in its modern form by John Hubbard in a series of papers beginning in 1963[? , ? , ?] (and also independently by Gutzwiller[?] and Kanamori[?]). Hubbard wrote that in writing down the Hamiltonian he “set up the simplest possible model containing the necessary ingredients”:

\[
H = -t \sum_{\langle i,j \rangle} \sigma (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}
\]

where \( \langle i,j \rangle \) indicates summation over nearest-neighbours on a lattice as shown in Fig. 32. The first term is the hopping or kinetic term, and the second accounts for the onsite repulsive interaction of the electrons. To date it has been applied to an ever-increasing range of materials from Mott insulators to high-\( T_C \) superconductors.

The innovation in the Hubbard model was including a term which accounts for the electron-electron correlation. This energy, \( U \), is the cost for two electrons to occupy the same site resulting from the

Figure 32.: Square lattice showing the hopping term, \( t \), between sites and the onsite repulsive term, \( U \), in the Hubbard model.
Coulomb repulsion. Adjusting the values of $U$ and $t$ allows one to obtain both metallic and insulating solutions to Eqn.\[46\] providing a simple yet powerful method for studying correlated-electron materials.

### 7.1.2 Computational approaches

Despite the simplicity of Eqn.\[46\] the general Hubbard model (HB) is in fact intractable, and so much active research looks for solutions to describe the phase diagram. Exact solutions for the HB are only possible in 1D\[?\], which were first found by Lieb and Wu\[?\]. Their phase diagram showed a transition to a Mott insulator at half filling when $U$ dominates $t$. When the model is moved away from exactly half filling by either hole or electron doping, the system recovers its metallicit.

For arbitrary dimension, exact solutions of the HB cannot be found, and so approximations must be employed to investigate the phase diagram. A summary of numerical solutions for the 2D is given in\[?\]. One special case, however, considers the HB at absolute zero where exact solutions can be found using the Lanczos algorithm (for example). Analytical methods such as slave-boson mean field theory and the Gutzwiller approximation have been extensively applied to finding solutions.

Numerical techniques like the Dynamical Cluster Approximation (DCA) and Dynamical Mean-Field Theory (DMFT) have been more successful but the rapid scaling of the computational resources required with the system size has hampered efforts in simulating large systems. For example for the DCA, the full model can only be simulated on $4 \times 4$ lattices at present. Despite this profusion of computational approaches, consensus has yet to be reached on an accurate numerical description of the phase diagram.

### 7.1.3 Experimental simulations

Ultracold-atom experiments are a unique toolbox for accessing the HB in the laboratory\[?\]. Lasers create a potential which is used to trap ultracold atoms. Here the atoms now take the role of the electrons which can hop from site to site. Since the lasers are highly controllable and a vast range of potentials can be created by different interference effects, a tunable lattice model can be simulated. The relative strength of the hopping parameters in Eqn.\[46\] can be combined into a single $t/U$ term which can be varied by adjusting the potential created by the lasers.

Both the 2D and 3D Hubbard models have been successfully simulated in cold-atom experiments. The metal-insulator transition has been demonstrated with the localization of atoms due to their mutual repulsion observed\[?\]. Furthermore by appropriate rearrangement of the lasers, several other models can be realized such as the Falicov-Kimball model\[?\] and graphene-like hexagonal lattices\[?\]. The main advantages of the cold-atom approach to investigating the HB are its clean and highly tunable capabilities. However there are
limitations to the geometries that can be created using a cold-atom approach, and the effects like chemical doping and disorder that exist in real materials are difficult to simulate.

### 7.1.4 High-temperature superconductivity

Since their discovery in the 1980’s, the cuprate superconductors have remained one of the most studied and most elusive class of materials to comprehensively understand[9, 10, 11]. They have the highest critical temperatures of all known superconductors, yet the details of the pairing mechanism are still unknown. The relevant features for high-$T_C$ superconductivity in the cuprates appear to be the quasi two-dimensional electronic structure, antiferromagnetism, a single-band at the Fermi level, and a spin-$\frac{1}{2}$ element. In addition, the superconductivity appears for a range of dopings, with a doping-dependent maximum $T_C$.

Consider, for example, the stoichiometric La$_2$CuO$_4$ cuprate parent compound with the valences ($\text{La}^{3+}$)$_2$$\text{Cu}^{2+}$($\text{O}^{2-}$)$_4$. The Cu$^{2+}$ has a $3d^9$ configuration. Naively we would expect it to be a metal, but in fact it is a Mott insulator. The simplest model of the cuprates considers a single Cu-$d_{x^2-y^2}$ band, however this is strongly hybridized with the $p_x$ and $p_y$ states on the neighboring oxygens[12]. The inclusion of more orbitals in a multi-band Hamiltonian has been extensively investigated, however the most efficient and accurate description remains an open question[13].

The isolated Cu-$d_{x^2-y^2}$ is a result of a Jahn-Teller that removes the degeneracy of two $e_g$ orbitals. Strongly related to the orbital degeneracy are the antiferromagnetic (AFM) correlations. In fact, the presence of orbital degeneracy has a detrimental effect to strong AFM correlations since it allows ferromagnetic alignment of spins on different orbitals. To suppress this tendency, the breaking of the degeneracy is required to increase the crucial cuprate physics of the antiferromagnetism. Several materials with spin-$\frac{1}{2}$ antiferromagnetism have been identified and studied, yet lack the non-degenerate band and hence the cuprate physics that results in high-$T_C$ superconductivity.

