Competing interactions in multiferroics and low-dimensional systems
van der Vegte, Marcus Antonius

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2010

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter 6

Incommensurate and ferroelectric states in materials with competing charge orders

Magnetically tuneable electric polarisation and giant magnetoelectric effects were recently found in frustrated magnets where competing interactions between spins result in states without inversion symmetry.[1; 2; 3; 4] Electric polarization was also observed in materials with acentric charge and orbital orders.[5; 6] It was recently predicted that the interplay between charge, orbital, and spin degrees of freedom in doped manganites results in coexistence of site-centred and bond-centred charge orders, which breaks inversion and makes these materials ferroelectric.[7] Here we approach the coexistence of two different charge orders from a phenomenological point of view and show that the resulting ferroelectric states are unstable against an incommensurate modulation of the electron density. This instability breaks the homogeneous states into ferroelectric domains separated by electrically charged domain walls. As temperature decreases and the amplitude of the charge modulation grows, the ferroelectric phase may become stable, but it still may contain a single domain wall with a negative free energy.

1This chapter is based on M. A. van der Vegte and M. Mostovoy, submitted to Physical Review Letters.
6.1 Introduction

Conducting chains are unstable against a periodic modulation of the electron charge or spin density that opens a gap in electron spectrum. The charge density wave in the chain with one electron per site doubles the lattice period and usually has maxima and minima either on the chain sites, in which case the chain remains equidistant, or on the chain bonds, in which case it gives rise to an alternation of long and short bonds. These two types of charge ordering are illustrated in Fig. 6.1 by the example of a chain of transition metal and ligand ions, where the site-centred charge density wave (s-CDW) is an alternation of charges on metal sites with the concomitant alternate displacements of ligands (Fig. 6.1a), while the bond-centred charge density wave (b-CDW) induces the alternate shifts of metal ions, resulting in the formation of dimers and a small modulation of ligand charges (Fig. 6.1b).

When these two orders are both present, the electron and ion charge density loses inversion symmetry and an electric dipole moment is generated in the chains. Ferroelectricity induced by the coexisting s-CDW and b-CDW orders was found in organic charge-transfer semiconductors, such as TTF-CA, with chains formed by stacked donor and acceptor molecules. At the so-called neutral-to-ionic transition pairs of neighbouring molecules form dimers, which triggers a transfer of charge from donors to acceptors and makes these systems polar. In this case the site- and bond-centred orders coexist and support each other. Ferroelectric transition was also observed in the (TMTTF)$_2$X charge-transfer salts (X = PF$_6$, AsF$_6$ and SbF$_6$), where the bond length alternation is imposed by the crystal structure, while the alternation of charges of the TMTTF molecules is induced spontaneously. Here the s-CDW and b-CDW compete and suppress each other, as both open a gap at the quasi-one-dimensional Fermi surface.

The competition between site- and bond-centred charge orders does not
Phenomenological model

In the quasi-one-dimensional system, shown in Fig. 6.2, the metal-ligand chains parallel to the $x$ axis form a two-dimensional array, in which neighbouring chains are displaced by half a lattice constant in the $x$-direction with respect to each other. Due to this displacement and interchain lattice interactions, alternate shifts of metal ions in one chain are coupled to alternate shifts of ligand ions in neighbouring chains and vice versa. Therefore, ordered states of this system are described by a two-dimensional order parameter, the first component of which, $\eta_1$, corresponds to the b-CDW in even chains and the s-CDW in odd chains (Fig. 6.2a) and vice versa for the second component, $\eta_2$ (Fig. 6.2b). Such states with differentiated chains, showing either site- or bond-centred ordering, will be called ‘OR’ states. They compete with the phases where the s-CDW and b-CDW are equally present in all chains, which we call ‘AND’ states and which are linear superpositions of the two
Incommensurate and ferroelectric states

Figure 6.2 Centrosymmetric charge orders in the chain array. (a), Bond-centred ordering in A-chains and site-centred ordering in B-chains, described by the order parameter $\eta_1$. As in Fig. 6.1, big and small circles are, respectively, transition metal and ligand ions, while arrows indicate their displacements in the ordered state. (b), Site-centred ordering in A-chains and bond-centred ordering in B-chains, described by the order parameter $\eta_2$. (c) and (d), The superpositions $\eta_1 \pm \eta_2$ with the bond- and site-centred orders present in all chains with equal weights. Yellow circles indicate inversion centers.

