Nonsoliton model for dielectric anomalies at the incommensurate-ferroelectric phase transitions in $[N(CH_3)_4]_2XCl_4$ ($X = Co,Zn$)

C. L. Folcia

Departamento de Física Aplicada I, Escuela Técnica Superior de Ingenieros Industriales y de Telecomunicación, Universidad del País Vasco, Alameda de Urquijo s/n, 48013 Bilbao, Spain

J. M. Pérez-Mato

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apartado Postal 644, Bilbao, Spain

The dielectric peaks observed at the phase transition between an incommensurate- and a commensurate-ferroelectric phase have usually been explained in terms of a soliton-regime model of the incommensurate phase. However, in the case of $[N(CH_3)_4]_2XCl_4$ ($X =$ Co, Zn), recent observations provide evidence for a strong coexistence of both the incommensurate and ferroelectric phases. This behavior seems to discard a proper soliton regime as a model for the phase transition. We show here that in fact the dielectric behavior of these compounds can be explained assuming that the incommensurate modulation remains approximately in a sinusoidal configuration in the whole temperature range of interest. In accordance with the experimental results, the model considers that the transition between the incommensurate phase (in a sinusoidal regime) and the ferroelectric phase has a first-order character. A divergency of the dielectric susceptibility of $[N(CH_3)_4]_2CoCl_4$ and $[N(CH_3)_4]_2ZnCl_4$ is predicted as the incommensurate modulation (always in a sinusoidal regime) passes through the commensurate value $q = \frac{2}{5}c^*$. The obtained divergency law differs from the usual Curie-Weiss law and is enough to reproduce in general terms the dielectric anomaly observed in $[N(CH_3)_4]_2CoCl_4$. In this comparison we use as input data the temperature dependence of the wave vector and the coexistence ratio of incommensurate and ferroelectric phases, which were determined in some recent x-ray measurements. The present model considers a modulated order parameter in the frame of a generalized Landau analysis, but it is the low-temperature threefold-ferroelastic commensurate phase that is taken as the reference for the order parameter. Previous incommensurate and commensurate phases are described by an adequate modulation of the order parameter. A generalization of this approach to any incommensurate system exhibiting successive "lockins" into different commensurate phases is also discussed.

I. INTRODUCTION

Incommensurate phases are often stable in a limited temperature range between two commensurate phases. As the temperature decreases, a simple sequence is observed: commensurate (normal)–incommensurate (IC)–commensurate (lock in).[1-3] The crystal structure is distorted at the normal-IC transition as a consequence of the instability of a mode with IC wave vector q.[2,3] The transition at lower temperatures from the IC phase to the commensurate one can be considered the result of the interaction between the modulation and the underlying crystal lattice. As a consequence, the distortion wave vector locks into a certain rational value, q_C, giving place to a periodic structure. In the case that q_C has the same symmetry as the IC wave vector, the IC phase is called type I, otherwise type II.[2]

The thermodynamic description of this simple phase sequence in the framework of the Landau theory for phase transitions can be achieved in terms of a modulated order parameter. The IC phase is considered as a modulation of the low-temperature commensurate structure,

which is taken as the reference phase. In the case of type-I IC phases, this modulation is introduced by means of an inhomogeneous complex amplitude $Q(x)$ of the normal mode, describing the primary distortion in the reference commensurate phase. The Landau free energy is then expressed as the integral of an energy density in terms of $Q(x)$ and other inhomogeneous coordinates of some coupled modes. The lattice interaction is described by means of anisotropic (umklapp) terms that drive the wave vector q to the commensurate value q_C. In general, this type of formalism predicts the existence of a soliton regime previous to a continuous or quasicontinuous transition from the IC to the commensurate (lock-in) phase. This model has usually been employed to describe the thermodynamic behavior of A_2BX_4 compounds and other IC materials.[4-11] The predicted soliton regime has been confirmed by several techniques including its direct observation by means of transmission electron microscopy.[12]