A two-band HB is believed to describe the low-energy physics of the cuprate superconductors with a half-filled Hubbard band comprised of the Cu-$d$ electrons. Indeed much of the computational efforts at solving the HB are focused on finding solutions for the two-band model of the cuprates[14]. Finding a further material that is described by the HB would not only allow the investigation of the HB in a new system, but would provide much-needed information for understanding high-temperature superconductivity in the cuprates.

### 7.1.5 Designing a single-Hubbard band material

To directly compare the Hubbard theory with experiment it would be advantageous to have a material with hopping directly between the correlated atoms, that is, a purely $d$-band. Our strategy for designing a single-Hubbard band material (that also happens to encom-
Figure 33: (a) The hexagonal-manganite structure of YMnO₃. Layers of Mn-O are separated by rare-earth ions (Y). The Mn and O atoms form trigonal bipyramids in which five oxygens surround each Mn ion. (b) The crystal field splitting on the transition metal ion due to the trigonal-bipyramidal environment. The 5-fold degenerate d-states split into 2-2-1 with a single non-degenerate band isolated from the other four.

pass many of the cuprate features) is to engineer a non-degenerate d-manifold from crystal-field considerations. This is manifested in the hexagonal-manganite crystal structure that has formed the focus of this thesis where the trigonal bipyramid crystal field results in an isolated band. The pentagonal bipyramidal, square antiprismatic, square planar and square pyramidal crystal fielding splittings also result in a non-degenerate band however these crystal structures are possibilities for future exploration.

This chapter is organized as follows:
(i) We describe the hexagonal-manganite crystal structure and the resulting crystal-field splitting,
(ii) We identify chemical compositions with the required electron count for a single-band Hubbard model material, and
(iii) We give results of DFT and DMFT calculations for structural optimization along with the electronic and magnetic properties of the candidate materials.

7.2 MATERIAL DESIGN

The high-symmetry $P6_3/mmc$ hexagonal manganite structure is shown in Fig. 33(a), and the corresponding trigonal bipyramidal crystal-field splitting of the Mn 3d levels in Fig. 33(b). At the centre of the polyhedra lies a transition-metal ion. These are surrounded by five anions, in this case oxygen, that form a trigonal bipyramid around the central transition metal. The 5-fold degeneracy of the isolated transition metal ion is broken into two doubly-degenerate orbital levels ($d_{xz}, d_{yz}$ and $d_{xy}, d_{x^2−y^2}$), and a single orbital $d_{z^2}$. The result of this is our desired non-degenerate orbital. Though structural distortions to the ferroelectric $P6_3cm$ and nonpolar $P3c$ are known to occur, they consist of polyhedral tiltings which do not alter the coordination environment and hence do not change the crystal-field splitting.

In Fig. 34 we show the calculated spin-polarized density of states for hexagonal YMnO₃. Above the Fermi level we see the isolated $d_{z^2}$
Figure 34: The calculated electronic structure for hexagonal manganite YMnO$_3$ with $E_F = 0$ eV. The spin-polarized DOS is shown with the orbitally-projected Mn-$d^2$ shaded in purple. The spin-polarized DOS for ferromagnetically-ordered Mn ions was calculated using GGA+U with $U = 8$ eV and $J = 0.88$ eV on the Mn-$d$ states using the Lichtenstein approach.

with little O-$p$ hybridization. However in YMnO$_3$, we have a $d^4$ configuration which will not fill the non-degenerate $d_{z^2}$ band, regardless of spin state. From this consideration none of the hexagonal manganite multiferroics are suitable candidates.

First we select ion combinations that will yield half-filling of this isolated $d$ band and allows for doping across the range from empty to filled band. To half-fill the $d_{z^2}$ band, we require a $d^9$ configuration, suggesting Cu$^{2+}$. Now we identify three classes of materials and the appropriate chemical compositions for this property: oxides, fluorides and sulphides. For the oxides, we deduce that ZrCuO$_3$ and SnCuO$_3$ are appropriate compositions since we find Cu$^{2+}$ when we combine a 4-valent A-site with the three O$^{2-}$. Likewise we require 4-valent A-sites for the sulphides ZrCuS$_3$ and SnCuS$_3$. In the case of the fluorides we need 1-valent A-sites since we have three F$^-$ giving LiCuF$_3$ and NaCuF$_3$.

Next we perform explicit band structure calculations for our candidate materials. For this initial band-structure screening, we therefore consider the high-temperature $P6_3/mmc$ because of its smaller unit cell.