‘OR’ states with equal weights, $\eta_1 \pm \eta_2$ (Figures 6.2c and 6.2d). Other superpositions, $A\eta_1 + B\eta_2$, will be called mixed states.

All such states were found in the vanadium dioxide VO$_2$, which has the high-temperature rutile structure with two sets of equidistant V chains displaced with respect to each other along the c axis.[21] Below 340 K it undergoes a metal-insulator transition into the symmetric monoclinic M$_1$ phase where V ions in all chains are paired by the alternate shifts along the chain direction. Furthermore, V ions show alternate shifts in the direction perpendicular to the c axis. These zigzag twists of V-V bonds result from the pairing of V ions in neighboring chains. Uniaxial pressure and doping induce the asymmetric monoclinic M$_2$ phase, where half of the chains are dimerized and half are twisted, and the triclinic phase interpolating between M$_1$ and M$_2$.[21; 22]

The differentiated ‘OR’ states shown in Figs. 6.2a and 6.2b are centrosymmetric. However, their inversion centers (yellow circles) are shifted with respect to each other, which is why a superposition of these states, in general, breaks inversion symmetry and induces an electric polarization along the chains. The exceptions are the symmetric and antisymmetric superpositions - the ‘AND’ states with inversion centers between the chains (Figures 6.2c

[Figure 6.2: Diagrams showing centrosymmetric charge orders in the chain array.](https://example.com/figure62)
and 6.2d). The coupling between the electric polarization, \( P_x \), and the charge ordering is described by the term

\[
f_{FE} = -\lambda P_x \eta_1 \eta_2 (\eta_1^2 - \eta_2^2)
\]

invariant under all symmetry operations from the space group of the model (see Appendix A). Another term in free energy of the model, allowed by symmetry, is the so-called Lifshitz invariant,

\[
f_L = -\kappa (\eta_1 \partial_x \eta_2 - \eta_2 \partial_x \eta_1),
\]

which favours a periodically modulated phase where \( \eta_1, \eta_2 \) and \( P_x \) vary along the chains.

Next we note that irrespective of symmetry properties of systems with two competing orders, the terms (6.1) and (6.2) are either both allowed or both forbidden by symmetry. Indeed, both contain a part transforming as \( \eta_1 \eta_2 \), both are anti-symmetric under \( 1 \leftrightarrow 2 \) and both contain a term transforming as \( x \). Therefore, close to a second-order transition into an ordered state the homogenous ferroelectric state induced by coexisting charge orders is inherently unstable towards a sinusoidal variation of the order parameters and the induced electric polarization that suppresses ferroelectricity.

As temperature decreases, the sinusoidal modulation of polarization, which in general is incommensurate with the lattice, transforms into an array of ferroelectric domains with opposite polarizations along the \( x \) axis, separated by relatively narrow domain walls where the charge density, \( \rho = -\frac{\partial P_x}{\partial x} \), is nonzero. The electric charges of the domain walls \( (\pm P_x \text{ per unit area}) \) alternate along the chains. When the domain wall free energy becomes positive, the lock-in transition into a uniformly dimerized ferroelectric phase occurs.