However, a wide number of materials exhibit a much more complicated sequence of IC and commensurate phases.[13] $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$, here-

after referred to as TMAZnCl$_4$ and TMACoCl$_4$, respectively, belong to this group. At high temperature, they are commensurate and isomorphous, its symmetry being given by the space group *Pmcn*. Close to room temperature, as the temperature is lowered, a sequence of modulated (IC and commensurate) phases is observed in both materials. The IC modulation is originated by the instability of a Σ_3 mode (following the notation of Bradley and Cracknell[14]) whose wave vector is $q=(\frac{2}{5}+\delta)c^*$, with $\delta \approx 0.02$. On decreasing the temperature the wave vector locks into the commensurate value $q=\frac{2}{5}c^*$ resulting in a fivefold-ferroelectric phase with space group $P2_1cn$.[13] Spontaneous polarization in the direction of the 2_1 helicoidal axis appears in this phase because of the coupling of the Σ_3 order parameter with a mode of wave vector $5q-2c^*$. In TMAZnCl$_4$, this ferroelectric phase transforms at lower temperature into a threefold ($q=\frac{1}{3}c^*$) monoclinic ferroelastic phase with space group $P112_1/n$, which is stable in an extended temperature range. On the other hand, in TMACoCl$_4$, the ferroelectric phase transforms into another short-range IC phase before the stabilization of a low-temperature ferroelastic phase similar to the one in TMAZnCl$_4$.[13] A complete characterization by means of differential thermal analysis (DTA), differential scanning calorimetry (DSC), and dielectric constant and thermal expansion measurements of the different phases and transition temperatures appearing in these compounds is given by Sawada, Yamaguchi, Suzuki, and Shimizu.[15,16]

The whole sequence of transitions in TMAZnCl$_4$ and TMACoCl$_4$ is usually described in terms of nonmodulated parameters. The order parameter is identified with the amplitude of the main distortion in each phase and is taken to be homogeneous. The different phases are then described by the variation of the distortion wave vector with temperature. The Landau free-energy expansions of the different phases are constructed in terms of these amplitudes, considering for each phase the eventual coupling with higher armonics giving place to spontaneous polarization or strains. Phase transitions are then described as first-order transitions due to the eventual crossing of the Landau potentials corresponding to the different phases.[17−20] This approach, which is purely focused on the reciprocal space, is useful for describing a transition sequence with any number of modulated phases. The model implies a sinusoidal or quasi-sinusoidal character of the modulation and excludes the existence of a soliton regime, as the one observed in some compounds.[12,21,22] As an alternative, the application of the "modulated order parameter" approach in this kind of system is not obvious at all, because of the ambiguity in the choice of the reference commensurate phase. Nevertheless, some attempts have been made by means of a formal reduction of the number of phases that are present in these materials to only the first three: normal, IC, and commensurate (fivefold).[11,23] This latter is taken as the reference commensurate phase, and further transitions to other modulated phases are not considered. Thus, the model becomes a simple transcription of the one employed for the K$_2$SeO$_4$ family compounds, leading to a

quasicontinuous lock-in transition through a soliton regime. In contrast to this prediction, the recently reported observation in TMACoCl$_4$ and TMAZnCl$_4$ of memory effects inside the apparent range of the ferroelectric phase evidenced for these compounds a strong coexistence of both the IC and ferroelectric phases in the whole temperature range of the latter.[24,25] This assumption has been confirmed by means of x-ray diffraction measurements of the modulation wave vector and the intensity of satellite reflections in the phase-transition sequence of TMACoCl$_4$ near room temperature.[26] Also, real-time x-ray synchrotron topography measurements performed in TMAZnCl$_4$ seem to indicate a strong coexistence of the ferroelectric and the IC phases.[27] These results discard a proper soliton regime as a model for the IC-ferroelectric ("lock-in") phase transition in TMACoCl$_4$ and TMAZnCl$_4$.

The dielectric peak observed at the phase transition from an IC phase (type I) to a commensurate ferroelectric one is usually explained in terms of a soliton-regime picture of the IC phase.[5,6] Discommensurations in the soliton regime separate regions with opposite polarization that become ferroelectric domains at the lock-in phase. In this picture, the increase of the dielectric susceptibility at the IC-ferroelectric transition is explained in terms of the decrease of the effective interaction between the discommensurations as the soliton density approaches zero. Consequently, the displacement of the discommensurations under a given electric field, and the resulting macroscopic polarization, become larger. However, according to the previous discussion, the dielectric anomalies observed in TMACoCl$_4$ and TMAZnCl$_4$ (Refs. 15, 16, 24, and 25) cannot be considered the result of a proper soliton regime. Therefore, the general dielectric behavior of these compounds must be otherwise explained. In this paper, a phenomenological model is presented that can in fact reproduce qualitatively the observed dielectric behavior assuming a first-order phase transition between the IC phase in a sinusoidal regime and the fivefold-ferroelectric phase. In particular, a divergency of the dielectric susceptibility of the IC phase is predicted when the IC modulation wave vector passes through the commensurate value $q=\frac{2}{5}c^*$. A preliminary report of this work is presented in Ref. 28.

