First-order multi-k phase transitions and magnetoelectric effects in multiferroic Co₃TeO₆

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A theoretical description of the sequence of magnetic phases in Co₃TeO₆ is presented. The strongly first-order character of the transition to the commensurate multiferroic ground state, induced by coupled order parameters corresponding to different wavevectors, is related to a large magnetoelastic effect with an exchange energy critically sensitive to the interatomic spacing. The monoclinic magnetic symmetry C2′ of the multiferroic phase permits spontaneous polarization and magnetization as well as the linear magnetoelectric effect. The existence of weakly ferromagnetic domains is verified experimentally by second harmonic generation measurements.

At variance with structural transitions which alter the lengths and orientations of the chemical bonds, the spin ordering occurring in magnetic phases has in most cases a negligible effect on the structural lattice. An important exception is represented by the class of magnetostructural transitions occurring in multiferroic compounds in which the magnetic ordering in the multiferroic phase induces simultaneously a change in the atomic structure, which permits the emergence of a spontaneous polarization. However, the measured changes of lattice parameters found in the multiferroic phases are generally small, i.e. of the order of 10⁻³ Å, and do not affect the second-order character of the transitions to these phases. Here, we describe theoretically the sequence of phases recently reported in Co₃TeO₆ in which a strongly first-order transition, characterized by substantial discontinuities of the lattice parameters and a remarkable delta-shape peak of the specific heat, yields a multiferroic ground state displaying magnetoelectric properties. The observed structural changes are related to the coupling between the magnetic order-parameters involved at the transition, which correspond to different propagation wave-vectors, in contrast with the standard situation found in multiferroic transitions where the coupled order-parameters generally pertain to the same k-vector.

Neutron powder diffraction studies show that below the paramagnetic phase described by the space group Gp = C2/c1′ the Co₃TeO₆ undergoes a sequence of three antiferromagnetic phases, summarized in Fig. 1. They are associated with three different k-vectors of the centred monoclinic Brillouin-zone: \( \vec{k}_1 = (0, 0.480, 0.055) \), \( \vec{k}_2 = (0, 0, 0) \) and \( \vec{k}_3 = (0, 1/2, 1/4) \).

I. The incommensurate Phase I, which emerges at \( T_N = 26 \) K, shows the coexistence of \( \vec{k}_1 \) and \( \vec{k}_2 \). The tran-
symmetries C2/c (Γ1), C2′/c′ (Γ2), C2′/c′ (Γ3) and C2′/c (Γ4). The magnetic structure proposed by Ivanov et al.\cite{Ivanov2008} from neutron data coincides with the C2′/c magnetic group which is therefore associated with a one-dimensional order-parameter, denoted ζ hereafter, corresponding to the single equilibrium state which minimizes below T_1 the canonical free-energy:

\[ F_2(ζ) = \frac{α_2}{2} ζ^2 + \frac{λ_1}{4} ζ^4 \]  

In absence of applied fields the magnetic symmetry of the phase does not allow the emergence of spontaneous polarization or magnetization components.

III. At T_2 = 17.4 K a commensurate phase III arises in which the neutron diffraction pattern corresponding to \( \vec{k}_2 \) persists coexisting with magnetic peaks associated with the commensurate wave-vector \( \vec{k}_3 \). Both sets of reflections are observed in the whole range of stability of the phase down to 1.6 K\cite{Ivanov2008} \( \vec{k}_3 \) is in general a position inside the Brillouin-zone, corresponding to a four-dimensional IR of \( G_p \), denoted \( \tau_1(\vec{k}_3) \), whose matrices are listed in Table 1. Keeping for the four order-parameter components the same notation \( (η_i = ρ_i e^{iθ_i}, i = 1, 2) \) as for phase I the transition free-energy reads

\[ F_3(ρ_1, ρ_2, θ_1, θ_2) = F_1(ρ_1, ρ_2) + \frac{β_3}{4} (ρ_1^4 \cos 4θ_1 + ρ_2^4 \cos 4θ_2) + \frac{β_4}{2} ρ_1^2 ρ_2^2 \sin (2θ_1 + 2θ_2) + \ldots, \]