### 6.3 Phase diagram

If \( LI \) is forbidden by symmetry, the phase diagram of the model only contains homogeneous states and is found by minimizing its free energy,

\[
f_0 = \frac{a}{2} \eta^2 + \frac{1}{4} \eta^4 \left( b + b' \sin^2 2\phi \right) + \frac{1}{6} \left( c + c' \sin^2 2\phi \right) \\
+ \frac{1}{8} \eta^8 \left( d + d' \sin^2 2\phi + d'' \sin^4 2\phi \right)
\]

(6.3)

where \( \eta \) and \( \phi \) are the polar coordinates in the plane: \( \eta_1 = \eta \cos \phi \) and \( \eta_2 = \eta \sin \phi \). To stabilize the Mixed state one has to expand free energy at least up to eighth-order terms in \( \eta \). The phase diagram with the competing uniformly
Incommensurate and ferroelectric states

Figure 6.3 Phase diagram of the chain array model. (a), Phase diagram obtained for the case the LI is forbidden by symmetry, containing only uniformly dimerized phases: the 'OR' state (Figs. 6.2a and 6.2b), the 'AND' state (Figs. 6.2c and 6.2d) and the ferroelectric (FE) state. The parameter $a$ along the vertical axis plays the role of temperature, while the parameter $b'$ along the horizontal axis determines the free energy difference between the 'AND' and 'OR' states. (b), The phase diagram for the case when the LI (6.2) is allowed. Here IC denotes the periodic incommensurate phase, while DW denotes the phase with a single domain wall. The parameters of the Landau expansion used to obtain these phase diagrams are: $b = 1$, $d'' = 2$ and $c = c' = d = d' = 0$ for $\kappa = 0.1$ and $\gamma = 1$. To plot the phase diagram in panel (b) we used $\kappa = 0.1$ and $\gamma = 1$.

The full phase diagram of the model including inhomogeneous phases is shown in Fig. 6.3b. It was obtained by minimizing $\int d^2x(f_0 + f_1)$, where

$$f_1 = \kappa \eta^2 \frac{\partial \phi}{\partial x} + \frac{\gamma}{2} \left[ \left( \frac{\partial \eta}{\partial x} \right)^2 + \eta^2 \left( \frac{\partial \phi}{\partial x} \right)^2 \right]$$

(6.4)

is the Lifshitz invariant (6.2) plus the second-order terms in gradients of the order parameters necessary to keep the gradients finite ($\gamma > 0$). The LI dramatically modifies the phase diagram (see Fig 3.b). A large part is now occupied by the incommensurate phase. Furthermore, the Mixed phase, which in this case is ferroelectric (FE), is separated from the centrosymmetric 'AND' and 'OR' phases by domain wall (DW) states containing a single domain wall. Their origin can be understood as follows. The free energy has the form of the action of a charged particle with the coordinates $(\eta_1, \eta_2)$ moving in...
Figure 6.4 Inhomogeneous states. (a), The incommensurate state shown as a closed trajectory in the $\eta_1\eta_2$ plane. White and (black) circles are minima of $f_0$ corresponding to 8 uniform ferroelectric states with positive (negative) polarization. (b), Domain wall states represented by trajectories between two minima of $f_0$ corresponding to ferroelectric states with opposite electric polarisations. Only the 4 domain walls with the lowest free energy are shown.

the potential $U_0 = -f_0(\eta, \phi)$ and a magnetic field $\propto \kappa$, $x$ playing the role of time. The homogenous 'AND', 'OR' and ferroelectric phases correspond to maxima of $U_0$, the incommensurate state corresponds to the rotational motion of the particle around the coordinate centre (Fig. 6.4a), while domain walls are the trajectories connecting two neighbouring maxima of the potential energy traversed in the direction determined by the sign of $\kappa$. There are in total 8 uniform ferroelectric states (minima of $f_0$ indicated by circles in Fig. 6.4a), of which 4 (white circles) have positive polarization and 4 (black circles) have negative polarization. In the incommensurate state the free energy of all domain walls (equal the action along the corresponding trajectory) is negative. Furthermore, the free energy of the domain wall where electric polarization varies from negative to positive is different from that where the polarization varies from positive to negative. In the DW state one domain wall has a negative free energy, while another one has a positive free energy. At the phase boundaries of the DW phases the free energy of one domain wall changes sign. Since the domain wall is charged, it can be moved by an applied electric field, so that the DW state is, in essence, also ferroelectric.
Figure 6.5 Ordered states in half-doped manganites. (a) and (b), The two energetically equivalent states, described by the order parameters $\eta_1$ and $\eta_2$, with the checkerboard charge disproportionation between the nominal Mn$^{4+}$ (circles) and Mn$^{3+}$ ions with the staggered orbital ordering on the Mn$^{3+}$ sites.[11][12] Arrows indicate their displacements of the Mn$^{4+}$ ions. (c) and (d), Superpositions $\eta_1 \pm \eta_2$, which show the displacement pattern of Mn ions and $P2_1nm$ space symmetry reported in ref. [14]. An orbital ordering in these states occurs without charge disproportionation.