7.3 COMPUTATIONAL DETAILS

The electronic structure calculations were performed within Density-Functional theory using the Vienna $ab$ initio Simulation Package (VASP) \[?, ?\] The electronic wavefunctions and density were expanded using a plane-wave basis set, and we used projector-augmented-wave
(PAW) potentials \cite{PAW} for core-valence separation. The exchange-correlation potential used was the generalized gradient approximation (GGA)\cite{GGA} and strong correlation effects were treated by means of the Hubbard+U scheme. Here we used the Dudarev method\cite{Dudarev} in which a \(U_{\text{eff}} = U - J\) accounts for the on-site \(U\) (Coulomb repulsion) and \(J\) (Hund’s rule exchange) on the metal \(d\) states. To choose an appropriate \(U_{\text{eff}}\) for hypothetical compounds (without spectroscopic data), we performed hybrid functional calculations to select an appropriate range. In the hybrid functional calculations, a HSE functional which comprised of 75\% PBE and 25\% exact Hartree-Fock exchange was used\cite{HSE}. This led us to choose a \(U_{\text{eff}}\) of 7 \(\text{eV}\) on the \(Cu-d\) states.

A \(10 \times 10 \times 4\) Gamma-centred k-point mesh was used for Brillouin-zone integrations. The plane-wave cut-off was set to 550\(\text{eV}\) and in performing the structural optimizations, we allowed the ions to relax until the Hellmann-Feynman forces were less than 1 \(\text{meV/Å}^{-1}\).

To treat the electron-electron correlations within the partially filled \(Cu-d_{z^2}\) bands at the Fermi level we used the Dynamical Mean-Field Theory (DMFT) approach\cite{DMFT}. We first expressed the Kohn-Sham Hamiltonian in a basis of maximally-localized Wannier functions for the \(Cu-d_{z^2}\) bands using the wannier90 code\cite{Wannier90}. We then used these as the noninteracting part \(H_0\) of a Hubbard Hamiltonian \(H = H_0 + H_{\text{int}}\). Here the \(H_{\text{int}}\) is the local electron-electron interaction comprising of the intra-orbital Coulomb interaction, \(U_{\text{DMFT}}\), and Hund’s rule coupling, \(J\). Here we used \(J = 0\) \(\text{eV}\) since we consider a single orbital, while we vary \(U_{\text{DMFT}}\) from 0 to 4 \(\text{eV}\). We used a continuous time hybridization expansion quantum Monte Carlo solver\cite{TRIQS} as implemented in the TRIQS 1.0 code\cite{TRIQS} to calculate the local Green’s function within DMFT at a temperature \(T = 1/(k_B\beta) = 290\text{K}\) (\(\beta = 40 \text{eV}^{-1}\)).

### 7.4 RESULTS – OXIDES

#### 7.4.1 Structural optimization

The results for the structural optimization for the \(P6_3/mmc\) structure of \(\text{ZrCuO}_3\) and \(\text{SnCuO}_3\) are given in Table 5. From simple ionic-radius considerations we would expect larger lattice parameters for the Zr oxides as Zr has a bigger ionic radius than Sn. However, we find that the lattice parameters for ZrCuO\(_3\) are slightly smaller than SnCuO\(_3\). In fact the Cu-F bond lengths in both compounds are almost the same.

#### 7.4.2 Electronic properties

With the optimized structure we next calculated the electronic properties for the ZrCuO\(_3\) and SnCuO\(_3\) compounds which are shown in Fig. 35 and Fig. 36 respectively. In both cases the density of states (DOS) around the Fermi level is comprised mainly of Cu-\(d\) and O-\(p\) states, which is shown in the orbitally-projected DOS for both compounds. The influence of the trigonal bipyramidal crystal field is ev-
7.4 RESULTS – OXIDES

<table>
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<th>a (Å)</th>
<th>c (Å)</th>
<th>Cu-F (in plane) (Å)</th>
<th>Cu-F (apical) (Å)</th>
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<tr>
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</tr>
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<td>2.08</td>
<td>1.84</td>
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<td>21.10</td>
<td>2.15</td>
<td>3.81</td>
</tr>
</tbody>
</table>

Table 5.: Calculated structural parameters for hypothetical oxides, fluorides and sulphides in the centrosymmetric hexagonal manganite structure with the $P6_3/mmc$ space group. The first two columns give the lattice parameters in the standard hexagonal setting with two formula units per unit cell.

Figure 35.: Band structure and total and orbital-projected density of states (DOS) for ZrCuO$_3$ in the hexagonal manganite structure. The Fermi level is set to 0 eV and is marked by the dashed line.

ident in the splitting of the Cu-$d$ states. The Fermi level intersects the Cu-$d_{z^2}$ band, which is almost although not fully separated from the other four Cu-$d$ bands due to its bandwidth of 1.2 eV. This arises from the significant hybridization between the Cu-$d_{z^2}$ and O-$p_z$ band, resulting from orbital overlap between the Cu ions and the apical oxygen ions. A completely split-off band with less anion hybridization would be more desirable for our target band structure.

In addition, for SnCuO$_3$, we find undesired Sn-$s$ states at $E_F$ (Fig. 36), making it less appealing for our single-band Hamiltonian. ZrCuO$_3$ is more promising with only Cu-$d_{z^2}$ and O-$p_z$ at $E_F$. 

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7.4.3 Sulphides

For completeness we also calculated the electronic structure of two sulphide compounds: ZrCuS$_3$ and SnCuS$_3$. For both of these cases the sulphide orbitals had a substantial overlap with states at $E_F$, removing any possibility for Hubbard-band behaviour.