which differs from \( F_1 \) by the \( β_3 \) and \( β_4 \) lock-in invariants. Phase III results from the coupling of the order-parameters \( η_i(\vec{k}_3) \) and \( ζ(\vec{k}_2) \) corresponding to the total free-energy

\[ F_T = F_3(ρ_i, θ_i) + F_2(ζ) - \frac{δ}{2} ζ^2 (ρ_1^2 + ρ_2^2), \]

where the \( δ \)-term represents the lowest-degree coupling between the two order parameters. Table 1 lists the

![Figure 2](image-url)

FIG. 2. (a) Paramagnetic unit-cell embedded into the 16-fold unit-cell of the multiferroic phase III of Co₃TeO₆. (b) Ferroelectric and weak ferromagnetic domains in phase III. In the text we use Cartesian instead of the monoclinic coordinates according to \( x \sim a, y \sim b, z \sim c. \)
under the conditions $\delta > \left(\frac{\beta_1 + \beta_2}{2}\right)^{1/2}$ and $\lambda_1 - \frac{4\beta^2}{|\beta_1 + \beta_2|} < -4\left(\frac{\beta_2}{3}\right)^{1/2}$, the phase corresponding to the sole “triggering” order-parameter $\zeta$ becomes unstable with respect to a phase in which both order parameters, $\zeta$ and $\eta \sim (\rho_1, \theta_1)$, are non-zero. In this phase $\zeta$ is frozen and $\eta$ determines the symmetry breaking process. The transition can be shown to occur discontinuously at a higher temperature than the transition temperature at which a phase with $\zeta = 0, \rho_1 \neq 0$ would appear. Accordingly, the triggering process, which is activated in the region of phase coexistence preceding the transition at $T_2$, is due to a large negative value of the interaction term for the coupling between the two order-parameters, which determines the value of the coupling coefficient $\delta$. Note that the first-order character of the transition to the multiferroic phase at $T_2$ is confirmed by the strong discontinuities (of the order of $10^{-2}$ A) observed in the lattice parameters and by a remarkably sharp peak of the specific heat. In contrast, the transition from the paramagnetic to the antiferromagnetic phase I is

\begin{table}[h]
\centering
\begin{tabular}{ccccccc}
\hline
(a) & (b) & (c) & (d) & (e) & (f) \\
\hline
1 & $P1'$ & $\zeta \neq 0, \rho_1 \neq 0, \rho_2 = 0, \theta_1 = 0$ & (-1, 0, 0) & 4 & (0, 1/2, 0) \\
2 & $P1'$ & $\zeta \neq 0, \rho_1 \neq 0, \rho_2 = 0, \theta_1 = \pi/4$ & (1/2, 3/2, 1) & 4 & (1/4, 3/4, 0) \\
3 & $P1$ & $\zeta \neq 0, \rho_1 \neq 0, \rho_2 = 0$ & (1/2, 1/2, 1) & 4 & (0, 0, 0) \\
4 & $C2'$ & $\zeta \neq 0, \rho_1 = \rho_2, \theta_1 = \theta_2$ & (0, 0, 4), (0, 2, 0), (1/2, 0, 0), (1/4, 0, 0) & 16 & (0, 5/8, 5/4) \\
5 & $P1'$ & $\zeta \neq 0, \rho_1 \neq 0, \rho_2 \neq 0, \theta_1 = 0, \theta_2 = -\pi/4$ & (0, 2, 0) & 8 & (0, 1/2, 0) \\
6 & $P1'$ & $\zeta \neq 0, \rho_1 \neq 0, \rho_2 \neq 0, \theta_1 = \pi/2, \theta_2 = -\pi/4$ & (1/2, 0, 0) & 8 & (1/4, 1/4, 1/2) \\
7 & $P1$ & $\zeta \neq 0, \rho_1 \neq 0, \rho_2 \neq 0$ & (0, 1, -2) & 8 & (0, 0, 0) \\
\hline
\end{tabular}
\caption{Seven possible choices (a) of the magnetic space groups (b) derived from the minimization of $F_T(\zeta, \rho_1, \theta_1)$ in Eq. (4). (c) Equilibrium values of the order parameters. (d) Basic translations of the conventional monoclinic or triclinic unit cells. (e) Multiplicity of the volume of the primitive paramagnetic unit cell. (f) Origin of the coordinates.}
\end{table}

