Polarization-flip phase transitions under an electric field in displacive systems with competing periodicities

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As an alternative to the usual Landau-Ginzburg-type continuous field approximation, a free energy featuring two anticrossed phonon branches and defined in a discrete lattice is proposed for dealing with modulated phases with inherent discrete lattice effects. Using this approach, it is shown that, at some threshold electric (or conjugate) field, phases may appear in the phase diagram of solids having several modulated phases of different periods. These phases are the result of the sign-reversal of a particular polar local mode in a spinlike modulation of the order parameter, and have indeed been recently observed in the modulated ferroelectric betaine calcium chloride dihydrate (BCCD). This type of field-driven *polarization-flip* transition had not been anticipated by previous theoretical approaches, including microscopic ones such as the ANNNI model. The model proposed also explains the quite peculiar topological features of the phase diagram under the electric field observed in BCCD.

I. INTRODUCTION

Solids with an incommensurate structural thermal instability can exhibit complex phase sequences as a function of temperature. In many of these materials, several intermediate commensurate phases exist where the structural modulation locks into different multiples of the period of the underlying basic lattice.[1] BCCD (betaine calcium chloride dihydrate) is the most conspicuous experimental case with more than 15 intermediate phases of different periods between room temperature and 0 K.[2] The instability mechanism is displacive with a clear soft-phonon branch,[3] but spin lattice models with competing interactions favoring different periods, as the ANNNI (axial next nearest neighbor Ising) model and its derivatives[4] seem sufficient to explain the basic features of its temperature phase diagram, in particular the polarization modulation in the different phases and the resulting dielectric properties.[2,5] The spins are associated to each semicell along the *z* direction and are identified with the (discrete) amplitude of a local mode, polar along the *y* direction. The local polarization, in general modulated along the *z* direction, is then represented by the average value of the spins on (semi)lattice *xy* planes. The polarization modulation is sinusoidal close to the initial incommensurate instability. But, according to dielectric and diffraction measurements, and in agreement with the ANNNI model, at lower temperatures, in subsequent commensurate phases, adquires simple spinlike one-dimensional commensurate sequences along the *z* direction. Thus, phases having modulation wave vectors $\mathbf{q}\equiv\gamma\mathbf{c}^*$ with $\gamma=\frac{1}{4}$ and $\frac{1}{5}$ (hereafter phases $\frac{1}{4}$ and $\frac{1}{5}$ have local-mode or *spin* sequences $\langle$4up4down$\rangle$ and $\langle$5up5down$\rangle$, respectively, or in short $\langle 4\rangle$ and $\langle 5\rangle$. The validity of this approximate description of the structual modulation has been recently confirmed by neutron diffraction experiments.[6] The modulation or *spin* sequences for phases corresponding to intermediate wave vectors can be readily envisaged from that of the simpler neighboring ones. Thus, for the phase $\frac{2}{9}$, with γ in between $\frac{1}{4}$ and $\frac{1}{5}$, the sequence would be $\langle 54\rangle$.[7] As the spin represents a local mode which is polar along the *y* direction, it comes out naturally from these rules that only phases with modulation wave vectors $\gamma=n/m$ with *n* even and *m* odd can be *y* polar, in agreement with more rigorous arguments.[8]

However, the microscopic or phenomenological models considered up to now have not anticipated the recently reported[9] peculiar features of the phase diagram of BCCD under electric field along the *y* direction (see Fig. 1). At nonzero field, the expected increase of the ranges of *y*-polar commensurate phases at the cost of the nonpolar ones is observed. But at some threshold fields new phases appear. In particular, above 17 kV/cm, approximately where the transition lines between phases $\frac{2}{11}$-$\frac{1}{5}$ and $\frac{1}{5}$-$\frac{2}{9}$ are about to meet, a new phase seems to exist in Fig. 1. From dielectric measurements Le Maire *et al.*[9] conjectured that this field-stabilized phase corresponds to a polar configuration $\langle 64\rangle$, being the result of a spin flip in the $\langle 5\rangle$ sequence of the nonpolar phase

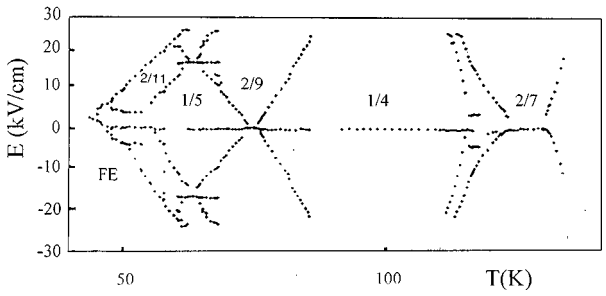

FIG. 1. Experimental phase diagram of BCCD as a function of temperature and electric field E_b as reported in Ref. 9.