7.5 RESULTS – FLUORIDES

Our strategy to increase the separation between the Cu-$d_{z^2}$ and the rest of the Cu manifold is to replace oxygen with a more ionic element – fluorine. The requirement for a $d^9$ electronic configuration leaves us with two proposals: LiCuF$_3$ and NaCuF$_3$.

7.5.1 Structural optimization

The calculated structural parameters of LiCuF$_3$ and NaCuF$_3$ are also given in Table 5. As expected from the large atomic radius of Na, the volume for the Na compound is slightly greater than that of LiCuF$_3$. The lattice constants for the fluoride class are greater than the oxides reflecting their more ionic nature. Again the apical Cu-F bond distance remains almost the same in the two structures being 1.85 Å for LiCuF$_3$ and 1.84 Å for NaCuF$_3$.

7.5.2 Electronic structure – DFT

Next we calculated the band structures and densities of states (DOS) for the fluoride compounds in the calculated equilibrium structures. Fig. 36 shows the bands and the total and orbital-projected densities of states of LiCuF$_3$. The expected crystal-field splitting with a non-degenerate band is found, which is half-filled at the Fermi level. The
other four Cu-\(d\) states are completely filled and are separated by a band-gap of \(\sim 0.2\) eV from the half-filled Cu-\(d_{z^2}\). Some hybridization of the Cu-\(d_{z^2}\) with F-\(p_z\) remains giving the bandwidth of \(\sim 1\) eV, however this is less hybridization than in the cuprate superconductors and so LiCuF\(_3\) is more single-band like. Note that we have two formula units in the calculation with the polyhedra pointing in different directions resulting in the two bands in the plot.

The band structure and density of states for the NaCuF\(_3\) compound are given in Fig. 38. Like the Li compound, we find the non-degenerate \(d_{z^2}\) band which is half filled at the Fermi level. The electronic structure is remarkably similar in the area surrounding the Fermi level since there is no contribution form the A site in this region. The only clear difference is that the crystal-field gap between the split-off band and the other Cu-\(d\) states is slightly larger in the NaCuF\(_3\) (\(\sim 0.3\) eV) compared to LiCuF\(_3\) (\(\sim 0.2\) eV).

7.5.3 Electronic structure – DFT+DMFT

To study the effect of explicit electron-electron correlations on the d-\(z^2\) band, we next applied DMFT to the LiCuF\(_3\) case. We first obtained the maximally-localized Wannier functions on the Cu sites using the wannier90 code\footnote{Wannier90} starting from Cu-\(d_{z^2}\) atomic projections. Fig. 39 shows the resulting Wannier functions. From these we can see that they have primarily \(d_{z^2}\) character with some \(p\) tails centered of the fluorine ions.

The trace of the local Green’s function at imaginary time \(\tau = \beta/2\) for LiCuF\(_3\) as calculated within DMFT is shown in Fig. 40. From the relation \(A(\omega = 0) = -\frac{1}{\pi} \lim_{\beta \to \infty} \beta G(\beta/2)\), this can be used as a measure of the spectral function at the Fermi level. We see there is a shift from \(\text{Tr}(G(\beta/2)) \neq 0\) to \(\text{Tr}(G(\beta/2)) \sim 0\) for \(U_{\text{DMFT}} \sim 1.25\) eV showing a metal-insulator transition.
Figure 38.: The calculated electronic structure for hexagonal-manganite NaCuF$_3$ with $E_F = 0$ eV. The band structure is shown on the left, with the total and orbital-projected density of states (DOS) shown on the right.

Figure 39.: Maximally localized Wannier functions by initial projection on $d_{z^2}$ depicted for one of the Cu sites.
Figure 40.: Trace of the local Green’s function at $\tau = \beta/2$ as a function of the interaction parameter $U$ for LiCuF$_3$.

Figure 41.: Spectral function for varying $U$ below and above the metal-insulator transition as a function of frequency $\omega$. The filled orbitals are shaded and the Fermi level is marked with the black line at 0 eV.

The calculated spectral functions for different values of $U_{DMFT}$ are shown in Fig. 41. These are calculated from the imaginary time Green’s functions by analytic continuation using the maximum entropy method[41]. We see that the system is metallic at $U = 0$ eV. As the interaction parameter $U$ is increased, lower and upper Hubbard bands emerge at either side of the quasiparticle peak. At $\omega = 0$ eV, the spectral weight gradually shifts from the quasiparticle peak to the Hubbard bands. Eventually the Mott transition occurs when the electron interactions are strong enough to cause the quasiparticle peak to disappear completely and a gap to appear. Consistent with the $\text{Tr } G(\beta/2)$ data, the system gaps above $U_{DMFT} = 1.25$ eV.
Figure 42.: Densities of states for doped LiCuF$_3$ calculated by artificially adding electrons and compensating with a background positive charge. (a) DOS for removing one electron per formula unit, (b) DOS for removing half an electron per formula unit, and (c) DOS for adding half an electron per formula unit. In each structure, the Fermi level is set to 0eV.
Finally we consider the possibility of doping by examining the effects of adding and removing electrons to the LiCuF$_3$ compound. In VASP, electrons can be artificially added (removed) without explicitly changing the ion configuration by compensating via a background positive (negative) charge. Fig. 43 shows the results for removing $\frac{1}{2}$ and $\frac{3}{2}$ electron, and adding $\frac{1}{2}$ electron per formula unit. As expected, the Fermi level shifts towards the valence band when electrons are removed, giving a completely unfilled Cu-$d_{z^2}$ band when $1$ e$^-$ per formula unit is removed. The Fermi level gradually shifts through this band as we increase the number of electrons, finally resulting in a completely filled Cu-$d_{z^2}$ band when $1$ e$^-$ per formula unit is added.