Figure 3 shows the distribution of magnetic domains in the monoclinic $xz$ plane. The image was gained by optical second harmonic generation (SHG) as described in Ref. 5. The orientation of the domain walls along an arbitrary direction in the $xz$ plane further confirms the 2' symmetry. This symmetry is also consistent with the presence of the $\chi_{xxx}$ and $\chi_{zzz}$ components of the SHG susceptibility tensor. Note, however, that it differs from the symmetry $m$ assumed in Ref. 5. In Ref. 5 only $t$-tensor components were considered as origin of the SHG signal since in magnetically induced ferroelectrics like MnWO$_4$ the SHG signal is always linearly coupling to the spontaneous polarization. In contrast, the SHG signal leading to Fig. 3 revealed that SHG in CTO is related to $c$-tensor components reproducing the weakly ferromagnetic order. SHG with $\chi_{xxx} \neq 0$, $\chi_{yyy} = 0$, and $\chi_{zzz} \neq 0$ as c-type susceptibilities leads to the magnetic symmetry 2'. Unfortunately, a recent discussion of our SHG data in Ref. 11 is still based on the assumption of SHG coupling to the electric polarization which lead to results inconsistent with the ones reported in this work.

Since the transitions to phases I and III result from the coupling of two order-parameters corresponding to distinct $k$-vectors they display necessarily a first-order character following the triggering mechanism proposed by Holakovsky in which one order-parameter triggers the onset of another order-parameter across the first-order discontinuity. The mechanism requires taking into account a sixth-degree invariant of the “triggered” order-parameter ($\zeta (\rho_1^2 + \rho_2^2)^{1/2}$) in the total free-energy $F_T$. Under the conditions $\delta > \left(\frac{\beta_1 + \beta_2}{2}\right)^{1/2}$ and $\lambda_1 - \frac{4\beta^2}{|\beta_1 + \beta_2|} < -4\left(\frac{\beta_2}{3}\right)^{1/2}$, the phase corresponding to the sole “triggering” order-parameter $\zeta$ becomes unstable with respect to a phase in which both order parameters, $\zeta$ and $\eta \sim (\rho_1, \theta_1)$, are non-zero. In this phase $\zeta$ is frozen and $\eta$ determines the symmetry breaking process. The transition can be shown to occur discontinuously at a higher

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{SHG image of a polished single-crystal platelet (thickness 50 µm) of Co$_3$TeO$_6$ at $T = 5$ K. Diagonal parallel stripes correspond to magnetic domain walls, whereas the gradual ringlike oscillation of brightness is caused by interference of the laser light in the sample. The incident light at $E = 1.29$ eV was propagating parallel to the crystallographic $y$ axis and polarized parallel to the direction of the domain walls, while the SHG light was polarized perpendicular to the domain walls.}
\end{figure}
weakly first-order with almost negligible lattice discontinuities and a standard specific heat anomaly. The transition from phase I to phase II which involves a single order-parameter has typical second-order transition features with no noticeable discontinuity of the lattice parameters.