$\frac{1}{5}$. Its polarization, larger than those of the neighboring phases $\frac{2}{11}$ ($\langle 65 \rangle$) and $\frac{2}{9}$ ($\langle 54 \rangle$), would explain the steady increase of its stability range at higher fields. Neutron scattering measurements under electric field have recently confirmed this hypothesis and directly detected the polarization flip change in the polarization modulation.[10] This transition has not been foreseen in studies of field effects on ANNNI-type Hamiltonians or in other microscopic displacive models.[11] Even Landau-type phenomenological analyses specially developed to derive electric field effects on BCCD have failed to predict such polar phases.[12]

Using an alternative quite general free-energy functional, we show here that, under some conditions, this kind of polarization-flip phase transitions under conjugate field can be, in fact, rather common in displacive systems with competing periodicities. The proposed potential reproduces the basic low-energy lattice-dynamics common to all these materials, while keeping, in contrast to the usual approaches,[12,13] the lattice discreteness of the order parameter configuration. This is sufficient for predicting the existence in the lowest temperature range of several commensurate phases with spinlike modulations, while the presence of flip transitions under a conjugate field seems rather ubiquitous.

II. A DISCRETE GENERALIZED LANDAU-GINZBURG POTENTIAL

The essential mechanism for the appearance of modulated phases (incommensurate and commensurate) in many dielectric systems is a strong coupling of a phonon branch, thermally soft at the Γ point, with a second low-energy stable phonon branch; both branches being, however, uncoupled at the Γ point. This basic scheme (which may be complicated by the presence of additional branches) is present in very different materials such as K_2SeO_4,[14] thiourea,[15] or BCCD.[3] Hence, a local description requires, at least, two local modes, which generate the configuration subspace associated to the two relevant branches. As the static modulation in the different phases takes place along a single direction, the configuration for a given thermodynamic phase can be described by the average value of the two local variables, say η_n and ξ_n, in lattice planes n along the modulation direction, and the problem becomes essentially one dimensional. A Landau-Ginzburg-type potential with an underlying one-dimensional discrete lattice can then be postulated for these local order parameters. This potential is expressed more efficiently using the so-called internal coordinate introduced in the superspace description of modulated structures:[16] if $\gamma \mathbf{c}^*$ is the primary wave vector of the modulation, the configuration of the order parameter η can in general be described by a modulation function $\eta(v)$ of period 1 along the internal coordinate v, so that the average value of the order parameter at the lattice point n, η_n, is given by $\eta(v_n)$ with $v_n = \gamma n$ (mod 1). An analogous function can be defined for the ξ configuration. The use here of a continuous ''internal'' coordinate to label the cells along the modulation direction does not imply any continuous approximation of the lattice, but allows us to separate on the real-space configuration the effect of the wave vector (real space period) from that coming from the particular form of the modulation. In the case of commensurate configurations, the number of physically relevant points in $\eta(v)$ and $\xi(v)$, $v_n = \gamma n$, is discrete and finite, while in an incommensurate configuration the set of distinct points v_n forms a dense set in the period $[0, 1)$. In terms of these modulation functions, the postulated free energy (per unit cell) is

$$
\begin{aligned}
F = \frac{1}{N}\sum_n \Phi(\gamma, v_n) = \frac{1}{N}\sum_n \Big\{ & 2(\tau - 1)\,\eta(v_n)^2 + \eta(v_n)^4 \\
& + \xi(v_n)^2 + \frac{\beta'}{4}\,\xi(v_n)^4 + \sigma\{[\eta(v_n + \gamma) - \eta(v_n)]\xi(v_n) \\
& - \eta(v_n)[\xi(v_n + \gamma) - \xi(v_n)]\} + \frac{\delta}{2}[\eta(v_n + \gamma) - \eta(v_n)]^2 \\
& + \frac{\delta'}{2}[\xi(v_n + \gamma) - \xi(v_n)]^2 - E\,\eta(v_n) \Big\}, \qquad (1)
\end{aligned}
$$

