

Electromagnon excitations in modulated multiferroics

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The phenomenological theory of ferroelectricity in spiral magnets presented in [M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006)] is generalized to describe consistently states with both uniform and modulated-in-space ferroelectric polarizations. A key point in this description is the symmetric part of the magnetoelectric coupling since, although being irrelevant for the uniform component, it plays an essential role for the nonuniform part of the polarization. We illustrate this importance in generic examples of modulated magnetic systems: longitudinal and transverse spin-density wave states and planar cycloidal phase. We show that even in the cases with no uniform ferroelectricity induced, polarization correlation functions follow the soft magnetic behavior of the system due to the magnetoelectric effect. Our results can be easily generalized for more complicated types of magnetic ordering, and the applications may concern various natural and artificial systems in condensed matter physics (e.g., magnon properties could be extracted from dynamic dielectric response measurements).

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The existence of magnetic materials that are also ferroelectrics¹⁻³ upsurge recurrent interest to study and to rationalize theoretically various models manifesting this possibility (see, e.g., Refs. 4-7). The recent discovery of ferroelectricity in a family of the so-called frustrated magnets (see, e.g., Ref. 8) is particularly instructive. In this case, ferroelectricity is a collateral effect of the magnetic ordering that, in contrast to earlier multiferroics, involves modulated structures.^{9,10} The current interest in this new class of ferroelectromagnets is twofold. On one hand the fundamental physics that result from the interplay between the electric and magnetic properties in these systems is not exhausted¹⁰ and, on the other hand, many potential applications arise from this interplay.¹¹

The appearance of a modulated magnetic structure is accompanied by a distribution of polarization due to the inhomogeneous magnetoelectric effect.¹² This universal effect is similar to so-called flexoelectric effect in liquid crystals.¹³ Microscopic studies have focused on the Dzyaloshinskii-Moriya interaction as the main source of the inhomogeneous magnetoelectric effect,⁴ and this idea seems also to be behind the phenomenological Landau-like approaches carried out until now in relation to ferroelectricity of magnetic origin.^{5,14,15} As a result, the main attention has been put to only antisymmetric parts of the effect (where the components of the magnetization enter in an antisymmetric combination). However, in a general case, the inhomogeneous magnetoelectric effect has also a nonvanishing symmetric part (see below). This is indeed the natural possibility from the phenomenological point of view,^{12,13} whatever the microscopic origin of this symmetric coupling.

In this paper we show that this symmetric part of the inhomogeneous magnetoelectric effect is a key ingredient in the full description of materials exhibiting modulated magnetic structures. When it comes to the uniform polarization, indeed, only the antisymmetric part of the magnetoelectric effect plays a role in the agreement with previous theoretical publications (see, e.g., Refs. 4, 5, and 15 and more details below). However, to describe nonuniform, i.e., modulated in space, polarizations, the magnetoelectric effect has to be con-

sidered in its full extent. This is precisely the case when addressing the so-called electromagnons, i.e., the normal modes characteristic of ferroelectromagnets that involve both polar modes and magnons in a hybridized way.^{2,16}

Electromagnons were theoretically predicted a long time ago considering uniformly ordered materials.¹⁶ This consideration has been recently extended to the case of an antiferromagnet that becomes ferroelectric and then, through the inhomogeneous magnetoelectric effect, this induces an incommensurate magnetic structure.¹⁷ The first experimental evidences about electromagnon have been reported for materials in which, showing no instability toward ferroelectricity in the absence of magnetism, it is the appearance of a modulated magnetic structure that makes them ferroelectrics.^{18,19} Unfortunately, all theoretical studies performed so far for this latter case have been restricted to only antisymmetric parts of the magnetoelectric coupling.^{14,20} We show below that, contrary to what is implicitly assumed in these works, both symmetric and antisymmetric parts of the inhomogeneous magnetoelectric effect contribute nontrivially to the interplay between the fluctuations of magnetization and polarization in multiferroics.