II. LANDAU FREE ENERGY

We use the modulated order parameter approach, but instead of the fivefold-ferroelectric phase, it is the threefold modulated ferroelastic phase of lower temperatures that is taken as the reference structure for the transition sequence. Accordingly, an order parameter is introduced whose homogeneous configuration corresponds to the threefold modulated phase. The IC and other commensurate phases are then described by an adequate space modulation of this order parameter.

In general, in the IC phase the static displacement $u(\mu,T)$ of the atom labeled μ in the unit cell positioned at T can be expressed as

$$u(\mu,T)=Q^{(q)}e(\mu,q)e^{iq\cdot T}+c.c. ,   (2.1)$$

where $Q^{(q)}$ is the normal coordinate corresponding to the IC wave vector and $e(\mu,q)$ is the μ component of the polarization vector of the normal mode. The displacement $u(\mu,T)$ may be also expressed in terms of a commensurate distortion with wave vector q_C if it is assumed that the normal coordinate is position dependent, thus

$$u(\mu,T)=Q^{(q_C)}(T)e(\mu,q_C)e^{iq_C\cdot T}+c.c. \ , \tag{2.2}$$

where

$$Q^{(q_C)}(T)=Q^{(q)}e^{i(q-q_C)\cdot T} \tag{2.3}$$

and it is assumed that $e(\mu,q)=e(\mu,q_C)$.

In our case $q_C=\frac{1}{3}c^*$. Considering T as a continuous variable and taking $Q^{(q_C)}=\rho(x)\exp[i\varphi(x)]$ we can write

$$u(\mu,x)=\rho(x)e(\mu,q_C)e^{i[(2\pi/3)x+\varphi(x)]}+c.c. \tag{2.4}$$

If $\varphi(x)=(2\pi/15)x$, the preceding expression becomes

$$u(\mu,x)=\rho(x)e(\mu,q_C)e^{i(4\pi/5)x}+c.c. \ , \tag{2.5}$$

which corresponds to a distortion with wave vector $q'_C=\frac{2}{5}c^*$. Therefore, the fivefold phase may be described by means of the normal coordinate $Q^{(c^*/3)}$, referred to the threefold normal mode, if its phase is assumed to vary in the form $\varphi(x)=(2\pi/15)x$ and the q dependence of the polarization vector is neglected.

Accordingly, in order to describe the thermodynamic behavior of the system (TMACoCl4 or TMAZnCl4), the following free-energy expansion for the IC phase is proposed:

$$f_{IC}(x)=\tfrac{1}{2}\alpha QQ^*+\tfrac{1}{4}\beta(QQ^*)^2+\tfrac{1}{6}\gamma_1(QQ^*)^3+\tfrac{1}{8}\gamma_3(QQ^*)^4$$

$$+\tfrac{1}{10}\gamma_4(QQ^*)^5-\frac{\gamma_2}{2}(Q^6+Q^{*6})-i\frac{\delta}{2}\left[Q\frac{dQ^*}{dx}-Q^*\frac{dQ}{dx}\right]+\frac{\kappa}{2}\frac{dQ}{dx}\frac{dQ^*}{dx}$$

$$-\frac{\xi}{2}(Q'^{10}+Q'^{*10})-\frac{\sigma}{2}P(Q'^5+Q'^{*5})+\frac{1}{2\chi_0}P^2-PE \ , \tag{2.6}$$

where the order parameter Q transforms according to the irreducible representation Σ_3 of the space group $Pmcn$ at the reciprocal space point $q_C=\frac{1}{3}c^*$ of the first Brillouin zone, P is the spontaneous polarization, and E an homogeneous electric field. Q' is defined as

$$Q'(x)=Q(x)e^{-(2\pi/15)x}=\rho(x)e^{i[\varphi(x)-(2\pi/15)x]} \tag{2.7}$$

and therefore transforms according to the irreducible representation Σ_3 but at the point $q'_C=\frac{2}{5}c^*$. The terms in expression (2.6) with coefficients ξ and σ become homogeneous for the fivefold phase when $\varphi(x)=(2\pi/15)x$.

The terms with coefficients δ and κ are the Lifshitz invariant and the usual elastic term favoring an inhomogeneous and an homogeneous configuration of Q, respectively. The terms with coefficient γ_2 and ξ are the lock-in terms that represent the interaction between the modulation and the crystal lattice driving the system to the threefold phase and the fivefold phase, respectively, as temperature decreases. As usual, it is assumed that only α is temperature dependent, $\alpha=\alpha_0(T-T_0)$.