where τ is a normalized temperature. The coupling term σ between the two local variables vanishes for homogeneous configurations favoring modulated ones. Anharmonicity is only included at a local level. Equation (1) is closely related with the Landau potential proposed by Levanyuk and Sannikov[17] for incommensurate systems of the so-called type II. Here, however, no continuous approximation is introduced; the η and ξ configurations are discrete although they are described along the continuous internal coordinate of the superspace formalism. Notice that the dependence on the wave vector parameter γ is here explicit and the real-space nearest neighbor of a given site with value $v = v_n$, having $v_n + \gamma$ as internal coordinate, is not necessarily the nearest site along the internal cordinate. Thus, the σ and δ terms, coupling neighboring sites, cannot in general be approximated by gradient terms, as done in usual Landau-Ginzburg-type functionals. In Fourier space, Eq. (1) represents two (anharmonic) phonon branches bilinearly coupled for $k \neq 0$ through the term σ, only one of them being a soft-phonon branch. We use reduced units so that the number of free coefficients in the potential is limited to a minimum. Equation (1) also contrasts with more complex microscopic effective Hamiltonians proposed in the literature:[18] the energetics has been reduced to its bare essentials with couplings only up to nearest neighbors and two modes per cell; the local variables have displacive character and no *a priori* spinlike feature is introduced; instead of an effective Hamiltonian, we reduce the problem to a Landau-type thermodynamic potential through the *ad hoc* introduction of the usual Landau hypothesis of a single quadratic coefficient linearly dependent with temperature and unstable below a certain temperature. For a given commensurate wave vector $\gamma = n/m$, the sum in Eq. (1) is reduced to m distinct terms, while if γ is incommensurate, it can be replaced by an integral along the internal coordinate

$$
F_{\mathrm{inc}} = \int_0^1 dv\, \Phi(\gamma, v),
$$

which for a given temperature should be minimized not only with respect the $\eta(v)$ and $\xi(v)$ configurations, but also with respect to the wave vector γ.

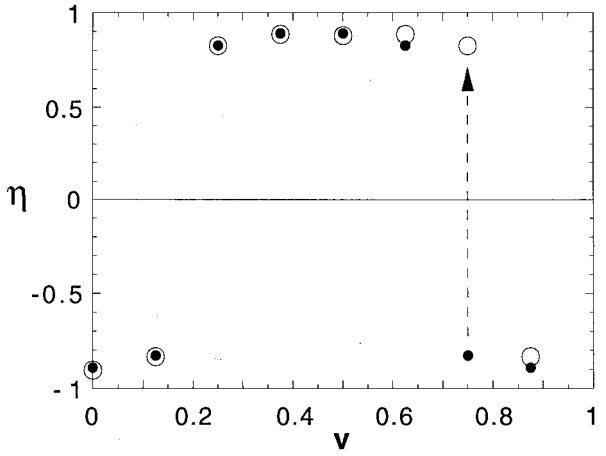

FIG. 2. Equilibrium configuration of the order parameter η in the modulated phase with $\gamma=\frac{1}{8}$ at a temperature $\tau=0.25$ under a field $E=4\times10^{-3}$ (solid points) for the model described in the text. This configuration coincides essentially with that derived at zero field. The empty circles correspond to the η configuration at the same temperature under a field $E=5\times10^{-3}$, showing the abrupt change of the modulation which can be described as a discrete ''flip'' of a local mode value.