To examine the possibility for experimental doping, we also look at the effect of chemical doping with oxygen on the electronic structure. Replacing one fluorine atom in our cell results in the chemical formula Li$_2$Cu$_2$F$_5$O$_1$, which has the effect of removing half an electron per formula unit. We calculated the relative energies of the substitution sites for the oxygen by replacing a fluorine ion with an...
oxygen ion for the three inequivalent fluorine sites, performing a full relaxation, and comparing the final energies. We found the in-plane fluorine sites to be lower in energy by $\sim 0.3$ eV per formula unit compared to those above and below the Cu atom. The resulting density of states (DOS) for the in-plane oxygen substitution is plotted in Fig. 43 where the orbital-projection from the O-\(p_z\) is displayed in pink. Notably, these oxygen states have very little overlap with the non-degenerate Cu-\(d_{z^2}\), and in fact, the area surrounding the Fermi level is remarkably similar to that given by the first method of simply adding electrons.

Potential routes to electron doping LiCuF\(_3\) include replacing some Li with Be or introducing F vacancies into the system. The influence of these dopants on the electronic structure by explicit calculation of the bands are left to future work.

### 7.5.5 Feasibility of synthesis

So far we have considered only hypothetical hexagonal-manganite structures. To consider the possibility for synthesis, we investigate the structural stability of a range of structural isomorphs for XCuF\(_3\) over a range of volumes. We take a large range of crystal structures adopting \(ABX_3\) chemistry, and apply both positive and negative hydrostatic pressure by scaling the lattice parameters. The fractional internal coordinates of the ions are kept fixed for each of these calculations to ensure that the original symmetry group was maintained throughout the calculation. The considered isomorphs are high-temperature hexagonal manganite (\(P6_3/mmc\)), low-temperature ferroelectric hexagonal manganite (\(P6_3/mcm\)), low-temperature nonpolar hexagonal manganite (\(P3c\)), cubic perovskite (\(Pm\bar{3}m\)), ilmenite (\(R\bar{3}\)), the ‘NaCuF\(_3\)’ structure (which corresponds to the ambient experimental ground state, \(P\bar{1}\)), the ‘CoGeO\(_3\)’ structure (\(C2/c\)), and two structural variants found in BaTiO\(_3\) – a rhombohedral (\(R3m\)) and a tetragonal (\(P4/mnm\)).

Fig. 44 shows the energy-volume curves for the various structural isomorphs for NaCuF\(_3\). As expected, the ‘NaCuF\(_3\)’ structure is equilibrium ground state structure, and this remains the case over a large range of volumes up to 69 Å\(^3\). Above this volume, the cubic perovskite, \(Pm\bar{3}m\) becomes favorable. For very large unphysical volumes there is a further crossover to the ‘CoGeO\(_3\)’ structure (\(C2/c\)).

However, the case is quite different for LiCuF\(_3\) in Fig. 45. Here, the overall ground-state structure is again the ‘NaCuF\(_3\)’ structure with an equilibrium volume of 58 Å\(^3\). However, for a very small expansion of the cell, the ground state becomes the hexagonal manganite structure, which remains stable for volume greater than $\sim 63$ Å\(^3\). Achieving the hexagonal manganite structure thus might be possible under a small amount of tensile strain. Again, beyond a very large volume of 78 Å\(^3\), the ‘CoGeO\(_3\)’ structure (\(C2/c\)) is stable.
Figure 44.: Structural stability calculations for a variety of NaCuF$_3$ isomorphs for a range of volumes. The NaCuF$_3$ structure is stable for smaller volumes, however for greater than 63Å$^3$, the hexagonal manganite structure is the ground state.

Figure 45.: Structural stability calculations for a variety of LiCuF$_3$ isomorphs for a range of volumes. The NaCuF$_3$ structure is stable for smaller volumes, however for greater than 63Å$^3$, the hexagonal manganite structure is the ground state.
7.6 DISCUSSION

7.6.1 Hubbard model and Mott-insulator

The fluorides LiCuF$_3$ and NaCuF$_3$ have the desired electronic properties that could – if synthesised – be modelled by a single-band Hubbard Hamiltonian. The expected metal-insulator transition upon application of a Hubbard-$U$ term is obtained using an LDA+DMFT approach for a modest $U_{DMFT} \sim 1.25$ eV. However, one must be cautious with the double treatment of the electron-electron correlation in these calculations. We first used a $U = 7$ eV in the DFT+U calculations to obtain a split off Cu-$d_{z^2}$ as anticipated from crystal-field considerations and in agreement with hybrid-functional calculations. We then applied the DMFT on this isolated band with a $U_{DMFT}$ of $1.25$ eV resulting in a metal-insulator transition. While this would seem to complicate our treatment of electron-electron correlations, in fact our DFT bands are very similar in character and band-width to our DFT+U bands with the DFT+U treatment acting as a ‘scissors operator’ to isolate the $d_{z^2}$ orbital. Because of this, we expect only small quantitative changes in the $U_{DMFT}$ value that causes the metal-insulator transition if the initial Wannier functions were constructed from results of an LDA calculation.

