Coupling of replicate order-parameters in incommensurate multiferroics

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Abstract
The specific properties of incommensurate multiferroic phases resulting from the coupling of order-parameter replicates are worked out using the illustrative example of iron vanadate. The specific properties of incommensurate multiferroics resulting from the coupling of replicate order-parameters [6]. These properties are illustrated here by the coupling of two antiferromagnetic order-parameters [2, 4, 5]. A different situation has been pointed out in the pyroxene NaFeSi$_2$O$_6$ [6], in which the onset of the ferroelectric phase results from the coupling of two order-parameters having the same symmetry but a different phase. The possibility of inducing an additional broken symmetry phase by replication of a single order-parameter was shown [6] to reflect the existence of an effective continuous symmetry which is broken at the transition to the ferroelectric phase, expressing the continuous rotation of the phase modulation mode (phason) associated with the free-sliding of the incommensurate spin wave formed in the multiferroic phase.

Phase transitions induced by the coupling of replicate order-parameters display a number of specific features, such as the stabilization of additional broken symmetry phases and a critical dependence of the dephasing between the order-parameters [6]. These properties are illustrated here by the theoretical description of the transition to the multiferroic phase observed in iron vanadate FeVO$_4$ which, due to the low triclinic symmetry of the paramagnetic phase [7, 8], constitutes an unambiguous example of transition induced by the coupling of order-parameter replicates. Expressing the transition order-parameter in terms of magnetic spin waves allows us to show that the order-parameter dephasing corresponds to the angle between spins forming pairs in the antiferromagnetic spiral structure, and that isotropic exchange interactions contribute to the stabilization of the ferroelectric phase.

One of the distinctive features of magnetic multiferroic materials is the existence of an incommensurate ferroelectric phase induced by the coupling of two antiferromagnetic order-parameters. In multiferroic compounds, such as TbMnO$_3$ [1], Ni$_3$V$_2$O$_8$ [2] or MnWO$_4$ [3] the two order-parameters display different symmetries, i.e. they transform as distinct irreducible representations (IRs) of the paramagnetic space group [2, 4, 5]. A different situation has been pointed out in the pyroxene NaFeSi$_2$O$_6$ [6], in which the onset of the ferroelectric phase results from the coupling of two order-parameters having the same symmetry but a different phase. The possibility of inducing an additional broken symmetry phase by replication of a single order-parameter was shown [6] to reflect the existence of an effective continuous symmetry which is broken at the transition to the ferroelectric phase, expressing the continuous rotation of the phase modulation mode (phason) associated with the free-sliding of the incommensurate spin wave formed in the multiferroic phase.

Phase transitions induced by the coupling of replicate order-parameters display a number of specific features, such as the stabilization of additional broken symmetry phases and a critical dependence of the dephasing between the order-parameters [6]. These properties are illustrated here by the theoretical description of the transition to the multiferroic phase observed in iron vanadate FeVO$_4$ which, due to the low triclinic symmetry of the paramagnetic phase [7, 8], constitutes an unambiguous example of transition induced by the coupling of order-parameter replicates. Expressing the transition order-parameter in terms of magnetic spin waves allows us to show that the order-parameter dephasing corresponds to the angle between spins forming pairs in the antiferromagnetic spiral structure, and that isotropic exchange interactions contribute to the stabilization of the ferroelectric phase.

Starting from the paramagnetic symmetry $P11'$ of FeVO$_4$, a single two-dimensional IR (denoted $\Gamma$) can be constructed in the general direction $k = (0.222, 0.089, 0.012)$ of the triclinic Brillouin-zone reported experimentally [7], the matrices of which are given in table 1. A symmetry analysis of the corresponding two-component order-parameter $(\eta_1 = \rho_1 e^{i\theta_1}, \eta_1^* = \rho_1 e^{-i\theta_1})$ shows that a single second-order transition to an incommensurate non-polar phase of point group 11' (phase I) can be induced by $\Gamma$, which coincides with the antiferromagnetic phase observed between $T_F = 22$ K and $T_F = 15$ K in FeVO$_4$ [7]. Since the propagation vector $k$ is nearly temperature-independent, a further symmetry breaking mechanism to the ferroelectric phase stable below $T_F$ cannot be obtained if we do not assume that a coupling takes place at $T_F$ between the order-parameter $(\eta_1, \eta_1^*)$ and a dephased copy $(\eta_2 = \rho_2 e^{i\theta_2}, \eta_2^* = \rho_2 e^{-i\theta_2})$ having the same symmetry, as already noted in [8]. Although they display the same symmetry the two order-parameters represent two different sets of antiferromagnetic spin waves. The two sets couple at $T_F$ but remain in phase, therefore preserving space inversion. At $T_F$ the phases are decoupled destroying space inversion and
resulting in a complex polar spiral structure. The free-energy expressing the coupling between the two order-parameter copies can be written:

\[
F = a_1 \rho_1^2 + b_1 \rho_2^2 + 2c_1 \rho_1 \rho_2 \cos \theta + \frac{a_2}{2} \rho_1^4 + \frac{b_2}{2} \rho_2^4 + \frac{c_2}{2} \rho_1^2 \rho_2^2 \cos 2\theta
\]

where \( \theta = \theta_1 - \theta_2 \). Figure 1 shows the phase diagram deduced from the minimization of \( F \) with respect to \( \rho_1 \), \( \rho_2 \) and \( \theta \). Below the range of stability of phase I \( (\theta = n\pi) \), the phase diagram contains an additional phase II of magnetic point group \( 11' \), corresponding to \( \theta \neq n\pi \), which displays a spontaneous polarization \( \vec{P} \) in a general direction, as observed below \( T_F \) in FeVO\(_4\) [7, 9]. The topology of the phase diagram of figure 1 is specific to replicate order-parameters, the symmetries of phases I \((11')\) and II \((11')\) representing, respectively, the minimal symmetry group induced by \( \Gamma \), defined as the invariance group of the general direction in the representation space, and the lowest symmetry group induced by the reducible representation formed by the sum of the two IRSs \( \Gamma + \Gamma \) corresponding to the kernel of the homomorphism of the paramagnetic space group \( G_p \) on \( \Gamma \).

The straight thermodynamic path shown in figure 1 can be parametrized as \( a_1 = \chi (T - T_F) + 4c_2 w \) and \( b_1 = \xi (T - T_F) + w \), where the constant parameters \( \chi \), \( \xi \) and \( w \) characterizing the path fulfill the condition \( \chi \xi (T - T_F)^2 + 4c_2 \xi (T_F - T_F) + 3c_1^2 = 0 \). It yields the property that the order-parameter amplitudes \( \rho_1 = (-a_2/2)^{1/2} \) and \( \rho_2 = (-b_2/2)^{1/2} \) vary non-critically at \( T_F \), while the dephasing \( \theta \) plays the role of the critical transition order-parameter, varying below \( T_F \) as:

\[
\sin \theta = \left( \frac{\chi w}{4c^2} + \frac{\xi}{w} \right)^{1/2} \sqrt{T_F - T}
\]

where the \( c \) parameter is defined here above by the parametrization of \( a_1 \). This property differs from the standard behaviour found in multiferroic phases induced by the coupling of order-parameters having different symmetries where the dephasing \( \theta = \pi/2 \) is constant and the order-parameter amplitudes \( \rho_i \) vary critically with temperature. We show below that the critical variation of \( \theta \) can be interpreted as the temperature dependence of the angle between paired spins which are parallel in phase I and become non-parallel in phase II. The equilibrium polarization deduced from the coupling free-energy \( F = a_i P_i \rho_1 \rho_2 \sin \theta + \lambda ij P_i P_j \), gives in triclinic basis:

\[
P^i = -\frac{1}{2} (\lambda^{-1})^{ij} \alpha_j \rho_1 \rho_2 \sin \theta.
\]

Close to \( T_F \) one gets \( P^i = \Lambda^i \sqrt{T_F - T} \) with \( \Lambda^i = -\frac{1}{2} (\chi w + 4c_2 \xi/2)^{1/2} (\lambda^{-1})^{ij} \alpha_j \). This power law and the correlated Curie–Weiss like sharp peak of the dielectric permittivity \( \varepsilon \) are consistent with the dependence on temperature of \( P(T) \) and \( \varepsilon(T) \) observed on single crystal [7] and polycrystalline [9] FeVO\(_4\) samples. It confirms the hybrid pseudo-proper character [10] of the ferroelectric transition which behaves critically as a proper ferroelectric, although the small value of \( |P| \) found below \( T_F \) (6–12 \( \mu \)C m\(^{-2}\)) is of the order of magnitude of an improper ferroelectric. Since inversion symmetry is broken at the transition, the system displays two ferroelectric domains [11] with opposed polarizations corresponding to opposed dephasings \( \pm \theta \).

Application of a magnetic field does not give rise to spectacular magnetoelectric effects in FeVO\(_4\), since only trivial couplings between the order-parameter and the magnetic field are allowed by the low symmetry of the system. Thus, biquadratic couplings of the order-parameter to the magnetic free-energy \( \mu_i M^j M^j \) yield a renormalization of the \( a_i, b_i \), and \( c_i \) coefficients in equation (1) explaining the observed shift of \( T_F \) to lower temperatures [8] with increasing magnetic field. Standard magnetoelectric couplings \( P^i M^j M^j \) are responsible for the progressive reduction and suppression of the multiferroic phase reported at high field [12]. Above \( 3 \) T a new ferroelectric phase is observed at slightly lower temperature than \( T_F \) [12], which can be interpreted either as the result of a magnetic field induced lock-in transition to a commensurate multiferroic phase of triclinic symmetry 1, or as a re-entrance of the multiferroic zero-field phase.