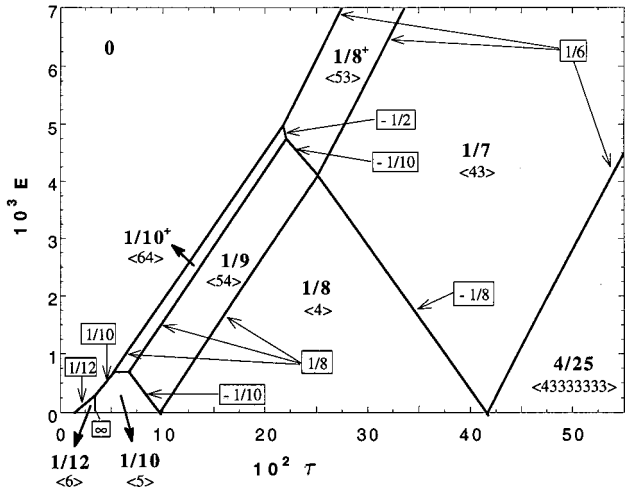

FIG. 3. Calculated low temperature (τ,E) phase diagram for the model described in the text. The wave vector γ and the η configuration for each phase is indicated; polarization-flipped phases are labeled by adding a sign + to the γ value. The scaling relations for the slopes of the interphase lines are shown in square frames. τ and E are dimensionless.

III. PHASE DIAGRAM

Within quite wide ranges for the values of the potential coefficients, a minimization at zero field of Eq. (1) and its incommensurate counterpart as a function of temperature yields a sequence of several phases, namely, an initial incommensurate phase plus several subsequent commensurate ones, with a final lock-in into a nonmodulated phase with $\eta\neq0$, $\xi=0$. The potential coefficients were fixed to $\beta'=90$, $\sigma=0.7076$, $\delta=0.2$, and $\delta'=1$; they were chosen without pretending to reproduce any real system in particular, only searching a maximal number of distinct commensurate modulated phases while keeping as ground state a nonmodulated $\eta\neq0$, $\xi=0$ configuration. The first instability at $\tau_I=1.0755$ into an incommensurate modulated phase of wave number $\gamma_I=0.16$ can be derived analytically. The subsequent phase diagram as a function of temperature and field was calculated numerically. As we were only interested in the relative stability of the commensurate phases well below T_i and their variation under the η-conjugate field (E), no effort was done to locate the stability range of the incommensurate phase, which in any case is limited to the higher temperature interval. As expected, close to τ_I, the spontaneous modulation $\eta(v_n)$ has a sinusoidal form, but quite rapidly, at lower temperatures well above the stability range of the commensurate phase $\frac{1}{8}$, the modulation function of η takes a steplike approximate form with two equal regions of opposite sign (see Fig. 2). The form of the modulation $\eta(v)$ hardly varies as temperature is further lowered, despite several transitions into different commensurate phases. Thus, the modulation attains a *soliton regime*[1] with respect to the final lock-in phase (the unmodulated polar ground state) and in all intermediate phases the local values of the order parameter can take essentially only two opposite values, acting *de facto* as a spin. Figure 2 shows the equilibrium values $\eta(v_n)$ for the $\frac{1}{8}$ phase, where a sequence $\langle4\rangle$ can be clearly seen. This compares well with the solitonlike atomic modulation functions observed in BCCD for $\gamma=\frac{1}{4}$ (Ref. 6) (the factor 2 between the two wave vectors comes from the fact that in BCCD the local mode is defined at every semicell). The invariance of the modulation function $\eta(v)$ at low temperatures explains the numerical rules relating the *spin* sequences in different phases.

The calculated phase diagram as a function of the η conjugate field is shown in Fig. 3 for the lower temperature range where locally the local mode η is close to saturation. In this temperature range, the transition lines between commensurate phases can be approximated by straight lines. Rather systematically at some threshold field, when two polar phases are about to ''squeeze out'' an intermediate nonpolar phase, a new polar phase with the same wave number is stabilized through the flip of a local-mode in the nonpolar sequence. As the local mode is nearly saturated at all sites for all competing phases, the equilibrium configuration hardly changes when the field is applied, except abruptly at these polarization-flip transitions. Thus, at $E\approx4\times10^{-3}$ a phase of wave vector $\frac{1}{8}$ (called $\frac{1}{8}^{+}$) with sequence $\langle53\rangle$ instead of $\langle4\rangle$ is stabilized (see Fig. 2) and its temperature stability range steadily grows at higher fields at the cost of the polar neighboring phases $\frac{1}{9}\langle54\rangle$ and $\frac{1}{7}\langle43\rangle$. A similar flip transition from the $\langle5\rangle$ to a $\langle64\rangle$ sequence happens for the $\frac{1}{10}$ phase.