In the constant amplitude approximation, that is, if only φ is x dependent and ρ is assumed to be homogeneous, the free-energy density (2.6) can be put in the form

$$f_{IC}(x)=\tfrac{1}{2}\alpha\rho^2+\tfrac{1}{4}\beta\rho^4+\tfrac{1}{6}\gamma_1\rho^6+\tfrac{1}{8}\gamma_3\rho^8+\tfrac{1}{10}\gamma_4\rho^{10}-\gamma_2\rho^6\cos6\varphi-\delta\rho^2\frac{d\varphi}{dx}$$

$$+\frac{\kappa}{2}\rho^2\left[\frac{d\varphi}{dx}\right]^2-\xi\rho^{10}\cos10\left[\varphi-\frac{2\pi}{15}x\right]-\sigma P\rho^5\cos5\left[\varphi-\frac{2\pi}{15}x\right]+\frac{1}{2\chi_0}P^2-PE \ . \tag{2.8}$$

On the other hand, the free energy corresponding to the fivefold-ferroelectric phase can be written as

$$F_C=\tfrac{1}{2}\alpha\rho^2+\tfrac{1}{4}\beta\rho^4+\tfrac{1}{6}\gamma_1\rho^6+\tfrac{1}{8}\gamma_3\rho^8$$

$$+(\tfrac{1}{10}\gamma_4-\xi)\rho^{10}-\sigma P\rho^5+\frac{1}{2\chi_0}P^2-PE \ . \tag{2.9}$$

First-order transitions between the IC and the fivefold-ferroelectric phase occur then at those temperatures for which the main free energy of the IC phase $F_{IC}=(1/L)\int_0^L f_{IC}(x)dx$ equals F_C, L being the crystal length along the wave-vector direction. The phenomenological coefficients appearing in (2.8) and (2.9) are assumed to be the same. The transition temperatures and the range stability of the ferroelectric phase will be strongly dependent on the actual values of the coefficients σ and ξ.

III. DIELECTRIC BEHAVIOR

Minimizing the free energy (2.8) the following expression for the polarization is obtained:

$$P=\chi_0E+\chi_0\sigma\rho^5\cos5\left[\varphi-\frac{2\pi}{15}x\right] \ . \tag{3.1}$$

Substituting this expression in (2.8)

$$f_{IC}(x) = \tfrac{1}{2}\alpha\rho^2 + \tfrac{1}{4}\beta\rho^4 + \tfrac{1}{6}\gamma_1\rho^6 + \tfrac{1}{8}\gamma_3\rho^8 + \tfrac{1}{10}\gamma_4\rho^{10} - \gamma_2\rho^6\cos6\varphi - \delta\rho^2\frac{d\varphi}{dx}$$

$$+ \frac{\kappa}{2}\rho^2\left[\frac{d\varphi}{dx}\right]^2 - \xi\rho^{10}\cos10\left[\varphi - \frac{2\pi}{15}x\right] - \sigma\chi_0E\rho^5\cos5\left[\varphi - \frac{2\pi}{15}x\right] - \frac{\chi_0}{2}\sigma^2\rho^{10}\cos^25\left[\varphi - \frac{2\pi}{15}x\right] - \frac{\chi_0}{2}E^2 . \quad (3.2)$$

The equilibrium value for the phase $\varphi(x)$ is obtained by minimizing the free energy above, with respect to the φ configuration. The resulting Euler-Lagrange equation is

$$\kappa\frac{d^2\varphi}{dx^2} = 6\gamma_2\rho^4\sin6\varphi$$

$$+ \left[10\xi + 5\frac{\chi_0}{2}\sigma^2\right]\rho^8\sin10\left[\varphi - \frac{2\pi}{15}x\right]$$

$$+ 5\sigma\chi_0E\rho^3\sin5\left[\varphi - \frac{2\pi}{15}x\right] . \quad (3.3)$$

Let us indicate with $\varphi_0(x)$ the equilibrium phase modulation when no electric field is applied to the sample ($E = 0$). According to (3.3), it satisfies

$$\kappa\frac{d^2\varphi_0}{dx^2} = 6\gamma_2\rho^4\sin6\varphi_0$$

$$+ \left[10\xi + 5\frac{\chi_0}{2}\sigma^2\right]\rho^8\sin10\left[\varphi_0 - \frac{2\pi}{15}x\right] . \quad (3.4)$$

Considering the field a small perturbation, φ_0 becomes $\varphi_0 + \Delta\varphi$ when the field is applied. Thus, linearizing expression (3.3), with respect to $\Delta\varphi$ and taking into account (3.4), we obtain

$$\kappa\frac{d^2\Delta\varphi}{dx^2} = \left[36\gamma_2\rho^4\cos6\varphi_0\right.$$

$$+ 10\left[10\xi + \frac{5\chi_0}{2}\sigma^2\right]\rho^8\cos10\left[\varphi_0 - \frac{2\pi}{15}x\right]\right]$$

$$\times\Delta\varphi + 5\sigma\chi_0E\rho^3\sin5\left[\varphi_0 - \frac{2\pi}{15}x\right] , \quad (3.5)$$

where the electric field is considered to be weak enough so that $\sigma\chi_0E\Delta\varphi \approx 0$.