We have also investigated a range of dopings for our leading candidate material, LiCuF$_3$, at the DFT level. We first artificially add electrons to the system and compare the result with chemical doping by oxygen substitution. The remarkable similarity between these two methods shows that the artificial-electron bath is accurate in treating doping for this system. Furthermore, we show that doping in this material could be realized by chemical substitution and could facilitate the exploration of the phase diagram of the single-band Hubbard model.

7.6.2 Cuprate-like features

Our single-band Hubbard material shares several characteristics with the cuprate superconductors. Previous attempts at reproducing cuprate features in new materials have primarily involved forming heterostructures to tune the crystal-field splitting. A promising route was proposed by Chaloupka and Khaliullin[?] by creating layered oxides of La$_2$NiMO$_6$. In a bulk crystal, the Ni-$d$ states are split in the crystal field to $b_2$ and $e_g$ states. With a $d^7$ electron count, this results in one electron in two degenerate $e_g$ bands. Upon introduction into a superlattice, the degeneracy of the two $e_g$ states is removed, resulting in two single bands with the lower now containing one electron. However, this is not what happens in reality, where charge-transfer physics (important for the late transition-metal series) needs to be considered for a full understanding. A Mott-Hubbard picture is not sufficient to describe the physics, and the result is not a single-band Hubbard model[?].

Following this strategy, a superlattice made from SrTiO$_3$ and SrFeO$_3$ monolayers was proposed with a diverse playground of lattice in-
stabilities, high polarizability and $p$-type conductivity in the SrTiO$_3$ layer[?]. When the ‘perfect’ cubic lattice geometry was imposed in the superlattice, cuprate-like Fermi surface nesting was found. However, upon full structure optimization it was found that the coupling of a Jahn-Teller instability and an octahedral rotation removed the cuprate-type behavior.

Our hypothetical material avoids common pitfalls in achieving cuprate-type behavior since instabilities like Jahn-Teller distortions are frustrated by our triangular lattice, however effects like charge disproportionation to Cu$^+/\text{Cu}^{3+}$ remain to be considered. The LiCuF$_3$ single-band Hubbard material shares several features with the cuprates. Our layered structure comprises of polyhedra of transition metals and anions (Cu and F here) which are separated by Li ions in a similar manner to the layering and reduced dimensionality the cuprates. Furthermore we have isolated a single Hubbard-like band at the Fermi level which comprises of a spin-$\frac{1}{2}$ element.

### 7.7 Future Directions

#### 7.7.1 Magnetism

Up to now we discussed non-spin-polarized calculations, however we expect strong antiferromagnetic (AFM) correlations in such compounds. The spins occupy triangular lattices, so we expect frustration to play the major role in determining the ground state magnetic ordering since they are antiferromagnetically coupled. Next we performed several collinear spin-polarized calculations to find the ground state magnetic structure for the fluoride class, with the simulation cell increased to allow for a variety of antiferromagnetic orderings. We do not consider spin-orbit coupling in these preliminary spin-polarized calculations. In the collinear limit, the ground state for both cases is found to be a frustrated AFM arrangement in which spins are coupled AFM in plane and out of plane. The energy lowering associated with the AFM order compared to the FM order is 4 meV per formula unit. Likely ground-states for this compound are $120^\circ$ spin-structures similar to those occurring in the $R\text{MnO}_3$ family. To verify this, non-collinear spin calculations must be performed which is postponed for future work.

#### 7.7.2 Exotic Superconductivity

*Collaboration with Dr. Peter Staar, ETH*

Ongoing work involves the calculation of the superconducting properties of LiCuF$_3$ using the Dynamical Cluster Approximation (DCA). Preliminary results hint at possible exotic superconductivity owing to the triangular Cu lattice. From this the superconducting temperature and the phase diagram will be explored computationally.
7.8 **Summary**

We have identified a class of materials with the hexagonal manganite structure, LiCuF$_3$ and NaCuF$_3$ whose low-energy behavior resembles a single-band Hubbard Hamiltonian. Using DFT and DMFT we characterized the electronic and structural properties of the material and observed the metal-insulator transition as predicted in the Hubbard model. Furthermore we discussed the implications for exotic superconductivity and similarity to the cuprate class of superconductors.