First, let us reconsider the uniform polarization that may arise due to the inhomogeneous magnetoelectric effect. To simplify our presentation and ease the algebra, we neglect crystalline-field anisotropy (a more realistic treatment does not affect our qualitative results). In this case, the magnetoelectric coupling term reads as

$$F_{EM} = -f_1 \mathbf{P} \cdot \mathbf{M} (\nabla \cdot \mathbf{M}) - f_2 \mathbf{P} \cdot [\mathbf{M} \times (\nabla \times \mathbf{M})], \quad (1)$$

where \mathbf{P} is the polarization and \mathbf{M} is the magnetization, and f_1 and f_2 are, in general, two different constants. The general form of this term is $-f_{kl,ij} P_k M_i \partial_l M_j$,¹² where the magnetoelectric tensor reduces to $f_{kl,ij} = f_1 \delta_{kl} \delta_{ij} + f_2 (\delta_{kl} \delta_{ij} - \delta_{kj} \delta_{li})$ in the isotropic case. Let us split the polarization into uniform $\bar{\mathbf{P}}$ and nonuniform (modulated) \mathbf{P}' contributions: $\mathbf{P} = \bar{\mathbf{P}} + \mathbf{P}'$. From the magnetoelectric term, we then can extract the following contribution to the free energy of the system:²¹

$$-f_{kl,ij}\bar{P}_k \int d\mathbf{r} M_i \partial_l M_j = \frac{\bar{P}_k}{2} \int d\mathbf{r} (f_{kl,ji} - f_{kl,ij}) M_i \partial_l M_j.$$

Thus, we see, the uniform polarization indeed couples to the magnetization only through the antisymmetric part of the magnetoelectric tensor. In the isotropic case that is $f_{kl,ij} - f_{kl,ji} = (f_1 + f_2)(\delta_{ki}\delta_{lj} - \delta_{kj}\delta_{li})$. Thus, as regards the uniform polarization, the relevant part of the magnetoelectric term [Eq. (1)] can be written as $-\frac{1}{2}(f_1 + f_2)\bar{\mathbf{P}} \cdot [\mathbf{M}(\nabla \cdot \mathbf{M}) - (\mathbf{M} \cdot \nabla)\mathbf{M}]$, which coincides with the expression given in (Ref. 5). However, it is important to keep in mind that there are actually two independent contributions, f_1 and f_2 , to the magnetoelectric coupling term.

Let us now turn our attention to the magnetic features of the modulated magnets discussed in, e.g., Ref. 10. As we have mentioned, in these systems ferroelectricity is induced by magnetism and does not appear spontaneously by itself. In addition, the magnetoelectric effect is typically weak in comparison to pure magnetic contributions into the free energy. Therefore, in the first approximation, when determining the magnetic structure and dynamics it is possible to consider the magnetization separately.

Most of these systems first undergo a transition from the magnetically disordered phase to a modulated structure similar to a longitudinal spin-density wave (LSDW);

$$\mathbf{M} = (M_1 \cos Qx, 0, 0), \quad (2)$$

and then to a structure similar to a planar cycloid (PC),

$$\mathbf{M} = (M_1 \cos Qx, M_2 \sin Qx, 0). \quad (3)$$

The dependence on \mathbf{P} of Landau free-energy density can be taken as $\frac{1}{2}\chi^{-1}P^2 + F_{\text{EM}}$, where χ is the dielectric susceptibility in the absence of magnetism²² and F_{EM} accounts for the magnetoelectric coupling. It can be easily seen that the inhomogeneous magnetoelectric effect [Eq. (1)] implies the appearance of ferroelectricity as a result of the PC structure, but not of the LSDW (Ref. 5).

A simple way to reproduce this sequence of transitions is by considering Landau free-energy density in the form,

$$F_M = \frac{a}{2}M^2 + \frac{b}{4}M^4 + \frac{1}{2} \sum_i M_i \hat{L}_i M_i, \quad (4)$$

where the differential operators \hat{L}_i describe the anisotropic softening that gives rise to the modulated structures. For small wave vectors one can approximate $\hat{L}_i = c\nabla^2$. The free energy [Eq. (4)] then is reduced to a familiar form (see, e.g., Ref. 23). Near the wave vector $\mathbf{Q} = (Q, 0, 0)$ of the modulated structures $a + \hat{L}_i \approx \alpha_i + c_x \nabla_x^2 + c \nabla_\perp^2$. Equation (4) is then a natural generalization of the free energy considered in Refs. 5 and 15 that provides the unified description of the spectrum at the relevant wave vectors (i.e., $\mathbf{q} = 0$ and $\pm\mathbf{Q}$). If $a, b, c > 0$, the system shows no instability with respect to uniform

