Magnetoelectric effects in the spiral magnets CuCl$_2$ and CuBr$_2$

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Abstract

The nature and symmetry of transition mechanisms in the spin-spiral copper halides CuCl$_2$ and CuBr$_2$ are analyzed theoretically. The magnetoelectric effects observed in the two multiferroic compounds are described and their phase diagram at zero and applied magnetic fields are worked out. The emergence of the electric polarization at zero field below the paramagnetic phase is shown to result from the coupling of two distinct spin-density waves and to be partly related to the Dzialoshinskii–Moriya interactions. Applying a magnetic field along the two-fold monoclinic axis of CuCl$_2$ yields a decoupling of the spin-density waves modifying the symmetry of the phase and the spin-spiral orientation. The remarkable periodic dependences of the magnetic susceptibility and polarization, on rotating the field in the monoclinic plane, are described theoretically.

Keywords: multiferroic, CuCl$_2$, CuBr$_2$, Landau theory

(Some figures may appear in colour only in the online journal)

1. Introduction

Two distinct symmetry properties of the spiral phases in multiferroic compounds allow understanding their specific magnetoelectric behavior. The first property is that time-reversal symmetry $T$ is preserved in the magnetic point group of the multiferroic phases. Such property derives from the incommensurate character of the spiral structures which partly lose their discrete translational symmetry but keep the point-group symmetry of the paramagnetic structure unless a macroscopic tensor emerges at the transition [1]. In the multiferroic phase the onset of a macroscopic polarization breaks space inversion but not time inversion. This has, on the one hand, the consequence to forbid a magnetization induced by an electric field but permits a magnetic field induced polarization. On the other hand only quadratic magnetoelectric effects are allowed. The other property typifying spiral multiferroic phases is that they result from the coupling of two antiferromagnetic order-parameters. Such coupling gives rise to a sequence of two second-order transitions: a first transition to a non-polar antiferromagnetic phase associated with a single order-parameter, followed by a second transition to the spin spiral ferroelectric phase associated with two coupled order-parameters. Consequently the transition to the multiferroic phase displays a hybrid pseudo proper ferroelectric character [2]: the small value of the ferroelectric polarization is that of an improper ferroelectric, but the critical behavior corresponds to a proper ferroelectric transition with a $T_c - T$ temperature dependence of the polarization and a Curie–Weiss like divergence of the dielectric permittivity.

The preceding description holds for incommensurate spin spiral in multiferroic oxides [3–5]. Recently multiferroic properties have been reported in the non-oxide compounds CuCl$_2$ and CuBr$_2$ [6–10] in which the ferroelectric properties coexisting with a spin spiral antiferromagnetic order are observed directly below the paramagnetic phase. In order to clarify this unusual situation we analyze theoretically the nature and symmetry of the order-parameters in the two copper halides at zero field (section 2). Expressing the order-parameter components in function of the spin-densities associated with the copper atoms we show that
the Dzialoshinski–Moriya cycloidal interactions are not exclusively involved in the emergence of the electric polarization, and they disappear when assuming a commensurate approximant of the incommensurate structure (section 3). In sections 4 and 5 we describe the complex magnetoelectric effects reported in CuCl2 [6] and CuBr2 [9]. Last (section 6) we summarize our results and briefly discuss the experimental observations reported in the copper oxides LiCuClO3 [11–14] and LiCuVO4 [15–17], in which the coupling between the transition order-parameters present some similarity with CuCl2 and CuBr2.

2. Phase diagram at zero field

The incommensurate wave-vector \( \mathbf{k} = (1, k_y, 0.5) \) arising at the transition to the spin-spiral phase, which takes place at \( T_N = 24 \text{ K} \) in CuCl2 \((k_y = (2\pi/\bar{b}) 0.226)\) [7] and \( T_N = 73.5 \text{ K} \) in CuBr2 \((k_y = (2\pi/\bar{b}) 0.235)\) [9] is located at the surface (R-line) of the monoclinic C Brillouin-zone. It is associated with two bi-dimensional irreducible representations [18] \( \Gamma_1 \) and \( \Gamma_2 \) of the paramagnetic space-group \( C2/m \Gamma \), the matrices of which are given in table 1. Denoting \( \eta_1 = \rho_1 \cos \theta_1, \eta_2 = \rho_2 \sin \theta_1 \) and \( \zeta_1 = \rho_3 \cos \theta_2, \zeta_2 = \rho_2 \sin \theta_2 \) the order-parameter components respectively associated with \( \Gamma_1 \) and \( \Gamma_2 \), the Landau free-energy corresponding to the reducible representation \( \Gamma_1 + \Gamma_2 \) reads:

\[
F = \frac{a_1}{2} \rho_1^2 + \frac{\beta_1}{4} \rho_1^4 + \gamma_1 \rho_1^6 + \frac{a_2}{2} \rho_2^2 + \frac{\beta_2}{4} \rho_2^4 + \gamma_2 \rho_2^6 + \frac{\gamma_6}{2} \rho_1^2 \rho_2^2 + \frac{\gamma_6}{2} \rho_1^2 \rho_2^2 \cos(2\theta_1 - 2\theta_2) + \frac{\gamma_6}{4} \rho_1^2 \rho_2^2 \cos^2(2\theta_1 - 2\theta_2) \tag{1}
\]

where \( a_i = a_i(T - T_c), a_2 = a_2(T - T_c) \) and \( a_1, a_2, \beta_1, \beta_2, \gamma_1, \ldots, \gamma_6 (i = 1−5) \) are phenomenological constants. Table 2 lists the symmetries of the stable phases that may arise below the paramagnetic phase at zero field deduced from a Landau symmetry analysis which requires considering an eighth degree term in \( F \) for stabilizing the full set of low-symmetry phases [19]. Because of the incommensurate character of the phases the symmetries correspond at zero field to grey magnetic point groups [20]. Column (d) of table 2 indicates the spontaneous components of the electric polarization emerging in each phase. One can verify that the \( P^a \) and \( P^c \) polarization components, observed experimentally at zero field in CuCl2, is induced by the reducible representation \( \Gamma_1 + \Gamma_2 \) for the equilibrium values of the order-parameter components \( \rho_1 = 0, \rho_2 = 0, \theta_1 - \theta_2 = (2n + 1)\pi/2 \), or equivalently \( \eta_1 = 0, \eta_2 = 0, \zeta_1 = 0, \zeta_2 = 0 \). It coincides with a phase of symmetry \( m' \) which allows a spin-spiral in the \( b-c \) plane. Figures 1(a) and (b) show the theoretical phase diagrams involving the phases listed in table 2 and the thermodynamic path corresponding to the paramagnetic to multiferroic phase.

The equilibrium polarization is determined by minimizing the dielectric contribution to the free-energy:

\[
F_D = \delta P^{az} \rho_1 \rho_2 \sin(\theta_1 - \theta_2) + \frac{1}{2\chi_0} \left[ (P^a)^2 + (P^c)^2 \right] \tag{2}
\]

where \( \chi_0 \) is the dielectric susceptibility in the paramagnetic phase. It yields \( P^{az} = -\delta \chi_0 \rho_1 \rho_2 \sin(\theta_1 - \theta_2) \) or equivalently \( P^{az} = \delta (\eta_1 \zeta_2 - \eta_2 \zeta_1) \). Therefore the equilibrium form of \( P^{az} \) in the multiferroic phase reduces to

\[
P^{az} = \delta \chi_0 \rho_1 \rho_2 \tag{3}
\]

i.e. the induced ferroelectricity has an improper character. Since the transition to the ferroic phase results from the coupling of two order-parameters it has a first-order character, \( \rho_1 \)

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**Table 1.** Irreducible representations \( \Gamma_1 \) and \( \Gamma_2 \) of the paramagnetic space-group \( C2/m \Gamma \) associated with the wave-vector \( \mathbf{k} = (1, k_y, 0.5) \). \( T \) is the time reversal operator. The matrices of \( \Gamma_1 \) and \( \Gamma_2 \) are given in complex form.

| \( C2/m \Gamma \) | \( \Gamma_1 \) | \( \Gamma_2 \) | \( \Gamma_1 \) | \( \Gamma_2 \) |
|-----------------|----------------|----------------|----------------|----------------|
| \( \eta_1 \) | \( \eta_2 \) | \( \eta_2 \) | (0 0 0) | (0 0 0) |
| \( \zeta_1 \) | \( \zeta_2 \) | \( \zeta_2 \) | (0 0 0) | (0 0 0) |

**Table 2.** Grey magnetic point groups (Column (b)) deduced from the minimization of the free-energy (equation (1)). Column (a): irreducible and reducible representations. Column (c): equilibrium values of the order-parameters. Column (d): spontaneous polarization components at zero magnetic fields.

