Significance of phase difference in magnetism and the magneto-electric effect.

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Abstract. For the new class of multi-ferroics, in which inversion symmetry is broken by magnetic ordering, a number of models have been developed to describe the exchange interactions that might give rise to net polarisation. We explore the importance of phase factors in these theories and how this concept brings together existing ideas within a common motif. Phase differences appear ubiquitous within the subject and they are fixed or free dependent upon the symmetry of the magnetic atoms. Further, we state restrictions upon which representations and co-representations a system displaying electric polarisation can order under.

1. Introduction
For macroscopic electric polarisation to arise in a material there can be no centre of inversion. Recently, a new class of ferroelectric materials have been discovered in which magnetic order, rather than atomic position, destroys centro-symmetry. The intimate relation between the magnetic and electric fields within such materials gives rise to a magneto-electric (ME) effect in which these ordering parameters are strongly coupled. Multi-ferroic striction has been much debated in recent years, and a number of exchange models have been developed to explain the origin of their net polarisation: existing theories have been summarized by Kimura [1]. While their common ground might seem sparse, we show that the role of phase dislocations in removing centro-symmetry brings together these existing theories.

2. Existing models
Consider two magnetic chains ordering under a modulation, with a phase difference \( \phi \) (Fig. 1 & 2). For simple, nearest-neighbor interactions between the chains the moments of the atoms in the second chain can be decomposed into components parallel and perpendicular to those in the first. The component parallel will be subject to super-exchange (SE) interactions [2] while the component perpendicular is subject to Dzyaloshinsky-Moriya (DM) interactions [3, 4]. From literature we highlight three expressions for net polarization in new multiferroics [5, 6, 7]:

\[
P = \gamma \chi_2 M_1 M_2 \sin \phi [\vec{Q} \times (\vec{a}_1 \times \vec{a}_2)]
\]

\[
p_0 = -\gamma q_m M_0^2 \frac{e_1}{2e_0^2} e^2 \sin 2\phi 
\]

\[
P^{ICM} = 4C \vec{S}_3 \cdot \vec{S}_4 \cos(2\pi (\frac{1}{4} + \delta_z) z') \cos(2\pi \delta_x (1 - x)) \cos(\epsilon) \sin \phi 
\]
Here, the terms $M_n$ are the amplitudes of magnetic components, $\vec{S}_n$ are spins on the $n^{th}$ atom, the other terms being constants. A factor of the type $\sin(n\phi)$ is common to all three expressions despite their differing contexts. This term represents a phase difference between interacting, modulated moments or local dipoles. Further, we refer to the quantum-mechanical work of H. Katsura [8], which derives a “reverse”-DM type interaction from considering the exchange Hamiltonian between two metal atoms. Katsura expresses his result, for both the one- and two-hole cases, as a triple crossed-product (here slightly expanded for clarity):

$$\vec{P} \approx -\frac{eV}{3\Delta} I \vec{e}_{12} \times \hat{r} |\vec{e}_1||\vec{e}_2| \sin\theta_{12}$$ \hspace{1cm} (4)

$$\vec{P} \approx -\frac{4e}{9} \left( \frac{V}{\Delta} \right)^3 I \vec{e}_{12} \times \hat{r} |\vec{e}_1||\vec{e}_2| \sin\theta_{12}$$ \hspace{1cm} (5)

Again, polarization is proportional to a term (or two in the one-hole system) which varies with $\theta$, the phase difference between two magnetic moments on interacting sites.

**Figure 1.** Two chains of modulated moments showing a phase difference. 1a) Phase-separated sinusoidal order. 1b) Phase difference between two chains with spiral order is realized as a constant angular differential; the third row is a super-position of the first two.

### 3. Discussion

The importance of phase in all of the preceding work is usually understated, though it has more recently received the attention deserved [6, 7]. Here, we highlight the universality of phase in these exchange mechanisms, and the underlying simplicity of symmetry arguments.

The salient results of the Mostovoy and Betouras et. al. can be derived from simple symmetry arguments. Ferro-electricity cannot arise in a system with a centre of inversion. Cosine waves have a centre of inversion every $\pi$ radians; when $\cos(Q.x) = 1$ for magnetic ordering (See Fig. 2). If no magnetic inversion centre is coincident with an inversion centre of the crystal structure then the centro-symmetry of the system is lost. Hence, for commensurate magnetic order to break centro-symmetry it must be displaced from the atomic lattice; this is equivalent to a phase-difference, $\phi_0$, at the centre of symmetry. For incommensurate ordering, every possible value of $\cos(Q.x)$ is realized in the crystal, and there must always be a magnetic centre of inversion coincident with one of the atomic lattice, negating any macroscopic polarisation. However, if there are several such spin density waves (SDWs) and their inversion centres are not coincident then the system becomes acentric once more: this is equivalent to a phase difference, $\phi$, between the SDWs. The quantitative calculations (Eq. 2 & 4) demonstrate that the magnitude of the net polarization is proportional to $\phi$; magnetic order not only breaks centro-symmetry, but it is strongly coupled to the polarization that arises.