Instead of looking for a formal solution of Eqs. (3.4) and (3.5), we drastically simplify the problem by vanishing the term in $\Delta\varphi$ at the right-hand side of (3.5), in accordance with the fact that it is of higher order in ρ than the term proportional to the field E. This approximation also implies to consider null the right-hand side of Eq. (3.4). Thus, it is assumed that if no electric field is applied the equilibrium phase modulation follows a linear law: $\varphi_0 = ax$, i.e., the IC structure is in a sinusoidal regime with the modulation wave vector $q = (\tfrac{1}{3} + a)c^*$. However, the effect of the threefold lock-in term with coefficient γ_2, which is the predominant one on the right-hand side of expression (3.4), is introduced in an approximate form by assuming a certain temperature dependence of a [$\varphi_0 = a(T)x$] and therefore a tempera-

ture variation of the modulation wave vector.

This situation is known to happen even in materials with a clear soliton regime. Such a regime is restricted to a narrow temperature interval close to the lock-in phase transition. In fact, the material properties can be well described using a sinusoidal configuration for the modulation, with a temperature-dependent wave vector, in most of the temperature range of the IC phase.

In this approximation, expression (3.5) for $\Delta\varphi$ reduces to

$$\kappa\frac{d^2\Delta\varphi}{dx^2} = 5\sigma\chi_0E\rho^3\sin5\left[\varphi_0 - \frac{2\pi}{15}x\right] , \quad (3.6)$$

which, replacing $\varphi_0 = a(T)x$, leads to the following solution:

$$\Delta\varphi = -\frac{\sigma\chi_0\rho^3E}{5\kappa\left[a(T) - \frac{2\pi}{15}\right]^2}\sin5\left[\varphi_0 - \frac{2\pi}{15}x\right] . \quad (3.7)$$

Consequently, in this approximation, the average modulation wave vector is not changed when the electric field is applied.

On the other hand, according to (3.1) the polarization $P(x)$ may be written as

$$P = \chi_0E + \chi_0\sigma\rho^5\cos5\left[\varphi_0 + \Delta\varphi - \frac{2\pi}{15}x\right] , \quad (3.8)$$

which can be expressed as $P_0 + \Delta P$, where $P_0(x)$ is the polarization with $E = 0$ and ΔP is given by

$$\Delta P = \chi_0E + \frac{\chi_0^2\sigma^2\rho^8E}{\kappa\left[a(T) - \frac{2\pi}{15}\right]^2}\sin^25\left[\varphi_0 - \frac{2\pi}{15}x\right] , \quad (3.9)$$

where only terms up to first order in $\Delta\varphi$ have been considered and expression (3.7) has been used.

The dielectric susceptibility defined as

$$\chi = \frac{1}{2L}\int_{-L}^{L}\frac{\Delta P}{E}dx \quad (3.10)$$

can then be finally calculated from (3.9). The final result is

$$\chi_{IC} = \chi_0\left[1 + \frac{\chi_0\sigma^2\rho^8}{2\kappa[a(T) - (2\pi/15)]^2}\right] , \quad (3.11)$$

where it has been taken into account that $\varphi_0 = a(T)x$.

Therefore, the dielectric susceptibility of the IC phase diverges when $a(T)$ approaches the value $2\pi/15$, that is, when the modulation wave vector approaches the value corresponding to the fivefold phase from higher or lower

values. This divergency is essentially due to the fact that the wavelength of the secondary polarization wave diverges when $\mathbf{q}$ becomes $\frac{2}{5}\mathbf{c}^*$.

Before reaching the wave vector of the IC modulation the value $\mathbf{q}=\frac{2}{5}\mathbf{c}^*$, on cooling or heating, the fivefold-commensurate-ferroelectric phase, whose free energy F_C is given in expression (2.9), becomes more stable leading to a first-order transition to this phase. Thus, it is clear that the maximum value of the dielectric susceptibility in a cooling or heating run depends on the temperature where the potentials F_{IC} and F_C cross each other. Also the undercooling and overheating phenomena of the corresponding metastable phases around this point should be considered (see Sec. IV). The phase diagram at normal pressure of TMAZnCl$_4$ (Refs. 15 and 18) indicate that there is a unique crossing point, and correspondingly only one IC phase is stable in this compound. On cooling, the fivefold commensurate phase transforms discontinuously into the ferroelastic threefold one. On the other hand, in the case of TMACoCl$_4$ (Refs. 15, 16, and 18) the fivefold-ferroelectric phase is sandwiched between two IC phases, and therefore two crossing points of F_{IC} and F_C should exist in this compound.