| (a) | (b) | (c) | (d) |
|------|------|------|------|
| \( \Gamma_1 \) | \( \Gamma_2 \) | \( \eta_1 \neq 0, \rho_2 = 0 \) | \( P^a, P^c \) |
| \( \eta_1 \neq 0, \rho_2 = 0 \) | \( P = 0 \) |
| \( \eta_1 = 0, \rho_2 = 0 \) | \( P = 0 \) |
| \( \theta_1 - \theta_2 = (2n + 1)\pi/2 \) | \( \Gamma_1 + \Gamma_2 \) | \( \Gamma_1 + \Gamma_2 \) | \( \eta_1 = 0, \rho_2 = 0 \) | \( P = 0 \) |
| \( \theta_1 - \theta_2 = n\pi \) | \( \theta_1 - \theta_2 = \text{arbitrary} \) | \( P^a, P^b, P^c \) | \( P^{az} \) |
and $\rho_2$ varying discontinuously across $T_N$. Therefore, $P^e$ and $P^z$ undergo an upward discontinuity at $T_N$ before increasing linearly below $T_N$, in agreement with the experimental curves of $P^e$ and $P^z$ measured for CuCl$_2$ by Seki et al [6]. The dielectric permittivity under $E^z$ field reported by these authors exhibits a sharp rising at $T_N$ before reaching a maximum at about 17 K followed by a continuous decrease on cooling. Minimizing successively $F_{E^z P^z}$ with respect to $P^z$ and $E^z$ yields the susceptibility component

$$\chi_{\alpha\alpha} = \frac{\partial^2 \delta \rho_{\alpha\alpha}}{\partial E^z \partial P^z}$$

where $\rho_1$ and $\rho_2$ are the order-parameter modulus at zero field. One gets below $T_N$:

$$\chi(T) \approx \chi_0 \left[ 1 + \frac{2 \delta^2}{\Delta} \left( \frac{\beta_1 \alpha_1 + \beta_2 \alpha_2}{\alpha_1 \alpha_2} \right) - 2(\gamma_2 - \gamma_1) \right]$$

where $\Delta = (\gamma_2 - \gamma_1)^2 - \beta_1 \beta_2$. $\chi(T)$ increases up to $T_{\text{Max}} = \frac{\alpha_1 \beta_1 + \alpha_2 \beta_2}{\alpha_1 \beta_2 - \alpha_2 \beta_1}$ before decreasing continuously with $T$, as observed experimentally [6].

3. Magnetoelectric interactions

In order to determine the nature of the magnetic interactions giving rise to the electric polarization one can express the order-parameter components in function of the spin-density components $\sum_{i=1}^{8} s_i$ associated with the copper atoms of the antiferromagnetic unit-cell [7]. Figure 2 shows the eight-fold unit-cell corresponding to an approximant of the infinite incommensurate unit-cell in $b$-direction of CuCl$_2$ and CuBr$_2$. Introducing the microscopic antiferromagnetic spin-density waves $L_i = s_i - s_j - s_k - s_l$, $L_{ij} = s_i - s_j - s_k$, $L_{kl} = s_k - s_l - s_j$, $L_{ij} = s_i - s_j + s_k$, one finds, by using projector techniques [19], that the order-parameter spin waves are spanned by the magnetic modes:

$$\eta_i(L_1, L_2, L_3, L_4), \eta_j(L_2, L_4, L_3), \zeta_i(L_3, L_1, L_2), \zeta_j(L_4, L_2, L_3)$$

Assuming the magnetic moments confined in the $b$-$z$ plane, as reported from neutron diffraction measurements [7], the order-parameter spin waves read:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Theoretical phase diagrams at zero fields in the (a) $(\alpha_1, \alpha_2)$ and (b) $(\gamma_4, \alpha_2 - \alpha_1)$ planes assuming an eighth-degree expansion for the free-energy given by equation (1). All solid red curves in (b) and hatched red curves in (a) are second-order transition lines, whereas the solid red curve in (a) denotes a first-order transition line. Figure (a) shows that the paramagnetic $C2/m'$ to polar $m'$ phase transition should occur across the region of stability of a non-polar $2/m'$ phase or directly across a first-order transition as observed experimentally.}
\end{figure}
The polarization components \( P_{\alpha z} \approx \eta_1 \zeta_2 - \eta_2 \zeta_1 \) is formed by two types of bilinear invariants \( s_i^b s_j^b \): (1) Antisymmetric invariants \( \sum_{i,j} (s_i^b s_j^b - s_j^b s_i^b) \) with \((i, j) = (1-4)\) or \((5-8)\) representing the Dzialoshinskii–Moriya (DM) ‘cycloidal’ interactions \([21]\) between the spin-densities associated with atoms \((1-4)\) or \((5-8)\); (2) Invariants \( \sum_{i,j} (s_i^b s_j^b \pm s_j^b s_i^b) \) representing anisotropic exchange interactions \([22]\) between the magnetic moments of atoms \(i = 1 \) to 4 and \(j = 5 \) to 8.