In the work of Katsura the central concept is the triple cross product, the DM like interaction between two neighbouring sites (Eq. 5 & 6), this is only non-zero in systems
Figure 2. A commensurate SDW upon a line of atoms: black circles represent magnetic atoms upon sites of inversion symmetry; arrows represent their magnetic moment; open circles denote centres of inversion for the SDW. Note that, as axial vectors, magnetic moments are not reversed by inversion. a) \( \phi_0 = 0 \), Lattice and SDW inversion centres coincide; the system is centro-symmetric. b) \( \phi_0 \neq 0 \), None of the SDW or lattice inversion centres coincide; the system is acentric.

Figure 3. The orbits of magnetic moments described by two perpendicular cosine waves for various phase differentials: a) \( \phi = 0 \); b) \( \phi = \frac{\pi}{6} \); c) \( \phi = \frac{\pi}{3} \); d) \( \phi = \frac{\pi}{2} \). The component axes are at an angle of \( \frac{\pi}{4} \) to the magnetisation axes. The evolution of the ordering is continuous with \( \phi \); co-linear for \( \phi = 0 \), then elliptical until circular spirals appear for \( \phi = \frac{\pi}{2} \).

showing spiral ordering of the magnetic moments. The usual way to express the magnetic moment in a spiral is \( \vec{M} = M_1 \vec{e}_1 \cos(\vec{Q} \cdot \vec{x}) + M_2 \vec{e}_2 \sin(\vec{Q} \cdot \vec{x}) + M_3 \vec{e}_3 \), where \( \vec{e}_1, \vec{e}_2, \vec{e}_3 \) form an orthogonal basis and \( \vec{Q} \) is the propagation vector. An alternative, representation is \( \vec{M} = M_a [(\vec{e}_1 + \vec{e}_2) \cos(\vec{Q} \cdot \vec{x}) + (\vec{e}_1 - \vec{e}_2) \cos(\vec{Q} \cdot \vec{x} + \phi)] + M_b \vec{e}_3 \). This form allows us to consider the action (and meaning) of a phase difference between the perpendicular components of a magnetic spiral. Such a phase shift defines the spirals ellipticity; in extemis the ordering becomes co-linear (Figure 2). This argument can be reversed; when structures show a change from collinear to spiral ordering we can consider this as a phase shift between two components; as this phase shift evolves a measurable change in ellipticity would be observed, and the resulting polarisation should be correlated to the ellipticity of the magnetic ordering. This correlation is well demonstrated in TbMnO\(_3\) [9]; the relevant graphs are reproduced for convenience (Figures 4 & 5). Thus, key to any DM type striction is the evolution of a phase difference between perpendicular SDWs, which induces a spiral ordering.

This simple concept can be extended to include charge ordering (charge density waves) as well as magnetic ordering (spin density waves). Charge density waves are scalar fields and, as such, transform under inversion in the same way pseudo-axial vectors. Hence, by the same arguments, inversion symmetry is destroyed when a CDW is displaced (in phase) from the lattice inversion centres or from a SDW in the same system.

One of the (many) advantages of using representation theory for analysing such magnetic orderings is identification of fixed phase factors in a system. For spirals composed of multiple basis vectors, the relative phase between each is free; this is true even if joined under co-representational analysis [10]. The definitions of the anti-unitary operator leaves an unprescribed factor of modulus 1 [12], synonymous with a phase difference between the IRs brought together by the operator itself [10, 11]. If the magnetic order is represented by a single, 1-dimensional IR then the phase difference is fixed between atoms related by symmetry or lattice translations. Further, we can read directly from the irreducible representations (IRs) of the group whether...
inversion is preserved. If the crystallographic space group is invariant under inversion then there are two possibilities. When the magnetic \( k \)-vector is invariant under inversion the system will retain its centre of inversion if (and only if) the system orders under an IR in which inversion is represented by the appropriate unitary matrix. When \( k \) is not invariant under inversion, then the system can only be centro-symmetric when ordering under a co-representation of type \( a \).

4. Conclusions
Phase differences between physical, electrical and atomic orderings give rise to interesting interactions, yet this freedom of a system is seldom considered. Indeed, phase difference appears ubiquitous in the emergence of magneto-electricity and spiral magnetic ordering; either by rendering a system acentric, or through reverse-DM interactions which arise between phase separated sites. However, phase differences between sites which are not symmetry related and between a material’s magnetic and atomic orderings is rarely addressed in refinement of magnetic data. It is clear from this review that assuming \( \phi_0 = 0 \) for a magnetic ordering will often be wrong in a multi-ferroic material. Further we have shown that the potential for ferro-electricity can be determined from the IR tables of the spin and charge density waves under which the system orders. Understanding the role of phase displacements, and how they are restricted by symmetry will be a key step in our developing understanding of these exciting materials.

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