The anomalous behavior of χ at the normal-IC transition could also be reproduced if a coupling term of the form $\eta(QQ^*)P^2$, with $\eta > 0$, were included in the Landau free-energy density expansion (2.6). This term would lead to a renormalization of χ_0 in (3.11) that becomes ρ dependent, $\hat{\chi}_0=(1/\chi_0+2\eta\rho^2)^{-1}$. A slight decrease of χ below the normal-IC transition temperature is then predicted,[5,7] which has been observed experimentally in TMACoCl$_4$ and TMAZnCl$_4$.[15,16] Nevertheless, this term is not essential to explain the divergency of χ as the commensurate value of the wave vector is approached.

IV. COMPARISON WITH EXPERIMENTAL RESULTS

The real dielectric behavior can be reproduced by the previous phenomenological model if the fact of the coexistence of the IC and the commensurate-ferroelectric phases is taken into account. Experimental data with respect to the coexistence degree and the volume ratio of both phases have been obtained by means of x-ray diffraction.[26] These results show that a clear coexistence of both phases is present in almost the whole range of stability of the ferroelectric phase. The bulk ferroelectric phase is of improper type and has in principle no strong anomalous dielectric susceptibility. Therefore, we can expect that the observed dielectric susceptibility follows approximately the law

$$\chi=r(T)\chi_{IC}(T)+[1-r(T)]\chi_0 , \tag{4.1}$$

where $r(T)$ is the volume ratio of IC phase in the sample and $\chi_{IC}(T)$ is given by Eq. (3.11).

In the case of TMACoCl$_4$, the dielectric susceptibility according to (3.11) and (4.1) can then be written in units of the vacuum dielectric permittivity ϵ_0 as

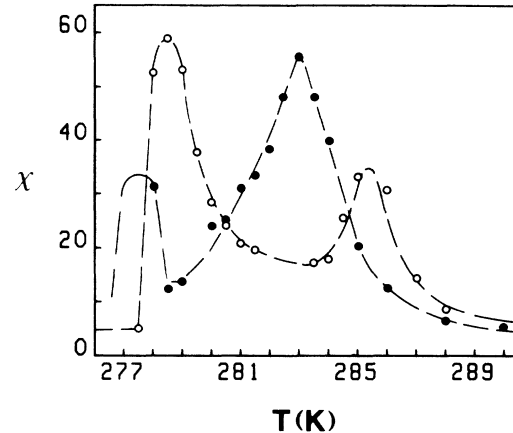$$\chi=5\left[1+\frac{5rCI^4}{(q-\frac{2}{5})^2}\right] , \tag{4.2}$$

FIG. 1. Dielectric susceptibility values for TMACoCl$_4$ calculated from expression (4.2) and x-ray data. Solid and open circles represent the cooling and heating run, respectively. The dashed lines are only a guide for the eye.

where the experimental value of $\chi_0\approx 5$ for this compound has been considered. In (4.2), the order parameter amplitude has been substituted by the total integrated intensity of the satellite profile I, which can be considered approximately proportional to the square of the amplitude of the order parameter. q represents the modulus of the modulation wave vector in units of c^*, which satisfies $2\pi(q-\frac{2}{5})=(a-2\pi/15)$. Experimental values of the IC volume ratio $r(T)$, the wave vector $q(T)$, and the satellite integrated intensity $I(T)$ can be taken from the mentioned x-ray diffraction experiments.[26] The theoretical values of χ obtained from (4.2) using these data are represented in Fig. 1 for $C=9.0\times10^{-9}$. If we consider the simplicity of the model with a single adjustable parameter, the agreement with the observed dielectric behavior in TMACoCl$_4$,[24,28] as shown in Fig. 2 is excellent.
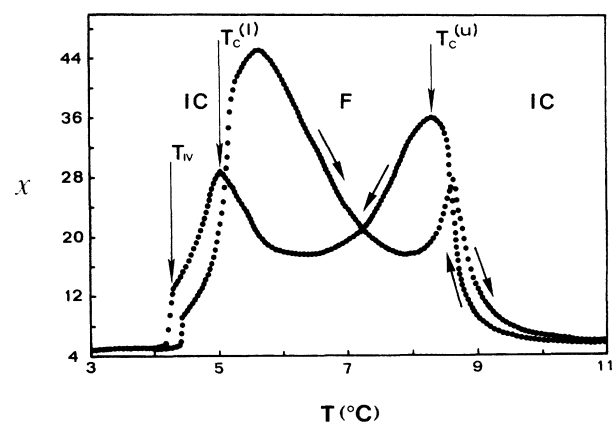