It has to be noted that taking into account the equilibrium conditions \( (\eta_2 = 0, \eta_1 = 0) \) fulfilled by the spin-density components in the cycloidal spin-wave phase yield:

\[
\eta_1 = a_1 (s_i^b - s_j^b) + a_2 (s_j^b - s_i^b + s_i^z - s_j^z)
\]

\[
\eta_2 = b_1 (s_i^b - s_j^b) + b_2 (s_j^b - s_i^b - s_i^z + s_j^z)
\]

\[
\zeta_1 = c_1 (s_i^b + s_j^b + s_i^z - s_j^z) + c_2 (s_i^b - s_j^b)
\]

\[
\zeta_2 = d_1 (s_i^b - s_j^b - s_i^z + s_j^z) + d_2 (s_j^b - s_i^b)
\]

These conditions cancel the antisymmetric DM interactions which are replaced by anisotropic exchange interactions \( \sum_{i,j} s_i^b s_j^b \). It suggests that the DM interactions are inherent to the incommensurate character of the spin spiral, but are not required for the stabilization of the commensurate cycloid in the eight-fold unit-cell approximant assumed in our description.

4. Magnetoelectric effects in CuCl₂

Two types of magnetoelectric effects have been reported in CuCl₂ by Seki et al \([6]\).

(1) Under increasing \( H^b \) field the \( P^a \) and \( P^c \) polarization components decrease and vanish above a threshold field of about 4 T at 5 K. This is interpreted by Seki et al \([6]\) as a tilting of the spin-spiral from the \( bc \)-plane to the \( ac \) plane. Under applied \( H^b \) field, time-reversal is broken and the magnetic point-group symmetry \( m \) of the spin spiral phase reduces to \( m \). The dependence of \( P^a \) and \( P^c \) on \( H^b \) is obtained from the magnetodielectric and magnetic contributions to the free-energy which read:

\[
F_{MP} = \frac{1}{2} \mu_0 (M^b)^2 (P_{\alpha z})^2 + \delta P_{\alpha z}^0 \rho_1 \rho_2 \sin(\theta_1 - \theta_2) + \frac{(P^a)^2}{\lambda_{uu}} + \frac{(P^c)^2}{\lambda_{zz}}
\]

\[
F_{MH} = \frac{1}{2} \mu_0 (M^b)^2 - M^b H^b
\]

Minimizing \( F_{MP} \) with respect to \( P_{\alpha z} \), and \( F_{MH} \) with respect to \( M^b \), and putting \( \theta_1 - \theta_2 = -\frac{\pi}{2} \) yields:

\[
P^a = \frac{\delta \rho_1 \rho_2}{1 + \frac{\mu_0}{\mu_0} (H^b)^2}, P^c = \frac{\delta \rho_1 \rho_2}{1 + \frac{\mu_0}{\mu_0} (H^b)^2}
\]