A different manifestation of magnetoelectricity can be found in the toroidal effects which can be predicted in the ferroelectric phase of FeVO\(_4\). Under applied field \( \vec{B} \) the toroidal free-energy is:

\[
F^T = g_0 T^i T^i + \alpha_0 T^i B^i \rho_1 \rho_2 \sin \theta
\]
where $T^I = k_f B^f$ are the induced toroidal moment components and $\kappa^I_{ij} = -\frac{1}{2} \rho_1 \rho_2 \sin \theta (g^{-1})^{li} \alpha_{ij}$ the magnetotoroidal susceptibility components. It yields:

$$T^I = K^I \sqrt{H_F} - T$$

(5)

with $K^I = -\frac{1}{2} (\chi w + 4 \tilde{c}_w) \frac{1}{2} (g^{-1})^{li} \alpha_{ij} B^j$. Equation (5) shows that at constant field the toroidal moment varies critically as the spontaneous polarization at zero fields. Since all components of the magnetotoroidal tensor are non-zero the induced toroidal moment should not orient along $\vec{B}$.

To gain insight into the microscopic spin states forming the magnetic structures, one can express the transition order-parameter replicates le us consider the six spins contained in the unit-cell with $n = \bar{n} + \bar{p}b + qc$, with $m = 1$ or $-1$ for atoms (1, 2, 3) or (1, 2, 3), respectively, one can write:

$$\tilde{\vec{z}}_{n}^{m,\mu} = \sum_{i} \left[ \vec{U}_{i} \text{e}^{ik \cdot \vec{R}_{n}}, \vec{W}_{i}^{*} \text{e}^{-ik \cdot \vec{R}_{n}} \right]$$

(6)

where $\vec{U}_{i}$ and $\vec{W}_{i}$ are spin waves transforming as $\Gamma_i$ for each $j$ and each space component. It yields 18 spin waves which are copies of $\eta$ and $\eta^*$. Equation (6) can be written in real form as:

$$\tilde{\vec{z}}_{n}^{m,\mu} = \rho_{i}^{m} \cos(k \vec{R}_{n}) - m \vec{W}_{i} \sin(k \vec{R}_{n})$$

(7)

where $\vec{U}_{i} \vec{W}_{i}$ are replicas of $\eta$ and $\eta^*$. Equation (7) can be written in real form as:

$$\tilde{\vec{z}}_{n}^{m,\mu} = \sum_{i} \left[ \vec{U}_{i} \cos(k \vec{R}_{n}) + m \vec{W}_{i} \sin(k \vec{R}_{n}) \right]$$

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where $\vec{U}_{i}$ and $\vec{W}_{i}$ are replicas of $\eta$ and $\eta^*$. Equation (7) can be written in real form as:
Expanding the constraints given by equations (12) to the commensurate or incommensurate, polar or non-polar phases exchange interactions. Considering interactions between first-neighbouring cells are involved. Below phase I, we consider the simple situation where only the stability limits of phase II. In order to show that these interactions between first-neighbouring cells are involved.

The possibility of stabilizing additional phases by coupling two dephased order-parameters having the same symmetry, i.e. transforming as the same irreducible representation of the parent phase, was first noted in superconductors [13] which involve a breaking of the continuous gauge symmetry. Let us consider an example of the replication mechanism was described in ferroelectric liquid crystals [14] in which the continuous rotational symmetry is broken at the transition to the ferroelectric phase. Although structural and magnetic phase transitions correspond to discrete symmetry breaking processes which do not give rise to additional phases by order-parameter replication, transitions to incommensurate structural or magnetic structures permit a realization of the replication mechanism, as shown in the present work for the multiferroic transition in FeVO₄. This is because the thermodynamic features of the transition are driven by an effective continuous group generated by the images of the crystallographic translations in the order-parameter space.

\[
\vec{u}_1 + \vec{w}_2 = \vec{u}_2 + \vec{w}_1 = 0,
\]

\[
\vec{u}_1 \cdot \vec{w}_2 + \vec{u}_2 \cdot \vec{w}_1 = 0
\]

and \( H \) becomes:

\[
H = \alpha(\vec{u}_1^2 + \vec{w}_1^2) + \beta(\vec{w}_1^2 + \vec{u}_2^2) + 2\gamma(\vec{u}_1 \cdot \vec{w}_1 + \vec{u}_2 \cdot \vec{w}_2)
\]  

\[
(13)
\]

Phase I corresponds to \( \vec{u}_1 = \pm \vec{u}_2 \) and \( \vec{w}_1 = \pm \vec{w}_2 \). Accordingly, the exchange Hamiltonian has the constant value \( H_0 = \frac{h}{2}(\alpha + \beta) \). The stability of this phase can be tested by varying slightly the four vectors \( \vec{u}_1, \vec{u}_2, \vec{w}_1, \vec{w}_2 \).