FIG. 2. Dielectric susceptibility vs temperature of TMACoCl$_4$ for cooling and heating runs. The IC-ferroelectric $[T_c^{(u)}]$, ferroelectric-IC $[T_c^{(I)}]$, and IC-threefold (T_{IV}) phase transitions on cooling are indicated. The dielectric susceptibility value is given in relative units with respect to the vacuum dielectric permittivity.

In particular, the asymmetry between the two successive dielectric peaks for both heating and cooling runs is reproduced.

The form of the predicted dielectric behavior is the result of the combined effect of the temperature dependence of the three parameters $r(T)$, $q(T)$, and $I(T)$. In the temperature range of Fig. 1, the value of $q(T)$ in the IC phase observed experimentally varies approximately between 0.414–0.404 and 0.394–0.388 above and below the commensurate value (0.400), respectively (see Ref. 26). This variation is enough to produce a significant contribution to the dielectric anomaly. However, the temperature variation of the order-parameter amplitude, included in expression (4.2) through the value of the integrated intensity I, is essential for the final form of the predicted behavior. In fact, if the exponent 4 for the total intensity in (4.2) is changed to 3.5 or 4.5, a very different theoretical behavior from that one shown in Fig. 1 is obtained.

V. GENERALIZATION OF THE MODEL

The present phenomenological model allows a suitable description of the dielectric susceptibility behavior of TMACoCl$_4$ and TMAZnCl$_4$. The temperature dependence of the order parameter phase φ (and as a consequence of the wave vector q) is assumed to be caused by the lock-in term with coefficient γ_2 in the free-energy density expansion (2.6), which becomes homogeneous in the threefold phase. The order parameter was referred to this threefold phase and, in a sinusoidal approximation, a divergency of the dielectric susceptibility was predicted when the wave vector q passes through the intermediate commensurate value $\frac{2}{5}c^*$, as a consequence of the coupling term σ between the polarization and the order parameter.

It is obvious that this result can be directly generalized to any system where a polarization wave coupled to the main modulation exists, provided that its wavelength diverges for a certain commensurate value of the wave vector of the main modulation. The resulting behavior is independent of the origin chosen for the phase φ and of the type of interaction between the modulation and the underlying crystal lattice. In fact, expression (3.11) does not depend on either γ_2 nor on the fact that the crystal cell becomes threefolded at the lock-in phase. The dielectric susceptibility diverges as a direct consequence of the possibility of the polarization wave to be deformed by the electric field, and it is reasonable to expect that this deformation will become easier as the wavelength increases.

Let us consider a hypothetical system, where the coupling between the polarization P and the order parameter $Q = \rho e^{i\theta}$ of the IC distortion leads to the following free-energy expansion:

$$f(x) = f_0 - \sigma P \rho^m \cos(m\theta) + \frac{1}{2\chi_0}P^2 - PE , \qquad (5.1)$$

where f_0 represents the part depending only on the order parameter. In (5.1), we take as a homogeneous reference for the order parameter the polar commensurate phase corresponding to a certain commensurate value of the

modulation wave vector of the type $\mathbf{q} = (n/m)\mathbf{a}_i^*$ so that an x-independent configuration of ρ and θ corresponds to this phase. Minimizing $f(x)$ leads to

$$P = \chi_0 E + \chi_0 \sigma \rho^m \cos(m\theta) . \qquad (5.2)$$

Next, we assume that for zero electric field ($E = 0$) the structural modulation can be approximated by a sinusoidal configuration, so that the phase θ_0 can be expressed as $\theta_0 = k(T)x$. The temperature dependence of $k(T)$ is considered to be caused by umklapp terms in f_0 in such a way that $k(T)$ is a continuous function of temperature taking positive and negative values. The zero value for k corresponds to the commensurate-ferroelectric phase.