which shows that \( P^a \) and \( P^c \) decrease with increasing \( H^b \) field. The vanishing of the polarization components above a threshold field \( H^b \approx 4 \) T in CuCl₂ at 5 K is obtained when \( \rho_1 \rho_2 = 0 \), i.e. when \( \rho_1 = 0 \) or \( \rho_2 = 0 \). It means that above 4 T a decoupling of the two order-parameters \( \rho_1 \) and \( \rho_2 \) occurs, only one order-parameter remaining active Therefore the monoclinic symmetry \( m \) at low field increases to \( 2/m \) above 4 T, consistent with the interpretation by Seki et al \([6]\) suggesting that the \( bc \) spin-spiral phase becomes unstable with a tilting towards a spin-spiral located in the \( ac \) plane. Assuming, for example, \( \rho_1 = 0, \rho_2 = 0 \) the theoretical description of the \( ac \) spin spiral above 4 T requires taking into account two copies (replica) of the corresponding order-parameter, i.e. \((\eta_1, \eta_2)\) and \((\eta'_1, \eta'_2)\), which couple to form the spin spiral. Note that the phases \( \theta_1 \) and \( \theta'_1 \) of the two order-parameter copies have to be identical (\( \theta_1 = \theta'_1 \)) in order to cancel the magnetoelectric coupling interaction \( P_{\alpha z}(\eta_1 \eta'_2 - \eta_2 \eta'_1) \). Note also that the increase of symmetry from \( m \) to \( 2/m \) with increasing field realizes a field-induced ferroelectric-to-paraelectric phase
transition which corresponds to the sharp peak observed for the dielectric permittivity component $\varepsilon_{xx}$ at 4 T. Figure 3 shows the thermodynamic path followed from the ferroelectric phase to one of the centro-symmetric phases of symmetry $2/m$ under $H^0$ field. (2) On rotating the magnetic field $H$ within the $a$-$\alpha z$ plane Seki et al. [6] report another type of magnetoelectric effect consisting of a periodic dependence of the magnetic susceptibility and polarization components in function of the angle $\theta_H$ between the magnetic field and the a axis. Upon rotation of the field the spiral plane also rotates as to being always perpendicular to the field, resulting in changes in the respective values of $P^0$ and $P^\omega$. Application of a magnetic field within the $a$-$\alpha z$ plane reduces the $m'1$ symmetry at zero-field to $m'$, inducing magnetization components $M^e$ and $M^\omega$. The magnetic free-energy involving the couplings between the order-parameter and the magnetization components reads:

$$F_{MH} = A(\rho_i) \frac{(M^e)^2}{2} + B(\rho_i) \frac{(M^\omega)^2}{2} + C(\rho_i)M^eM^\omega - H^0M^e + H^0M^\omega.$$  

(10)

with $A(\rho_i) = \mu_{11}^0 + \nu_{11\alpha}^1 + \nu_{21\alpha}^2$, where $\mu_{11}^0$ is the magnetic permeability and $(\nu_{11\alpha}, \nu_{21\alpha})$ are constant coupling coefficients between the order parameter invariants $(\rho^1_1, \rho^1_2)$ and $C(\rho_i)$. Minimizing $F_{MH}$ with respect to $M^e$ and $M^\omega$ gives $M^e = (CH^e - BH^\omega)/\Delta$ and $M^\omega = (CH^\omega - AH^e)/\Delta$ where $\Delta = C^2 - AB$. Therefore, one has:

$$M^e + M^\omega = \frac{(C - A)H^e + (C - B)H^\omega}{\Delta} = M(\cos \theta_H + \sin \theta_H)$$  

(11)

Taking into account the magnetic field dependence of (1) the order parameters, which vary as $\rho^\omega(z) \approx -\frac{\omega}{\pi} - \nu_{1\alpha}(H^e)^2 - \nu_{1\alpha}(H^\omega)^2 - \nu_{1\alpha}H^eH^\omega$ and $\rho^e(z) \approx -\frac{\omega}{2\pi} - \nu_{2\alpha}(H^e)^2 - \nu_{2\alpha}(H^\omega)^2 - \nu_{2\alpha}H^eH^\omega$, and (2) the lowest degree approximations of $C - A \approx \nu_{1\alpha} + \nu_{1\alpha}(H^e)^2 + \nu_{1\alpha}(H^\omega)^2 + \nu_{1\alpha}H^eH^\omega$ and $C - B \approx \nu_{1\alpha} + \nu_{1\alpha}(H^e)^2 + \nu_{1\alpha}(H^\omega)^2 + \nu_{1\alpha}H^eH^\omega$, and putting $H^e = H\cos \theta_H$, $H^\omega = H\sin \theta_H$ one gets $M^e + M^\omega \approx (\cos \theta_H + \sin \theta_H)(\lambda_1H + H^\omega(\lambda_2 + \lambda_3 \cos 2\theta_H + \lambda_4 \sin 2\theta_H))$, where the $\lambda_i (i = 1 - 4)$ are smoothly field-dependent coefficients. Therefore, the total magnetic susceptibility defined by Seki et al. [6] as $\chi = \frac{M}{H} = \frac{M^e + M^\omega}{H(\cos \theta_H + \sin \theta_H)}$ can be approximated under the form:

$$\chi(\theta_H) = \lambda_1 + H^\omega(\lambda_2 + \lambda_3 \cos 2\theta_H + \lambda_4 \sin 2\theta_H)$$  

(12)

Figure 4 shows the periodic $\theta_H$-dependence of $\chi$ for two different values of the field $H_1 < H_2$, consistent with the experimental curves measured by Seki et al. [6] at 1 T and 7 T.