magnetizations. Furthermore, if $\alpha_x < \alpha_y < \alpha_z$, in the spirit of arguments presented in Refs. 5 and 15, one can see that the free energy is minimized by the LSDW modulation in the parameter range $\alpha_x < 0$, $\alpha_y > 0$, while the PC configuration occurs when $\alpha_x < 0$ and $3\alpha_x \lesssim \alpha_y \lesssim \alpha_x/3$ (with $\alpha_z > 0$ in both cases).

At this point, it is worth making the following comment on the label ‘‘improper ferroelectrics’’ that is frequently put to the systems of our interest (see, e.g., Ref. 10). Within the above scenario M_y or, more precisely, its $\pm\mathbf{Q}$ Fourier components, can be seen as the order parameter of the LSDW-paraelectric \leftrightarrow PC-ferroelectric transition. In the LSDW-paraelectric state [Eq. (1)] has a term coupling M_y and P_y linearly so, in view of this linearity, the system should be labeled as proper rather than improper ferroelectric.²⁴ This is in fact manifested in the corresponding anomalies.⁵

As regards the dynamics, we are interested in the low-frequency excitations of the system. In the magnetically ordered phases, not too close to the transition points, these excitations are associated with variations of the magnetization in which its modulus is conserved. Thus the excitations are described by the Landau-Lifshitz equation,²³

$$\dot{\mathbf{M}} = \gamma \mathbf{M} \times \mathbf{H}_{\text{eff}}, \quad (5)$$

where γ is a constant and $\mathbf{H}_{\text{eff}} = (\hat{L}_x M_x, \hat{L}_y M_y, \hat{L}_z M_z)$.

The dispersion relations and correlation functions of our interest are obtained by linearizing this equation about the corresponding configurations of equilibrium. Then it is convenient to consider first of all the LSDW structure [Eq. (2)], and then a virtual transverse spin-density-wave (TSDW) modulation,

$$\mathbf{M} = (0, M_2 \sin Qx, 0). \quad (6)$$

This would be the structure obtained from Eq. (4) if, contrary to what we assumed for the LSDW, α_y becomes negative with $\alpha_x > 0$. This structure TSDW is of interest in its own right and besides, it turns out that the low-lying normal modes of the PC case can be found as the superposition of the normal modes associated with LSDW and TSDW structures. This notably simplifies the corresponding calculations.

Skipping a large amount of tedious (although straightforward and simple) algebra, we come to the following results. They are obtained under the same assumptions as those for the static problem. That is, assuming that the anharmonicity is weak and that the spatial dispersion such that the generalized stiffness presents well defined minima only at the wave vectors $\mathbf{q} = 0, \pm\mathbf{Q}$. This allows us to decouple the modes \mathbf{q} and $\mathbf{q} \pm \mathbf{Q}$ from the rest.²⁵ For our purposes, higher-order satellites can be neglected.

As it could be expected, the low-lying modes of the LSDW represent independent oscillations of the magnetization along the y and z axes. The corresponding dispersion relations are such that

$$\omega_{y,z}^2(\mathbf{q}) = \begin{cases} 2m_x^2(\alpha_{z,y} - \alpha_x + c_x q_x^2 + c q_\perp^2)(-\alpha_x + c q^2), & \mathbf{q} \rightarrow 0, \\ m_x^2(\tilde{\alpha}_{z,y} - 2\alpha_x + c q'^2)(\alpha_{y,z} - \alpha_x + c_x q_x'^2 + c q_\perp'^2), & \mathbf{q} = \mathbf{Q} + \mathbf{q}' (q' \rightarrow 0). \end{cases} \quad (7)$$

Here $m_x = \gamma M_1/2$ and the quantities $\tilde{\alpha}_i$ are defined such that $\hat{L}_i e^{\pm i2Qx} = \tilde{\alpha}_i e^{\pm i2Qx}$. It is worth noticing that the closer the transition is, the smaller is the gap obtained at small wave vectors. Not only because of the smallness of m_x , what influences trivially on the whole spectrum, but also because $\alpha_x \rightarrow 0$. In fact, very close to the transition point $\omega_{y,z}(q \rightarrow 0) \sim q$. The gap obtained close to the wave vector of the modulation, on the contrary, is not so sensitive to the smallness of α_x .