When the electric field is applied θ_0 becomes $\theta_0 + \Delta\theta_0$, and proceeding as in the specific case above, within the same approximations, the following expressions are derived:

$$\Delta\theta = -\frac{\sigma\chi_0 E\rho^{m-2}}{m\kappa k^2}\sin(m\theta_0) , \qquad (5.3)$$

$$\Delta P = \chi_0 E + \frac{\chi_0^2\sigma^2\rho^{2m-2}E}{\kappa k^2}\sin^2(m\theta_0) , \qquad (5.4)$$

which are completely analogous to expressions (3.7) and (3.9). Finally, for the dielectric susceptibility we obtain

$$\chi_{IC} = \chi_0\left[1 + \frac{\sigma^2\chi_0\rho^{2m-2}}{2\kappa k^2}\right] , \qquad (5.5)$$

which diverges when $k \to 0$ from positive or negative values. It is only a consequence of the coupling of the polarization with the order parameter leading to an homogeneous polarization $P = \chi_0(E + \sigma\rho^m)$ when k vanishes.

Thus, it results that the dielectric susceptibility shows a divergency when the symmetry of the IC modulation corresponds to that of a ferroelectric phase, even if a soliton configuration does not occur.

VI. CONCLUSIONS

We have shown that the IC phase in compounds like TMAXCl$_4$ ($X = $ Co,Zn) can exhibit a dielectric non-Curie-Weiss divergency when its modulation wave vector approaches the commensurate value associated with the ferroelectric phase, while keeping a sinusoidal configuration. Essentially, the model simply considers a transition to the threefold lock-in phase in a similar way as in K$_2$SeO$_4$ type compounds, but taking into account the coupling of the order parameter with magnitudes (here the polarization) that vanish at the lock-in phase but have a relevant influence at the previous modulated phases. The divergency of the dielectric susceptibility of the IC phase is simply due to the presence of a polarization wave in the system, whose wavelength becomes infinite at a given temperature. The effective dielectric susceptibility is then obtained by taking into account the temperature-dependent volume ratio of the IC phase in the coexisting region with the polar phase. The coexistence of both the IC and the ferroelectric phases considered in the model is based on the experimental evi-

dence (see Ref. 26). The corresponding IC-ferroelectric first-order phase transition is shown to be consistent with the anomaly of the dielectric susceptibility experimentally observed. It should be pointed out that this anomaly is much weaker (1 order of magnitude) than in compounds with a clear soliton regime such as Rb_2ZnCl_4.[7]

This model has also been generalized for any IC system that exhibits successive lock ins in different polar commensurate phases. In general, it is not necessary to assume a soliton configuration to explain the dielectric peaks in the dielectric behavior. A dielectric anomaly of the type given in Eq. (3.11) can be considered a general feature for an IC phase whose wave vector crosses a rational value associated with a polar commensurate phase. However, the magnitude of the effect predicted depends strongly on the order of the order parameter power appearing in (3.11). This exponent increases linearly with the order of the rational value considered for the wave vector, so that the anomaly is negligible for long period commensurate modulations.

The essential approximation introduced is the assumption of a sinusoidal regime for the modulation configuration in the temperature range considered, despite the fact that the modulation wave vector is temperature dependent. This simplification is expected to work well in any IC system whose wave vector is not close to a low-order commensurate lock-in value. This could be the case of deuterated thiourea when its modulation wave vector crosses the commensurate value $\frac{1}{8}$. The symmetry of this system allows the stabilization of a polar phase with $q = \frac{1}{8}$ when a bias electric field is applied to the sample.[29] The observed dielectric peak when q crosses the value $\frac{1}{8}$ at zero-bias field has then been explained assuming that the oscillating field employed in the measurement was capable of stabilizing this phase in a small temperature interval.[29,30] However, according to the present formulation, the dielectric peak at zero field can be simply explained without assuming any stabilization of the ferroelectric phase, even in a reduced temperature interval.

The model proposed by Ishibashi[11] and by Omari, Godefroy, Dvorák, and Janssen[23] for the IC-ferroelectric transition in $TMAZnCl_4$, takes into account only the existence of the fivefold-ferroelectric phase, without considering the low-temperature modulated phases. Thus, a behavior completely analogous to that of the compounds of the K_2SeO_4 family is predicted, including a soliton regime previous to a quasicontinuous lock-in transition into the fivefold commensurate phase. Thus, this model cannot explain the strong discontinuous character of the IC-ferroelectric transition in $TMAZnCl_4$ and $TMACoCl_4$, as has been observed by x-ray topography[27] and x-ray diffraction.[26] In contrast, the present formulation explains the general features of the behavior observed in $TMAZnCl_4$ and $TMACoCl_4$, including the dielectric behavior, and excludes the existence of a soliton regime as the approximation to the fivefold phase, in agreement with the first-order character of the IC-ferroelectric phase transition.

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