At constant magnitude of the applied field the dependence of the polarization components on the orientation of the field can be deduced from the magnetodielectric contribution to the free-energy. For the $P^0$ component this contribution reads:

$$F_{MP} = \left(\frac{P^0}{2}\right)^2 \frac{1}{\chi_{aa}} + \delta_{aa}(M^e)^2 + \delta_{aa}(M^\omega)^2 + \delta_{aa}(M^eM^\omega)$$  

(13)

Minimizing with respect to $P^0$ with $\theta_1 - \theta_2 = -\pi/2$, and taking into account the lowest-degree approximation of $\rho_1\rho_2$ in function of the field, which is:

$$\rho_1\rho_2 \approx \left(\frac{\omega}{\pi}\right)^2 [1 + H(\lambda_\alpha \cos \theta_H + \lambda_\omega \sin \theta_H)]$$

and an analogous expression for $P^\omega(\theta_H)$:
with increasing and magnetic free-energy and for \( \rho \) (1)

The \( \chi \rho \) into , reversing the sign of at 9 T, and a decrease

under which yield:

fitting parameters (in 10

by\textit{et al} [6]. Reversing the field \( P \) dependent part of \( \rho \)

the coupling of the same bi-dimensional order-parameters

emergence of an electric polarization below

for a \( Hb \) phase in presence of magnetic field which is lowered to

m

deduce from the dielectric measurements the symmetry of the

incommensurate helical spin

bulk CuCl 2, neutron powder diffraction patterns by Zhao

The observed

[9]

confirm the existence of an incommensurate helical

regime of \( P \) observed on cooling from 60 K to 10 K. Note

in this respect that the absence of decrease of \( P(T)\) down to

10 K suggests that a single ferroelectric phase is stabilized on

cooling below \( T_N \) in CuBr 2.

A sharp rising of the dielectric permittivity \( \varepsilon(T) \) at

Corresponding to a increase of the maximum polarization with

H. Equation (16) is also consistent with the saturated

of the maximum dielectric permittivity \( \varepsilon_{\text{max}}(T) \) with increasing H. The first effect can be derived from the magneto-dielectric

free-energy \( F_{\text{PM}} = \frac{\rho^2}{2m^2} + \frac{\delta P M^2 \rho^2}{2} \) and magnetic free-energy

\( F_{\text{M}} = \mu_0 \frac{M^2}{2} + \frac{\delta_0 \rho^2}{2} + \frac{\delta_2 \rho^2}{2} - \mu H \) which yield:

\begin{equation}
\chi(H) = \chi(0) + D(\rho) \left( 1 - \frac{H^2}{\mu_0 + \delta_1 \rho^2 + \delta_2 \rho^2} \right)
\end{equation}

where \( D(\rho) = -1 \chi_0^2 \left( \frac{\rho^2}{\alpha_1} + \frac{\rho^2}{\alpha_2} \right) > 0 \) for \( \alpha_1 < 0 \) and \( \alpha_2 < 0 \).

Therefore with increasing field the dielectric susceptibility decreases, as reported in [9].
6. Summary, discussion and conclusion

In summary, our proposed theoretical analysis shows that the multiferroic phase transitions occurring in CuCl₂ and CuBr₂ are induced by the coupling of two distinct antiferromagnetic spin-wave order parameters which lead, across a first-order transition, to an incommensurate polar phase of monoclinic symmetry $m_1'$ displaying a typical improper ferroelectric behaviour. The set of spin-density components spanning the order-parameters have been worked out. They indicate that the emergence of an electric polarization results from combined Dzialoshinskii–Moriya (DM) antisymmetric interactions and symmetric anisotropic exchange interactions. Interestingly, the antisymmetric interactions are cancelled when assuming a commensurate approximant of the magnetic structure instead of the actual incommensurate structure. It indicates that the DM interactions which are required for stabilizing the spiral structure and suppressing the inversion symmetry, contribute only partly to the electric polarization. This conclusion differs from the interpretation by Seki et al [6] of the dielectric properties of CuCl₂ in terms of an exclusive inverse DM interaction [23].