Expanding the constraints given by equations (12) to the first-order shows that only five independent parameters \( (\omega^2, \delta u_{1x}, \delta u_{1y}, \delta w_{1y}, \delta w_{2y}) \), where \( \omega^2 = \delta u_{1x}^2 + \delta u_{1y}^2 + 2\delta u_{1z}^2 \), determine the stability of phase I. At the second order the Hamiltonian reads:

\[
H = H_0 + \alpha(\omega^2 + \delta u_{1x}^2 + \delta u_{1y}^2 + \beta(\omega^2 + \delta w_{1y}^2 + \delta w_{2y}^2) + 2\gamma \delta u_{1x} \delta w_{2y} + \delta w_{1y} \delta w_{2y}).
\]  

\[
(14)
\]

The transition from phase I to the multiferroic phase II associated with the wavevector \( \vec{k}_c \) occurs when \( \frac{\partial H_0}{\partial \vec{k}_c} = 0 \) and \( |\alpha(\vec{k}_c)| = |\gamma| \) or \( |\beta(\vec{k}_c)| = |\gamma| \). These equations give, respectively, the equilibrium value of \( \vec{k}_c \) in phase I and the stability limits of phase II. In order to show that these limits exist and that a polar phase can actually be stabilized below phase I, we consider the simple situation where only interactions between first-neighbouring cells are involved.

In this case the non-zero coefficients in equation (10) are \( h_{0}^{1-1} \), \( h_{2}^{1+1} \), \( h_{2}^{1+1} \) and one has:

\[
\alpha(\vec{k}_c) = h_{0}^{1-1} + (2h_{1}^{11} + h_{0}^{1-1} + h_{1}^{-11}) \cos \vec{k}_c \cdot \vec{a} + (\vec{a} \rightarrow \vec{b}) + (\vec{a} \rightarrow \vec{c})
\]

\[
\beta(\vec{k}_c) = (2h_{1}^{11} - h_{0}^{1-1} - h_{1}^{-11}) \cos \vec{k}_c \cdot \vec{a} + (\vec{a} \rightarrow \vec{b}) + (\vec{a} \rightarrow \vec{c})
\]

\[
\gamma(\vec{k}_c) = 4(h_{1}^{1-1} - h_{0}^{1-1}) \sin \vec{k}_c \cdot \vec{a} + (\vec{a} \rightarrow \vec{b}) + (\vec{a} \rightarrow \vec{c})
\]  

\[
(15)
\]

If, for instance, \( h_{1}^{11} > 0 \) and \( h_{0}^{1-1} < 0 \) then one finds a minimum of \( H_0 \) at \( \vec{k}_c = (\frac{\pi}{a}, 0, 0) \) and \( \alpha \) becomes \( h_{0}^{1-1} - (2h_{1}^{11} + h_{0}^{1-1} + h_{1}^{-11}) + (2h_{1}^{11} + h_{0}^{1-1} + h_{1}^{-11}) + (2h_{1}^{11} + h_{0}^{1-1} + h_{1}^{-11}) \), with an analogous expression for \( \beta \) and \( \gamma \) = 0. When the \( h_{0}^{1-1} \) and \( h_{1}^{11} \) coefficients vary, \( \alpha \pm \gamma \) and \( \beta \pm \gamma \) take positive and negative values. The stability of the non-polar phase depends only on the two parameters \( \sigma = h_{0}^{1-1} - 2h_{1}^{11} + h_{1}^{11} + h_{1}^{-11} + h_{0}^{1-1} + h_{1}^{-11} \) and \( \tau = - (h_{0}^{1-1} + h_{1}^{11}) + (h_{0}^{1-1} + h_{1}^{-11}) + (h_{0}^{1-1} + h_{1}^{-11}) \), where \( \sigma > h_{0}^{1-1} \). The corresponding phase diagram in the \( \sigma - \tau \) plane is shown in figure 3. Thus the non-polar phase I and polar phase II can both be stabilized by isotropic exchange interactions. Considering interactions between spins belonging to more distant unit-cells would stabilize commensurate or incommensurate, polar or non-polar phases depending on the values of the \( h_{0}^{11} \), \( h_{1}^{11} \), \( h_{1}^{11} \) coefficients of the exchange Hamiltonian. However, since no assumption is made about the actual values of the interaction coefficients, one cannot exclude that in \( h_{0}^{11} \), \( h_{1}^{11} \) space, the region of the phase diagram in which the polar phase is stable would actually be forbidden.
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