The reasons for the peculiar topology of the phase diagram in Fig. 3, analogous to the one observed in the lowest temperature range of the experimental case of Fig. 1, are the approximate saturation of the local mode values in all relevant phases and the Clausius-Clapeyron-type relation $dE/dTc=-(\Delta S_1-\Delta S_2)/(P_1-P_2)$, where ΔS_i and P_i are the (temperature constant) excess entropies and polarizations of the two neighboring phases.[9] Except for a common constant, the (approximate) polarization of a given commensurate phase can be derived directly from its wave vector γ_i and the resulting spin sequence. The excess entropy of the commensurate phases can, on the other hand, be assumed to vary smoothly with the wave number, i.e., $\Delta S_i=A\gamma_i$ where

A is common to all phases and γ_i is the wave vector of the particular commensurate phase. In fact, this approximate linear relation is confirmed in our model and is known to be also approximately valid in a real system such as BCCD.[19] We expect then $(dE/dTc)_{1-2} \propto (\gamma_2 - \gamma_1)/(P_1 - P_2)$ and except for a common constant, the slopes only depend on the wave vectors of the two neighboring phases. Thus, we have $(dE/dT_c)_{\frac{1}{8}-\frac{1}{7}} = -(\frac{1}{8})A$, while $(dE/dT_c)_{\frac{1}{9}-\frac{1}{8}} = +(\frac{1}{8})A$, explaining the symmetry of the triangular squeezing of the nonpolar phase $\frac{1}{8}$ in Fig. 3. This rule also explains other regularities of the line slopes both in the phase diagram of the model (Fig. 3) and in the experimental results of BCCD (Fig. 1). Note for instance in Fig. 3 the parallelism of the lines between phases $0\text{-}\frac{1}{8}^+$, $\frac{1}{8}^+\text{-}\frac{1}{7}$ and $\frac{1}{7}\text{-}\frac{4}{25}$, all having a slope $(\frac{1}{6})A$ according to the rule above.

Although no effort was made to replicate any particular system, the phase diagram for the free-energy (1), already exhibits topological features analogous to those in BCCD, demonstrating in a general simple context that polarization-flip transitions are rather commonplace. An Heuristic argument can be considered to explain the fact that the flip transition takes place when the stability ranges of the neighboring polar phases are about to cross. At the crossing point both phases could in principle coexist, and this would stabilize the polarization-flipped configuration at a local level as an interface. Thus, for the case of phases $\frac{1}{9}$, $\frac{1}{8}$, and $\frac{1}{7}$ in Fig. 3, the coexistence of configurations $\langle 54 \rangle$ and $\langle 43 \rangle$ would imply at the interfaces local configurations $\langle 53 \rangle$ corresponding to the spin-flipped phase $\frac{1}{8}^+$. Note, however, that the apparent quadruple point in Fig. 3 resolves into two triple points in a larger scale. Probably these rather plausible flip transitions were not foreseen in previous studies because situations were not considered where the order parameter is close to local saturation in a large part of the phase diagram. It is intriguing, however, that in analogous modulated magnetic systems with competing periodicities such as CeSb no analogous magnetic field-driven transitions have been observed. Although phases related by a spin flip can be observed in the phase diagram of this magnetic system, the topology of the diagram is rather different and the magnetic field alone does not transform from one configuration to the spin-flipped one.[20]

IV. CONCLUSIONS

Summarizing, a free-energy potential with a displacive order parameter defined in a discrete lattice and featuring two anticrossed phonon branches is sufficient to reproduce the thermal stabilization of spinlike order-parameter modulations with different commensurate periods. The potential does not introduce a continuous approximation in real space and includes in a single framework both the free-energy of incommensurate and commensurate configurations through the use of the internal coordinate of superspace formalism. A field conjugate to the order parameter stabilizes additional ''polar'' phases through the ''flip'' of one local order parameter without changing the periodicity of the system. The present model reduces the mechanism of the structural instability to its bare essentials within a lattice-dynamical approach, and shows that these polarization-flip phase transitions can be a rather universal feature in systems with competing periodicities. The model also explains the peculiar topological features of the phase diagram under electric field observed in BCCD, which can be described by approximate scaling rules of general validity.

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