Similar expressions are found for the TSDW structure [Eq. (6)]. In this case, the low-lying modes are associated with oscillations of the magnetization along the x and z axes. Their dispersion relations can be obtained from Eq. (7) by replacing $y \leftrightarrow x$ in m_x , α_i , and $\tilde{\alpha}_i$.

As we have mentioned, these results for the LSDW and TSDW structures merge in the PC case. Three low-lying normal modes are found such that the modulus of the magnetization is conserved in this latter structure. The modes associated with oscillations along the x and y axes coincide with that obtained previously for the TSDW and LSDW modulations, respectively. Consequently, they have the same dispersion relations. The mode representing oscillations along the z axis, however, is composed by the modes associated with the same type of oscillation in the TSDW and LSDW cases. In consequence, its dispersion relation can be expressed such that $\omega_{z,PC}^2(\mathbf{q}) = \omega_{z,LSDW}^2(\mathbf{q}) + \omega_{z,TSDW}^2(\mathbf{q})$.

Let us now turn our attention to the fluctuations. Since the softness of the system is in its magnetic part, fluctuations of the magnetization $\delta\mathbf{M}$ will play the main role. Once Eq. (5) is linearized, the corresponding correlation functions,

$$M_{ij}(\mathbf{q}) \equiv \langle \delta M_i(\mathbf{q}, \omega) \delta M_j(-\mathbf{q}, -\omega) \rangle, \quad (8)$$

can be found with the aid of the fluctuation-dissipation theorem.²³ Within a first approximation, the polarization will follow these fluctuations in accordance with the magnetoelectric coupling [Eq. (1)]. This results in fluctuations of the polarization $\delta\mathbf{P}$ of magnetic origin, i.e., electromagnons, whose correlation functions,

$$P_{ij}(\mathbf{q}) \equiv \langle \delta P_i(\mathbf{q}, \omega) \delta P_j(-\mathbf{q}, -\omega) \rangle, \quad (9)$$

can be expressed in terms of the previous quantities [Eq. (8)]. The hybridization between magnons and polar modes reflects also in the form of cross correlation functions $\langle \delta P_i \delta M_j \rangle$. Within our approximation, these cross correlations can also be expressed in terms of the quantities [Eq. (8)]. However since they essentially reveal the same information (see e.g. Ref. 26), we omit them in the following.

As regards magnetic correlation functions, the ‘‘non-diagonal’’ components are zero for the structures of our interest ($M_{ij}=0$ if $i \neq j$). In addition, $M_{xx}=0$ in the LSDW case while $M_{yy}=0$ in the TSDW one. Close to the relevant wave vectors, the nonvanishing correlation functions are such that $M_{ii}^{-1}(\mathbf{q}) \propto \tau \{ [\omega^2 - \omega_i^2(\mathbf{q})]^2 + \tau^{-2} \omega^2 \}$, where τ is the (phenomenological) relaxation time of the corresponding oscillations.

The fluctuations of the polarization of magnetic origin can be described in terms of the quantities M_{ii} . These fluctuations are such that the soft magnetic behavior at $\mathbf{q} \approx \pm \mathbf{Q}$ reflects in dipole polarization excitations with small wave vectors.

And reversely, the soft magnetic response at $q \rightarrow 0$ reflects in polarization excitations with $\mathbf{q} \approx \pm \mathbf{Q}$, as can be seen in further formulas. Note also that the magnetoelectric coefficients f_1 and f_2 enter separately in the following results. That is, not only through the combination $f_1 + f_2$ that determines the antisymmetric part of the magnetoelectric effect and, consequently, the space average of the polarization of the system. [The \mathbf{q} -dependence associated with χ (Ref. 22) is implicit in these formulas.]

