Dielectric constant in the incommensurate phase of Rb_2ZnCl_4

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The incommensurate-commensurate phase transition in Rb_2ZnCl_4 is investigated by dielectric measurements. The steep increase of ϵ and the small difference between the Curie-Weiss and the transition temperature favor the interpretation that the transition is of second order. The Curie-Weiss law is found to be obeyed just above the transition. A Landau-type theory for the linear as well as nonlinear response of a multisoliton lattice is developed which can account very well for $\epsilon(T)$ in the whole incommensurate phase.

At present at least 10 dielectric crystals are known which undergo a sequence of paraelectric (P)–incommensurate (IC)–commensurate (C) structural phase transitions[1] and are ferroelectric in their commensurate phases. Whereas the investigations of upper P-IC phase transition have led to a satisfactory agreement between the experiment and the theory, this is not the case for the "lock-in" IC-C phase transition.[2] The order of the transition and the corresponding critical behavior cannot be regarded as settled, from the experimental[3,4] as well as from the theoretical[5,6] point of view.

The onset of ferroelectricity in Rb_2ZnCl_4 at $T_c = -81$ °C and the P-IC transition at $T_I = 27$ °C have been first reported by Sawada *et al.*[7] Recently, various techniques have been applied to the study of the incommensurate phase in this crystal[3,4,8,9] and its isomorphs K_2SeO_4, Rb_2ZnBr_4, etc. In this Communication, we report the results of a dielectric study which for the first time clearly show that the IC-C phase transition in Rb_2ZnCl_4 is of the second order. The static dielectric constant ϵ follows a Curie-Weiss behavior in the vicinity of the transition. We also show that a Landau-type theory can describe surprisingly well the variation of the dielectric constant in the whole incommensurate phase.

The sample was first cooled to liquid-nitrogen temperature and then the measurement was performed along a axis[7] on heating. The IC-C transition temperature was determined from the intercepts of $1/\epsilon$ vs T lines close to the transition as $T_c = 196.36$ K. The Curie-Weiss temperature of the IC phase is $T_1 = 196.31$ K. The small difference $T_c - T_1$ is indicating that the transition is of the second order. It should be pointed out also that the values of ϵ at $T \sim T_c$ are several times larger than those reported by other authors,[4,7] demonstrating that our crystal was grown better and has less defects. This agrees with conclusions of the recent work of Hamano *et al.*[4] where the dielectric properties of Rb_2ZnCl_4 were studied with special attention paid to the thermal hysteresis phenomena in the IC as well as C phases. Strong dependence of the thermal hysteresis on the defect concentration in the mixed $(Rb_xK_{1-x})_2ZnCl_4$ crystal supports the interpretation that the pinning of phase solitons by defects is the cause for the observed thermal hysteresis in Rb_2ZnCl_4.

The temperature dependence of $\log(\epsilon - \epsilon_0)$ vs $\log(T - T_c)$ in the incommensurate phase is presented in Fig. 1. ϵ_0 is determined from the value of ϵ measured at P-IC transition temperature $T_I = 304.24$ K as $\epsilon_0 = 13.0$. In the interval $0.4 < T - T_c < 3$ K the data can be fitted with the power law $\epsilon - \epsilon_0 \propto (T - T_c)^{-\gamma}$ with $\gamma = 1.01 \pm 0.05$ which is consistent with the Curie-Weiss behavior. This is not the case for the commensurate side of the transition where, on heating, a much steeper variation of ϵ was observed.

Rb_2ZnCl_4 belongs to the symmetry group for which the thermodynamic potential density in the presence

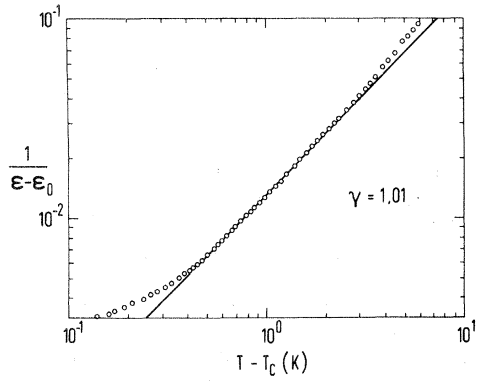

FIG. 1. Log-log plot of the reciprocal dielectric constant vs $T - T_c$ in the incommensurate phase of Rb_2ZnCl_4, where $T_c = 196.36$ K. In the temperature range $0 < T - T_c < 4$ K the best fit with the power-law behavior is obtained for a critical exponent $\gamma = 1.01 \pm 0.05$.