Several open questions remain for future consideration. The magnetic ground state remains to be determined by performing noncollinear spin DFT calculations. The influence of doping on the magnetic properties is an interesting question since interruption of the Cu triangular lattice could in principle remove the frustration caused by the triangular magnetic lattice. On a technical level, the ‘double double-counting’ from the inclusion of a $U$ in both the DFT and DMFT treatments should be formally addressed. The influence of strain on LiCuF$_3$ has two potential effects: It could stabilize the hexagonal manganite structure over the global ground state, and in addition the impact of strain on the electronic structure remains to be investigated. Finally we will address the superconducting properties of LiCuF$_3$ with collaborators using DCA to calculate the transition temperature and the phase diagram.
Never gonna give you up.
– Rick Astley

In this thesis we explored the wide range of low and high energy physical theories that are applicable to the multiferroic hexagonal manganites.
8.1 Topological and geometric defects

We first reviewed the requirements for topological defect formation in general systems and summarized the strict symmetry requirements for a phase transition to be described in the language of homotopy theory. We compared topological defects to geometric defects which are caused by an incompatibility of local ordering rules after a phase transition and the space in which it is defined. We discussed how the underlying difference between topological defects and geometric defects is that global symmetry changes can remove geometric defects, which is not the case for topological defects.

8.2 The Kibble-Zurek mechanism in multiferroics

We next applied homotopy theory to topological defects found in multiferroic hexagonal manganites. Using this we explored an early-universe theory – the Kibble-Zurek mechanism – which predicts qualitatively and quantitatively the topological defects that form during a quench through a phase transition.

Following the appropriate symmetry analysis and the isolation of the relevant parameters from ab initio calculations, we predicted the Kibble-Zurek scaling behavior in YMnO$_3$ for the first time in a multiferroic crystal. This was confirmed by quenching experiments. However, several open and ongoing questions remain from this work which we now summarize.

While the material showed Kibble-Zurek scaling for the slower range of cooling rates, an unexpected downturn was observed in experiments at fast cooling rates. In the thesis we suggested several possible causes for this, however a thorough investigation would look at whether this is material-dependent or a more fundamental feature of non-equilibrium phase transitions.

The topological description is, of course, only strictly valid for continuous symmetry, whereas our final state exhibits a discrete, 6-fold degeneracy. It would be interesting to study similar behavior in other systems to establish the limits for which topological characteristics can be used to describe discrete symmetry breaking in condensed matter systems.

Finally, we used the critical exponents from Monte Carlo simulations of the 3D XY model which is the universality class of the phase transition. However, the experimental determination of the dynamic critical exponents is lacking for this system to compare with these theoretical values. Matching the dynamical critical exponents to those predicted by theory would unambiguously validate the Kibble-Zurek prediction.

8.3 Tuning spontaneous-symmetry breaking in multiferroics

Spontaneous symmetry breaking is ubiquitous in physics from cosmic-strings in the early universe to vortices in superconductors. In this thesis we proposed that the phase transition in InMnO$_3$ is described...
by a Mexican-hat potential using a combination of symmetry analysis, Landau theory and density functional theory calculations. In fact the details of the potential can be systematically tuned and manipulated by chemistry.

We described the formation of topological defects in the material and how the combination of these defects with the two ground state crystal structures determines the domain and domain wall formation. A surprisingly duality between the domains and domain walls was revealed – for ferroelectric domains we find nonpolar domain walls, and for nonpolar domain we find ferroelectric domain walls. Finally we identified new third structure bringing a unity to topological defect and domain wall formation in the multiferroic hexagonal manganites.

Tuning between the ferroelectric and nonpolar states is achieved experimentally by Ga doping. Future directions include investigating other routes to tuning between the ground states such as other chemistries and strain.

Here we classified the electronic and structural properties without addressing magnetism. The Mn spins form a triangular lattice with antiferromagnetic coupling and so adopt $120^\circ$ noncollinear arrangements. A future direction is to investigate the influence of the Ga doping at the Mn site on the magnetic behavior where we expect it to disrupt the triangular frustration of the Mn ions.

8.4 DESIGNER SINGLE-BAND HUBBARD MATERIAL

The Hubbard model is of significant interest to several branches of condensed-matter physics since it is believed to encompass much of the low-temperature behavior of cuprate superconductors. We designed a single-band Hubbard material by first identifying the desired band structure, and then using chemical and material constraints to identify several classes of materials that fulfill our electronic requirements. Following this we calculated the structural stability and electronic properties of our hypothetical materials, and identified a promising candidate, LiCuF$_3$, for synthesis.

Several open areas remain to be investigated in this material. So far we have performed collinear magnetic calculations and shown that the ground state is antiferromagnetic. However the lattice is triangular and so we expect a noncollinear spin structure to relieve the frustration caused by antiferromagnetic coupling.

We showed that the structure can be doped, however more extensive characterization of the impact of doping remains to be carried out. We thus far examined the case for doping on the fluorine site; next substitution on the Li or Cu sites could be considered. Interestingly, doping on the Cu site could have an interesting effect on the magnetism since it would, in principle, disrupt the triangular frustration.

An ongoing collaboration involves the calculation of the superconducting properties using the dynamical cluster approximation (DCA). Based on these results several avenues of exploration are possible. For example, in our current structure we have an isotropic triangular lattice of Cu ions. An interesting question would be the influence
of an anisotropic triangular structure on the electronic and superconducting properties.