The different magnetoelectric effects observed in CuCl₂ and CuBr₂ under applied magnetic fields have been described theoretically by considering the couplings existing between the order-parameters, the polarization and the magnetization. In particular, the disappearance of the polarization above a threshold magnetic $H^P$ field has been shown to result from a decoupling of the order-parameters which are coupled at zero fields. It suggests that the coupling of the spin-waves inducing the antiferromagnetic spin-spiral is weak and sensitive to the applied field.

Although directional magnetoelectric effects on single crystal of CuBr₂ remain to be investigated in more details, the effects reported by Zhao et al [9] from powder sample measurements show a remarkable coincidence with those observed in CuCl₂, despite a difference of about 50 K for their transition temperatures: the same spin-wave order-parameter symmetries are activated in CuCl₂ and CuBr₂, involving the same interactions between the spin-densities and similar couplings between the induced polarization and magnetization components. This coincidence is due to the similarity of their structures, consisting of undistorted triangular lattices involving halide ions. However the presence of copper ions should also be important in the determination of the specific multiferroic properties in CuCl₂ and CuBr₂. In this respect, it can be noted that the high temperature transition to a spin spiral phase in cupric oxide CuO, that was initially reported to occur directly from the paramagnetic phase [24, 25] was later shown to take place in two steps [26, 27] with an intermediate phase having a remarkably narrow range of stability.

The copper oxides LiCu₂O₂ and LiCuVO₄ present some similar features with CuCl₂ regarding the order-parameter coupling which permits the emergence of a spin spiral multiferroics. A symmetry analysis of the sequence of sinusoidally modulated and helical ellipsoidal spin structures, arising respectively at $T_{N1} = 24.5$ K and $T_{N2} = 23$ K below the orthorhombic $Pmm21$ paramagnetic structure of LiCu₂O₂, shows that two copies of the four-dimensional order-parameter associated with the wave-vector (0.5, 0.174, 0), with different phases; are required for a consistent description of the experimental observations [11–14]. The coupling of these order-parameter replica yields a point-group symmetry $mm2_1V$ for the ferroelectric ellipsoidal phase consistent with a
spontaneous polarization $P^*$ at zero field and a magnetic structure with four magnetic domains in the $a$-$b$ plane. Applying $H^\parallel$, $H^\perp$ or $H^\bot$ fields lowers respectively the symmetry of the multiferroic phase to $mmm'$, $m'm'm'$, and $m'm'm'$, preserving the polarization along $c$. Under high fields the $P^*$ polarization disappears indicating a decoupling of the order-parameters. It yields a centrosymmetric monoclinic phase of symmetry $2/m$ associated with a single four component order-parameter. Note that replica of the same order-parameter have been previously shown to be involved in the theoretical description of the multiferroic phases of NaFeSi$_2$O$_6$ [28] and FeVO$_4$ [29].

The experimental observations reported for the multiferroic phase in LiCuVO$_4$ [15–17], stable below $T_N=2.5$ K, can be shown to involve the four two-dimensional irreducible representations, denoted $\tau(i=1–4)$ in Kovalev tables [18], of the Imma space-group of the paramagnetic phase, associated with the wave-vector $(0, 0.532, 0)$. At zero magnetic field one pair of irreducible representations $(\tau_1 + \tau_2$ or $\tau_2 + \tau_1$) gives rise to the multiferroic phase displaying the monoclinic symmetry $Z_2$, consistent with the emergence of a polarization $P^\parallel$ and with the preservation of $P^\parallel$ under $H^\parallel$ field. Applying a $H_a$ field decouples the preceding pair, and another pair of irreducible representations is formed $(\tau_1 + \tau_2$ or $\tau_2 + \tau_1$) inducing the observed spin flop, with an onset of a phase of symmetry $Z_2$ consistent with the reported $P^*$ polarization.

In conclusion, clarifying the nature of the coupling between the antiferromagnetic spin-density wave order-parameters leading to the emergence of multiferroic phases and the eventual modification of these couplings under applied magnetic fields, constitute an essential step for understanding their macroscopic properties and the nature of the underlying microscopic interactions. In most cases the coupled order-parameters have different symmetries corresponding to different irreducible representations of the paramagnetic space-group. However, in the multiferroic phases of some compounds, such as NaFeSi$_2$O$_6$, FeVO$_4$ or LiCu$_2$O$_2$, the coupled order-parameters, although corresponding to different spin-density waves, display the same symmetry, being associated with the same irreducible representation of the paramagnetic group. The coupling between replica of the same order-parameter is specific to continuous symmetry groups and cannot occur when a discrete symmetry is broken [30]. It therefore indicates that a continuous symmetry can be broken at the transition to a multiferroic phase, which can be identified as the continuous rotation of the phase modulation mode (the phason) characterizing transitions to incommensurate structures [19].