6.4 Discussion

These results directly apply to realistic materials with charge ordering described by two-component order parameters. In vanadium dioxide the ferroelectric coupling and the Lifshitz invariant are both forbidden by symmetry (see Table 2 in Appendix A). Here the order parameters $\eta_1$ and $\eta_2$, describing the monoclinic M$_2$ phase with differentiated dimerized and twisted chains, have the same inversion center, so that the monoclinic M$_1$ and triclinic phases, which are superpositions of and , are also centrosymmetric.

On the other hand, for doped manganites both $f_{FE} = -\lambda_b P_b \eta_1 \eta_2 (\eta_1^2 \eta_2^2)$, inducing polarization along the $b$ axis, and $f_L = -\kappa (\eta_1 \partial_y \eta_2 - \eta_2 \partial_y \eta_1)$ are allowed by symmetry (Table 6.3 in Appendix A). Here the order parameters $\eta_1$ and $\eta_2$ describe the two degenerate structures with the checker board charge...
disproportionation and staggered orbital ordering (Figs. 5a and b).[11; 12] These orders double the lattice period along the \( b \) axis and reduce the high-temperature \( Pbnm \) symmetry down to \( P2_1/m \). The superpositions of these two states with equal weights, \( \eta_1 \pm \eta_2 \), have an orbital ordering but no charge disproportionation (Figs. 6.5c and d) and belong to the \( P2_1nm \) space group reported for \( \text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3 \).[14] In the case of manganites, however, also the dimerized states, \( \eta_1 \pm \eta_2 \), break inversion symmetry and induce the electric polarization, \( P_a = \eta_1 \eta_2 \), along the \( a \) axis.[19; 23] This polarization is induced by the combination of the dimerization of Mn ions and the orthorhombic distortion of the perovskite \( \text{RMnO}_3 \) structure, and has the same origin as the polarization \( P \parallel a \) in the collinear E-phase of multiferroic manganites[24] and the excitation of magnons by the electric of light \( e \parallel a \) in manganites with a non-collinear spiral ordering.[25]

Since the amplitude of the charge and orbital modulation in manganites is small,[13; 17] the Lifshitz invariant \( f_L \) can suppress a uniform ferroelectric state in a wide temperature interval. One obvious physical origin of this invariant is electron doping. Less obviously, this term is also generated by the expansion of the harmonic lattice energy of the simple model discussed above in powers of gradients of the order parameters. This may explain the incommensurate phase observed in ferromagnetic manganites at precisely half doping.[26][27] The expected commensurate state appears together with an antiferromagnetic ordering,[28] which apparently plays an important role in stabilization of the ferroelectric phase.[7; 23]

### Appendix 6.A  Symmetry arguments

In all considered examples in this chapter the space group elements: two-fold (screw) axes, (glide) mirrors and inversion are represented two-by-two matrices of the types: \( \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix} \) or \( \begin{pmatrix} 0 & c \\ d & 0 \end{pmatrix} \), where \( a^2 = b^2 = c^2 = d^2 = 1 \), as the states \( \eta_1 \) and \( \eta_2 \) are physically different from the states \( \eta_1 \pm \eta_2 \) and cannot be transformed into each other. Direct inspection shows that under such transformations the fifth-order magneto-electric coupling and LI are either both allowed or both forbidden by symmetry. In the remaining of this appendix the symmetry properties of the chain array model, vanadium dioxide and Manganites are discussed.