Our hydrostatic pressure calculations hint that the hexagonal manganite structure may be stabilized for volumes slightly larger than equilibrium. A natural question is then whether tensile strain could produce the same effect. Strain will also influence the electronic properties and so a full investigation of the strain effects should be performed. Anisotropic triangular lattices could be experimentally realized by doping or by strain.

A technical question that remains unanswered in this work is whether or not the 'double double-counting' of the electron-electron interaction parameter $U$ in both the DFT and DMFT is a cause for concern. An initial investigation will vary the DFT+U parameter and examine the resulting impact on the spectra calculated by DMFT for various values of $U_{DMFT}$. 
APPENDIX A: NOMENCLATURE FOR GROUPS

A.1 DISCRETE GROUPS: CYCLIC GROUPS $\mathbb{Z}_n$

A cyclic group is one which is generated by a single element. The number of distinct elements in a group is referred to as the order of the group. $\mathbb{Z}_n$ denotes a cyclic group of order $n$.

A.1.1 $\mathbb{Z}_2$: Finite cyclic group of order 2

The cyclic group of order 2 has two elements, say $e$ and $x$ with $ex = xe = x$ and $e^2 = x^2 = e$ with the multiplication table given in Table 6. In terms of condensed matter, it describes disconnected order parameters with two possible degenerate solutions, for example in the Ising model.

<table>
<thead>
<tr>
<th>element</th>
<th>$e$ (identity)</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$</td>
<td>$e$</td>
<td>$x$</td>
</tr>
<tr>
<td>$x$</td>
<td>$x$</td>
<td>$e$</td>
</tr>
</tbody>
</table>

Table 6.: Multiplication table for $\mathbb{Z}_2$.

A.1.2 $\mathbb{Z}_3$: Finite cyclic group of order 3

The cyclic group of order 3 has two elements, say $e$ and $x$ and $x^2$ with $x^l x^m = x^{l+m}$ with the exponent reduced mod 3. The multiplication table is given in Table 7. The 3-state clock model is described as having $\mathbb{Z}_3$ symmetry.

<table>
<thead>
<tr>
<th>element</th>
<th>$e$ (identity)</th>
<th>$x$</th>
<th>$x^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e$</td>
<td>$e$</td>
<td>$x$</td>
<td>$x^2$</td>
</tr>
<tr>
<td>$x$</td>
<td>$x$</td>
<td>$x^2$</td>
<td>$e$</td>
</tr>
<tr>
<td>$x^2$</td>
<td>$x^2$</td>
<td>$e$</td>
<td>$x$</td>
</tr>
</tbody>
</table>

Table 7.: Multiplication table for $\mathbb{Z}_3$. 
The unitary group of degree \( n \), called \( U(n) \), is the group of \( n \times n \) unitary matrices with the group operation of matrix multiplication. The simplest case is for \( n = 1 \) is the group \( U(1) \) which is also the circle group. \( U(1) \) is made up of all complex numbers with absolute value 1 under multiplication and can be parameterized by the angle of rotation \( \theta \):

\[
\theta \mapsto z = e^{i\theta} = \cos\theta + i\sin\theta.
\]  \hspace{1cm} (47)

The Mexican-hat potential has \( U(1) \) symmetry, with the phase corresponding to a particular choice of \( \theta \).
## APPENDIX B: SUBGROUP GENERATORS

### B.1 Generators for selected subgroups of \( P6_3/mmc \)

<table>
<thead>
<tr>
<th>P3c1</th>
<th>P63cm</th>
<th>P3c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3+</td>
<td>3+</td>
<td>3+</td>
</tr>
<tr>
<td>0, 0, z</td>
<td>0, 0, z</td>
<td>0, 0, z</td>
</tr>
<tr>
<td>3−</td>
<td>3−</td>
<td>3−</td>
</tr>
<tr>
<td>0, 0, z</td>
<td>0, 0, z</td>
<td>0, 0, z</td>
</tr>
<tr>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>( x, -x, z )</td>
<td>( x, -x, z )</td>
<td>( x, -x, z )</td>
</tr>
<tr>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>( x, 2x, z )</td>
<td>( x, 2x, z )</td>
<td>( x, 2x, z )</td>
</tr>
<tr>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>( x, 2x, z )</td>
<td>( x, 2x, z )</td>
<td>( x, 2x, z )</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3+</td>
</tr>
<tr>
<td>0, 0, ( \frac{1}{4} ); 0, 0, z</td>
<td>0, 0, ( \frac{1}{4} ); 0, 0, z</td>
<td>0, 0, z; 0, 0, 0</td>
</tr>
<tr>
<td>6−</td>
<td>6−</td>
<td>3−</td>
</tr>
<tr>
<td>0, 0, ( \frac{1}{2} ); 0, 0, z</td>
<td>0, 0, ( \frac{1}{2} ); 0, 0, z</td>
<td>0, 0, z; 0, 0, 0</td>
</tr>
<tr>
<td>m</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
<td>( x, x, z )</td>
<td>( x, 0, z )</td>
<td>( x, y, z )</td>
</tr>
<tr>
<td>m</td>
<td>m</td>
<td>m</td>
</tr>
<tr>
<td>( x, y, z )</td>
<td>( x, y, z )</td>
<td>( x, y, z )</td>
</tr>
</tbody>
</table>

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