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References

[1] Dvorák V, Janovec V and Ishibashi Y 1983 J. Phys. Soc. Japan 52 2053
[2] Tolédano P 2009 Phys. Rev. B 79 094416
[3] Fiebig M 2005 J. Phys. D: Appl. Phys. 38 123–52
[4] Eerenstein W, Mathur N D and Scott J F 2006 Nature 442 759
[5] Kimura T 2007 Ann. Rev. Mat. Res. 37 387
[6] Seki S, Kurumaji T, Ishiwata S, Matsui H, Murakawa H, Tokunaga Y, Kaneko Y, Hasegawa T and Tokura Y 2010 Phys. Rev. B 82 064424
[7] Banks M G, Kremer R K, Hoch C, Simon A, Ouladdiaf B, Broto J M, Rakoto H, Lee C and Whangbo M H 2009 Phys. Rev. B 80 024404
[8] Lee C, Liu J, Whangbo M H, Koo H J, Kremer R K and Simon A 2012 Phys. Rev. B 86 060407
[9] Zhao L et al 2012 Adv. Mat. 24 2469
[10] Sakhnenko N V and Ter Oganessian V P 2012 Phys. Solid State 54 311–5
[11] Seki S, Yamasaki Y, Soda M, Matsuura M, Hirota K and Tokura Y 2008 Phys. Rev. Lett. 100 127201
[12] Yasui Y, Sato K, Kobayashi Y and Sato M 2009 J. Phys. Soc. Japan 78 084720
[13] Rasyidi A et al 2008 Appl. Phys. Lett. 92 262506
[14] Kobayashi Y, Sato K, Yasui Y, Moyoshi T, Sato M and Kakurai K 2009 J. Phys. Soc. Japan 78 084721
[15] Naito Y, Sato K, Yasui Y, Kobayashi Y, Kobayashi Y and Sato M 2007 J. Phys. Soc. Japan 76 023708
[16] Banks M G, Heidrich-Meisner F, Honecker A, Rakoto H, Broto J M and Kremer K J 2007 J. Phys.: Condens. Matter 19 145227
[17] Mourigal M, Enderle M, Fäk B, Kremer R K, Law J M, Schneidewind A, Hiess A and Prokofiev A 2012 Phys. Rev. Lett. 109 027203
[18] Kovalev O V 1965 Irreducible representations of the space groups Russian Monographs and Texts on the Physical Sciences (New York: Gordon and Breach)
[19] Tolédano J C and Tolédano P 1987 The Landau theory of phase transitions: application to structural, incommensurate, magnetic, and liquid crystal systems Lecture Notes in Physics (Singapore: World Scientific)
[20] Perez-Mato J M, Ribeiro J L, Petricek V and Aroyo M I 2012 J. Phys.: Condens. Matter 24 163201
[21] Dzyaloshinskii I E 1964 Sov. Phys.—JETP 19 960–71
[22] Whangbo M H, Koo H J and Dai D 2003 J. Solid State Chem. 176 417
[23] Katsura H, Nagaosa N and Balatsky A V 2005 Phys. Rev. Lett. 95 057205
[24] Kimura T, Sekio Y, Nakamura H, Siegert T and Ramírez A P 2008 Nat. Mater. 7 291
[25] Tolédano P, Leo N, Khalayavin D D, Chapon L C, Hoffmann T, Meier D and Fiebig M 2011 Phys. Rev. Lett. 106 257601
[26] Villarreal R, Quirion G, Plumer M L, Poirier M, Usui T and Kimura T 2012 Phys. Rev. Lett. 109 167206
[27] Wang Z, Qureshi N, Yasen S, Mukhin A, Ressouche E, Zherlitsyn S, Skourski Y, Geshov J, Ivanov V, Gospodinov M and Skurnyrev V 2016 Nat. Commun. 7 10295
[28] Mettout B, Tolédano P and Fiebig M 2010 Phys. Rev. B 81 214417
[29] Mettout B and Tolédano P 2012 J. Phys.: Condens. Matter 24 086002
[30] Mettout B, Tolédano P and Lormann V 1996 Phys. Rev. Lett. 77 2284–7