The dielectric contribution to the free-energy $F_D = -\nu P_y \zeta^2 (\rho_1^2 \rho_2^2 \cos 2(\theta_1 + \theta_2)) + \frac{P_y^2}{\varepsilon_{yy}}$ yields the equilibrium value of $P_y$ below $T_2$:

$$P_y = \nu \epsilon_{yy} \zeta^2 \rho_e^4 \cos 4\theta_e$$

At $T = T_2$, $P_y$ undergoes an upward discontinuity, imposed by the first-order character of the transition. On further cooling it increases as $\approx (T_2 - T)^2$, since the $\zeta$ order-parameter is frozen in phase III. A similar temperature dependence holds for the spontaneous magnetization components $M_x$ and $M_z$. From the spontaneous magnetic contribution to the free-energy in phase III

$$F_M = \mu_u M_u \zeta \rho_e^2 \cos 2(\theta_1 + \theta_2) + \frac{M^2}{2 \varepsilon_{uu}}$$

(with $u = x, z$), one gets

$$M_u = -\chi_{uu} \mu_u \zeta \rho_e^4 \cos 4\theta_e$$

as the equilibrium value below $T_2$. Application of magnetic fields along $x$ or $z$ yields a renormalization of the transition temperature according to

$$T_2(H_u) = T_2(0) - \frac{\alpha}{\chi_{uu} \mu_u} \cos^2 \theta_u^0 H_u^2$$

Where $\alpha = \alpha_0(T - T_2(0))$ is the coefficient of $\rho_e^2$ in $F_T$. For $\mu_u > 0$ the transition temperature is lowered under application of a magnetic field and $T_2(0) - T_2(H_u)$ increases quadratically with $H_u$, as observed in Co$_3$TeO$_6$ under $H_z$ field. The magnetic susceptibility components $\chi_{uu} = \frac{M_u}{H_u}$ are obtained by minimizing the field-induced contribution to the free-energy $F_M(H_u) = \mu_u M_u H_u \zeta^2 \rho_e^2 + \frac{M^2}{2 \varepsilon_{uu}} - H_u M_u$. This reveals

$$\chi_{uu} = \chi_{uu}^0 (1 - \mu_u \zeta^2 \rho_e^2)$$

Therefore the discontinuous jump of the order-parameter $\rho_e(T_2)$ coincides with a drop of $\chi_{uu}(T_2)$ the magnitude of which decreases with increasing field up to a threshold field corresponding to $\rho_e(H_u^0) = \frac{1}{\zeta \sqrt{\rho_e}}$ above which $\chi_{uu}$ undergoes an upward discontinuity at $T_2(H_u)$. This behaviour is verified experimentally for $H_z$ with a threshold field $H_z^c \approx 12 T$. The slight decrease with temperature observed for $\chi_{zz}$ below $T_2$ indicates a slight increase of the order-parameter within the multiferroic phase, with an almost step-like dependence on temperature across the transition. As a consequence of this Heaviside-like behaviour the specific heat $C$ which is proportional to the order-parameter derivative displays a delta-shape like behaviour across $T_2$. This remarkable property of the first-order multiferroic transition in Co$_3$TeO$_6$, which has been previously observed at the first-order ferromagnetic transition in Fe$_2$P, is reminiscent of structural transitions having a reconstructive mechanism as observed, for example, at the fcc-hcp transition in cobalt. However, in Co$_3$TeO$_6$ the symmetry-breaking mechanism involved at $T_2$ is not of the reconstructive type since the C2’ symmetry of phase III is group-subgroup related to the C2’/c symmetry of phase II. Therefore the strong discontinuities reported for the lattice parameter, at $T_2$ should correspond to a strong magnetoelastic coupling with an exchange energy critically sensitive to the interatomic spacing. This is in agreement with the large spin lattice coupling deduced by Her et al. from the magnetic hysteresis curves and with the direct exchange pathway corresponding to the shorter Co-Co distances existing in phase III (see Fig. 12 in Ref. [14] for the neighbouring atoms Co(5)-Co(5), Co(2)-Co(5), Co(3)-Co(3) and Co(4)-Co(4). The strong magnetoelastic effect is favored by the coupling between the order-parameters $\zeta$ and $\eta$. Here, the already existing antiferromagnetic order-parameter $\zeta$ triggers the emergence of the order parameter $\eta$, which is reflected by the transition discontinuity.