of the external electric field can be written as[1,10]

$$f(x)=\frac{\alpha}{2}QQ^*+\frac{\beta}{4}(QQ^*)^2+i\frac{\delta}{2}\left(Q\frac{dQ^*}{dx}-Q^*\frac{dQ}{dx}\right)$$
$$+\frac{\kappa}{2}\frac{dQ}{dx}\frac{dQ^*}{dx}-\frac{\gamma}{2}(Q^6+Q^{*6})$$
$$+\zeta(Q^3+Q^{*3})P+\frac{\eta}{2}QQ^*P^2+\frac{P^2}{2\chi_0}-PE \quad , \quad (1)$$

where Q, Q^* correspond to the basis of the Σ_2 representation at $\vec{k}=(2\pi/3a, 0, 0)$. The polarization P along the a axis plays a role of a secondary-order parameter. The temperature enters only via $\alpha=\alpha_0(T-T_0)$. In the Landau expansion (1) we have retained solely the lowest essential terms for the description of the IC phase. Whereas the Lifshitz term is crucial for the onset of the IC structure, the lock-in transition is driven by anisotropy terms Q^6+Q^{*6} and $(Q^3+Q^{*3})P$ which are both of sixth order in Q, when after minimization P is eliminated from expression (1). Although the contribution of the QQ^*P^2 invariant is expected to be small, it is essential for the slight kink in ϵ observed at the P-IC transition.

We substitute the two-component order parameter Q,Q^* by its polar representation $Q=\rho\exp(i\varphi)$ and employ the constant amplitude approximation[2] $\rho(x)=\rho_0$ which is at least qualitatively correct within the whole IC phase, what can be recognized from complete numerical solutions of models[5] analogous to (1). When we minimize the free-energy density (1) with respect to P, we get

$$f(x)=f_0+\delta\rho_0^2\frac{d\varphi}{dx}+\frac{\kappa\rho_0^2}{2}\left(\frac{d\varphi}{dx}\right)^2$$
$$+2\zeta E\bar{\chi}_0\rho_0^3\cos 3\varphi-2(\gamma+\zeta^2\bar{\chi}_0)\rho_0^6\cos^2 3\varphi \quad , \quad (2)$$

where all x independent terms are condensed in f_0 and $\bar{\chi}_0$ is renormalized to $\bar{\chi}_0=1/(\chi_0^{-1}+\eta\rho_0^2)$.

Without the external field $E=0$ the minimization of the free energy $F=\int f(x)\,dx$ with respect to the phase $\varphi(x)$ leads to the time-dependent sine-Gordon equation. Solutions of similar equations have been first discussed by Dzyaloshinskii[11] and de Gennes[12] while recently the same procedure has been applied to the theory of the IC-C transition by Sannikov.[6,13] $\varphi(x)$ can be expressed via Jacobian elliptic function where the period x_0 of $\psi(x)=\varphi(x)-\pi x/3x_0$ is given by

$$x_0=\left(\frac{\kappa}{\gamma}\right)^{1/2}\frac{kK(k)}{3\rho_0^2} \quad , \quad (3)$$

and $\bar{\gamma}=\gamma+\zeta^2\bar{\chi}_0$. The parameter k is determined so that the condition $F=\min$ is fulfilled

$$\frac{E(k)}{k}=\frac{\pi\delta}{4\rho_0^2}(\kappa\bar{\gamma})^{-1/2} \quad , \quad (4)$$

where $E(k)$, $K(k)$ denote complete elliptic integrals. The temperature dependence of k and consequently x_0 in Eqs. (3) and (4) is mediated only through ρ_0 for which we use the simplest expression obtained from Eq. (1), $\rho_0=[\alpha_0(T_I-T)/\beta]^{1/2}$, best suited for the vicinity of the P-IC transition $T\sim T_I=T_0+\delta^2/\alpha_0\kappa$. The parameter k varies from $k\sim 0$ at $T\lesssim T_I$, where the order parameter varies approximately as $Q(x)=\rho_0\exp(i\pi x/3x_0)$, to $k=1$ at $T=T_c$ where the IC structure locks into one of $n=6$ stable commensurate configurations with $\cos^2 3\varphi=1$. For $T\gtrsim T_c$ wide commensurate regions are separated by domain walls or "phase solitons."