In the LSDW case we have

$$P_{xx}(\mathbf{q}) \sim f_1^2 \{ q_y^2 [M_{yy}(\mathbf{q} - \mathbf{Q}) + M_{yy}(\mathbf{q} + \mathbf{Q})] + q_z^2 [M_{zz}(\mathbf{q} - \mathbf{Q}) + M_{zz}(\mathbf{q} + \mathbf{Q})] \},$$

$$P_{yy}(\mathbf{q}) \sim g_{-2}^2(\mathbf{q}) M_{yy}(\mathbf{q} - \mathbf{Q}) + g_{+2}^2(\mathbf{q}) M_{yy}(\mathbf{q} + \mathbf{Q}),$$

$$P_{zz}(\mathbf{q}) \sim g_{-2}^2(\mathbf{q}) M_{zz}(\mathbf{q} - \mathbf{Q}) + g_{+2}^2(\mathbf{q}) M_{zz}(\mathbf{q} + \mathbf{Q}),$$

$$P_{xy}(\mathbf{q}) \sim f_1 q_y [g_{-2}(\mathbf{q}) M_{yy}(\mathbf{q} - \mathbf{Q}) - g_{+2}(\mathbf{q}) M_{yy}(\mathbf{q} + \mathbf{Q})],$$

$$P_{xz}(\mathbf{q}) \sim f_1 q_y [g_{-2}(\mathbf{q}) M_{zz}(\mathbf{q} - \mathbf{Q}) - g_{+2}(\mathbf{q}) M_{zz}(\mathbf{q} + \mathbf{Q})],$$

and

$$P_{yz}(\mathbf{q}) = 0,$$

where $g_{\pm 2}(\mathbf{q}) = (f_1 + f_2)Q \pm f_2 q_x$. In the case of a pure symmetric coupling ($f_1 = -f_2$), with no Dzyaloshinskii-Moriya-like contributions, all these correlation functions turn out to be $\propto q^2$. In consequence, the eventual importance of fluctuations of the polarization with small wave vectors is conditioned to the existence of a nonvanishing antisymmetric part in the magnetoelectric coupling. In any case, fluctuations with wave vectors $\mathbf{q} \approx \pm \mathbf{Q}$ are important irrespective to the above vanishing (they are entirely due to $f_1 \neq 0$). These ‘‘magnetic’’ softenings of optical phonons in the LSDW paraelectric state can be used to measure the corresponding coefficients f_1 and f_2 . This soft behavior in the absence of ferroelectricity has in fact been observed in Ref. 19.

Similarly, for the TSDW structure we find that

$$P_{xx}(\mathbf{q}) \sim f_2^2 q_y^2 [M_{xx}(\mathbf{q} - \mathbf{Q}) + M_{xx}(\mathbf{q} + \mathbf{Q})],$$

$$P_{yy}(\mathbf{q}) \sim g_{-1}^2(\mathbf{q}) M_{xx}(\mathbf{q} - \mathbf{Q}) + g_{+1}^2(\mathbf{q}) M_{xx}(\mathbf{q} + \mathbf{Q}) + f_1^2 q_z^2 [M_{zz}(\mathbf{q} - \mathbf{Q}) + M_{zz}(\mathbf{q} + \mathbf{Q})],$$

$$P_{zz}(\mathbf{q}) \sim f_2^2 q_y^2 [M_{zz}(\mathbf{q} - \mathbf{Q}) + M_{zz}(\mathbf{q} + \mathbf{Q})],$$

$$P_{xy}(\mathbf{q}) \sim f_2 q_y [g_{-1}(\mathbf{q}) M_{xx}(\mathbf{q} - \mathbf{Q}) - g_{+1}(\mathbf{q}) M_{xx}(\mathbf{q} + \mathbf{Q})],$$

$$P_{xz}(\mathbf{q}) = 0,$$

and

$$P_{yz}(\mathbf{q}) \sim -f_1 f_2 q_y q_z [M_{zz}(\mathbf{q} - \mathbf{Q}) + M_{zz}(\mathbf{q} + \mathbf{Q})],$$

where $g_{\pm 1}(\mathbf{q}) = (f_1 + f_2)Q \pm f_1 q_x$. As in the previous case, the relevance of fluctuations of the polarization with small wave vectors is made conditional on the antisymmetric part of the magnetoelectric coupling, while the relevance of fluctuations

with wave vectors close to that of the modulated structure is not.