The respective monoclinic symmetries of phases II and III permit a variety of magnetoelastic effects under applied magnetic or electric fields. For instance, in phase II applying a magnetic field $H_x$, induces contributions by $P_x$ and $P_z$ to the polarization which vary as $P_x \approx \zeta H_y$. In phase III one has $P_{x,z} \approx \zeta \rho_e^2 H_y$, i.e., at constant temperature $P_x$ and $P_z$ increase linearly with $H_y$ in both phases, while at constant field they increase with temperature as $(T_1 - T)^{1/2}$ in phase I and as $(T_2 - T)$ in phase III. Conversely, applying the magnetic field $H_x$ or $H_z$ in phase II induces a polarization $P_y \approx \zeta H_{x,z}$. In phase III an additional contribution to the spontaneous polarization $P_y$, namely $\Delta P_y \approx \zeta \rho_e^2 H_{x,z}$ is generated. Reversed magnetoelastic effects should also be observed in phases II and III with the onset of an induced magnetization $M_y$ depending linearly on electric fields $E_x$ or $E_z$. Additional contributions to the $M_x$ and $M_z$ components of the spontaneous magnetization are generated under an electric field $E_y$. Accordingly, our theoretical analysis suggests that magnetic-field-induced polarization components $P_x(H_z)$, $P_z(H_z)$ and $P_z(H_x)$ are not allowed. Their observation was reported earlier and should be related to a misorientation of the sample admixing a $y$ component to the $x$ axis. The possibility for such a misorientation was indeed pointed out by the authors of Ref. [5].

In summary, the observed properties of the sequence of three phases reported in Co$_3$TeO$_6$ have been described theoretically. The most striking feature of this phase sequence is the coexistence of propagation vectors in the incommensurate and commensurate multiferroic phases, the Brillouin zone-centre $\vec{k}_z$ vector, which persists in all three phases, coupling successively with the incommensurate $\vec{k}_1$-vector in phase I, and with its lock-in commensurate variant $\vec{k}_3$ in phase III. Another remarkable property is the strongly first-order-character of the multiferroic transition which relates both to the triggering mechanism coupling the $\vec{k}_2$ and $\vec{k}_3$ related order-parameters,
and to a strong magnetoelastic coupling. The sharp peak of the specific heat is shown to be consistent with the almost constant value of the spontaneous magnetization in the multiferroic state. Furthermore, a number of experimental observations of Ref. [5] have been scrutinized: The monoclinic symmetry of phase III is 2′ (instead of the m as previously proposed[5]). This permits a spontaneous weak magnetization (M_x, M_z), which is found to be in agreement with domain structures observed in SHG measurements. It also allows a spontaneous polarization P_y which has not been investigated before whereas contributions P_x,z ≠ 0 are no longer expected. The magneto-electric effects that should exist in Co_3TeO_6 have been worked out theoretically. A verification of these predictions, supported by the application of both magnetic and electric fields, is necessary for confirming the validity of the theoretical description presented in this article.

At last we emphasize that our theoretical analysis and conclusions differ in an essential manner from the symmetry analysis proposed in Ref. [11] for two reasons. (i) Scrutinization of the data reported in Ref. [5] lead to a revision of the magnetic symmetry and the direction of electric polarization. Since this is a very recent result it could be taken into account in the present work but not in Ref. [11]. (ii) In Ref. [11] mainly one dimensional order-parameters associated with the wave-vector $\mathbf{k}_2$ are considered. In contrast, we analyze the symmetries and physical properties of phases I and III as resulting from the coupling of order-parameters associated respectively with the wave-vectors ($\mathbf{k}_1$, $\mathbf{k}_2$) and ($\mathbf{k}_2$, $\mathbf{k}_3$), in agreement with the neutron diffraction data reported in Ref. [4]. In particular the field-induced component $P_z(H_x)$ discussed in Ref. [11] is shown to be absent in our description, whereas we predict the existence of a single spontaneous (zero-field) polarization component $P_y$.

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