**Chain array:** The space group of the two-dimensional chain array shown in Fig. 6.2 has three generators (omitting the identity operation): mirror \( m_x = (-x, y) \), screw axis \( \tilde{2}_x = (1/2 + x, 1/2 - y) \) and inversion \( I = (-x, -y) \). The coordinate origin coincides with the position of a transition metal site in
an undistorted lattice. The order parameters $\eta_1$ and $\eta_2$ describing the lattice distortions, shown in Figures 6.2a and 6.2b, form a two-dimensional irreducible representation that changes sign under the shift by one lattice constant in the $x$ direction. The transformation properties of this representation are given in Table 6.1.

<table>
<thead>
<tr>
<th></th>
<th>$m_x$</th>
<th>$2_x$</th>
<th>$I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_1$</td>
<td>(1 0)</td>
<td>(0 −1)</td>
<td>(1 0)</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>(0 −1)</td>
<td>(1 0)</td>
<td>(0 −1)</td>
</tr>
</tbody>
</table>

**Table 6.1** Transformations of the order parameters for the chain array model.

*Vanadium dioxide:* The symmetry of the high-temperature rutile structure of VO$_2$ is $P4_2/mnm$. Its generators are $2_c = (−x, −y, z)$, $\bar{4}_c = (−y + 1/2, x + 1/2, z + 1/2)$, $\bar{2}_b = (−x + 1/2, y + 1/2, −z + 1/2)$ and inversion $I_c = (−x, −y, z)$. The two V ions in the unit cell with the coordinates $(0,0,0)$ and $(1/2,1/2,1/2)$ give rise to two groups of chains in the $c$ direction. The wave vector in the charge-ordered state is $(0,1/2,1/2)$. Here $\eta_1$ describes the alternate shifts of V ions along the $c$ axis in the first chain and along the $b$ axis in the second chain. For $\eta_2$ it is the other way around. The transformation properties of the order parameter under the generators of the space group, which do not change the direction of the charge-density-wave vector, are shown in Table 2. Since both $\eta_1$ and $\eta_2$ are odd under inversion, the fifth-order magnetoelectric coupling and LI invariant are forbidden.

<table>
<thead>
<tr>
<th></th>
<th>$2_c$</th>
<th>$2_b$</th>
<th>$I_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_1$</td>
<td>(1 0)</td>
<td>(0 −1)</td>
<td>(0 −1)</td>
</tr>
<tr>
<td>$\eta_2$</td>
<td>(0 −1)</td>
<td>(1 0)</td>
<td>(−1 0)</td>
</tr>
</tbody>
</table>

**Table 6.2** Transformation properties of the order parameters for VO$_2$.

*Manganites:* The space group of the high-temperature structure of La$_{0.5}$Ca$_{0.5}$MnO$_3$ is $Pbnm$. We use the three (glide) mirrors, $\bar{m}_a = (−x + 1/2, y + 1/2, z)$, $\bar{m}_b = (x + 1/2, −y + 1/2, z + 1/2)$ and $m_c = (x, y, 1/2 − z)$, as its generators. The components $\eta_1$ and $\eta_2$ of the order parameter describe the two energetically equivalent states, where the charge and orbital orders double the lattice period along the $b$ axis (Figures 5a and 5b).[12] Their transformation properties are given in Table 3. The $\eta_1$ or $\eta_2$ reduces symmetry down to $P2_1/m$, the equal weight superpositions, $\eta_1 \pm \eta_2$, belong to the noncentrosym-
metric $P21nm$ space group reported for $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$.[14]

\[
\begin{array}{ccc}
\eta_1 & m_a & \tilde{m}_a \\
\eta_2 & \tilde{m}_b & m_c \\
0 & 1 & -1 \\
1 & 0 & 1
\end{array}
\]

Table 6.3 Transformation properties of the two-dimensional irreducible representation of $Pbnm$ group, describing the charge ordering in doped manganites.
Bibliography