Finally, armed with the knowledge of correlation functions for LSDW and TSDW structures, we are in the position to calculate the polarization correlation functions in the PC case as $P_{ij}^{\text{LSDW}} + P_{ij}^{\text{TSDW}} + \Delta P_{ij}$. Here the first two terms represent the correlation functions obtained in for the LSDW and TSDW modulations, respectively, and the third one is

$$\Delta P_{xx}(\mathbf{q}) \sim q_x^2 [f_1^2 \Pi_x(\mathbf{q}, \mathbf{Q}) + f_2^2 \Pi_y(\mathbf{q}, \mathbf{Q})],$$

$$\Delta P_{yy}(\mathbf{q}) \sim q_y^2 [f_2^2 \Pi_x(\mathbf{q}, \mathbf{Q}) + f_1^2 \Pi_y(\mathbf{q}, \mathbf{Q})],$$

$$\Delta P_{zz}(\mathbf{q}) \sim f_2^2 q_z^2 [\Pi_x(\mathbf{q}, \mathbf{Q}) + \Pi_y(\mathbf{q}, \mathbf{Q})],$$

$$\Delta P_{xy}(\mathbf{q}) \sim f_1 f_2 q_x q_y [\Pi_x(\mathbf{q}, \mathbf{Q}) + \Pi_y(\mathbf{q}, \mathbf{Q})],$$

$$\Delta P_{xz}(\mathbf{q}) \sim f_1 f_2 q_x q_z [\Pi_x(\mathbf{q}, \mathbf{Q}) + \Pi_y(\mathbf{q}, \mathbf{Q})],$$

and

$$\Delta P_{yz}(\mathbf{q}) \sim f_1 f_2 q_y q_z [\Pi_x(\mathbf{q}, \mathbf{Q}) + \Pi_y(\mathbf{q}, \mathbf{Q})],$$

where $\Pi_i(\mathbf{q}, \mathbf{Q}) = m_i^2 [M_{ii}(\mathbf{q} - \mathbf{Q}) + M_{ii}(\mathbf{q} + \mathbf{Q})]$. These additional contributions are relevant for the fluctuations with wave vectors close to $\pm \mathbf{Q}$. It is worth noticing that, within our approximations, there are no contributions $\propto m_1 m_2$ to these correlations functions.

In summary, we have presented the key aspects of the phenomenological theory of ferroelectricity of magnetic ori-

gin that allow one to treat consistently, on the same footing, uniform and nonuniform polarizations. One of its key points is the accounting for all the possible contributions, symmetric and antisymmetric ones, to the inhomogeneous magneto-electric effect. Considering the most representative modulated magnetic structures, we have employed this theory to study the corresponding fluctuations of magnetization and polarization. Our main findings are the following: (i) The aforementioned fluctuations turn out to be interdependent as long as magnetic order appears, irrespective of whether this order induces a uniform polarization or not. This implies that ferroelectricity may not be strictly necessary when addressing applications based on such an interplay. (ii) The softness of the system reveals in the form of large fluctuations at both small wave vectors and wave vectors close to that of the modulated structure. At small wave vectors, the fluctuations of the polarization of magnetic origin can be associated with the antisymmetric part of the magnetoelectric effect (which eventually gives rise to the uniform polarization of the system). At wave vectors close to that of the modulated structure, however, the situation is different. In this case, the fluctuations are due to both symmetric and antisymmetric parts of the effect. Consequently, in view of the relativistic nature of the antisymmetric part, one can expect here a leading role of the symmetric contribution (which has its origin in the exchange interaction).

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²¹To derive the latter expression, we transform the magnetoelectric tensor into $(f_{kl,ij} + f_{kl,ji})/2$ and integrate by parts one of the resulting terms.

²²Strictly speaking, in the absence of magnetism we should write $\frac{1}{2}(\chi_0^{-1} P^2 - \mathbf{E} \cdot \mathbf{P})$, where χ_0 is a constant and the field \mathbf{E} is caused by inhomogeneous distributions of \mathbf{P} . That is, the electric field obtained from the equations of electrostatics $\nabla \times \mathbf{E} = 0$ and $\nabla \cdot (\mathbf{E} + 4\pi \mathbf{P}) = 0$. This results into the susceptibility χ .

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