In the presence of an electric field $E\neq 0$, the differential equation for $\varphi(x)$ becomes of the double sine-Gordon type. The electric field deforms phase solitons so that the antisymmetry of $\varphi(x)$ around each soliton center is lost. Effectively, as presented in Fig. 2, this leads to the extension of commensurate regions with $\cos 3\varphi=1$ and to the compression of regions with $\cos 3\varphi=-1$, or vice versa. The period of $\psi(x)$ is now $2x_0$, where

$$x_0=\frac{1}{6}\left(\frac{\kappa}{2}\right)^{1/2}\int_0^{2\pi}\frac{du}{(z-\Delta\sin^2 u+\lambda\sin u)^{1/2}} \quad . \quad (5)$$

Here, $\Delta=2\bar{\gamma}\rho_0^4$ and $\lambda=2\rho_0\zeta\bar{\chi}_0E$. The minimization with respect to the "energy" parameter z leads to $E\neq 0$ analog of Eq. (4)

$$\int_0^{2\pi}(z-\Delta\sin^2 u+\lambda\sin u)^{1/2}du=\pi\delta\left(\frac{2}{\kappa}\right)^{1/2} \quad . \quad (6)$$

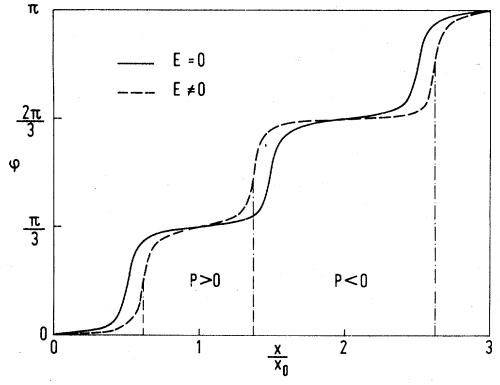

FIG. 2. Schematic representation of the effect of the electric field on the phase solitons near the IC-C transition.

The average polarization $\langle P \rangle$ is nonzero and is given by

$$\langle P \rangle = \bar{\chi}_0 E - \frac{\zeta \bar{\chi}_0 \rho_0^3}{3x_0} \left(\frac{\kappa}{2} \right)^{1/2} \times \int_0^{2\pi} \frac{\sin u \, du}{(z - \Delta \sin^2 u + \lambda \sin u)^{1/2}} \quad . \tag{7}$$

It should be mentioned, that the integrals of the above type can be expressed with the incomplete elliptic integrals.

Within the linear response to E at zero dc field and $T > T_c$, Eqs. (5) and (6) reproduce Eqs. (3) and (4), i.e., average intersoliton distance x_0 remains unchanged. For the susceptibility $\chi = \partial \langle P \rangle / \partial E$ we get from Eq. (7)

$$\chi = \bar{\chi}_0 + \frac{\zeta^2 \bar{\chi}_0^2}{\gamma + \zeta^2 \bar{\chi}_0} \left(\frac{E(k)}{(1-k^2)K(k)} - 1 \right) \quad . \tag{8}$$

For a simplified model a similar result has been reported in Ref. 13 where the IC-C transition is, however, regarded as first order. The most important consequence, which follows from Eqs. (4) and (8) and from the behavior of $E(k)$, $K(k)$ near $k \sim 1$, is that χ diverges at T_c according to the Curie-Weiss law $\chi \propto (T - T_c)^{-1}$. Namely, even slight deformation of $E = 0$ phase solitons and variations of derivatives $d\varphi/dx$ in commensurate regions leads near T_c to large variations in the intersoliton distances and consequently in $\langle P \rangle$. On the other hand, an analogous but simpler derivation for the C phase would show that $\chi \sim \bar{\chi}_0$ is nearly constant for $T \lesssim T_c$.

From Eqs. (5), (6), and (7) it is evident that even for larger dc field E the transition remains a sharp one; the transition temperature T_c is, however, shifted. From the condition for the transition $z = \Delta + |\lambda|$ and Eq. (6) we get in the weak-field regime

$$T_c(E) - T_c(E=0) = \frac{\zeta \bar{\chi}_0 \beta}{4\bar{\gamma}\alpha_0} |E| \left(1 + \ln \frac{8\bar{\gamma}\rho_0^3}{\zeta \bar{\chi}_0 |E|} \right) \quad , \tag{9}$$

where we have taken into account that there is no linear correction to ρ_0 due to $E \neq 0$. Apart from a logarithmic correction, Eq. (9) suggests a linear dependence of T_c on E. This indeed has been observed in Rb_2ZnCl_4.[4] Further aspects of the $E \neq 0$ regime will be discussed elsewhere.

The variation of linear response χ outside the critical region is within the presented theory governed only by three dimensionless parameters: $a = 4\zeta\alpha_0 \times T_I \sqrt{\kappa \chi_0 / \pi \beta \delta}$, determining the width of the IC phase, $b = \eta \alpha_0 \chi_0 T_I / \beta$, which is fixed by the magnitude of the kink in ϵ at T_I (see insert to Fig. 3), and $c = \gamma / \zeta^2 \chi_0$ denoting the relative contribution of the direct and polarization-induced anisotropy terms in Eq. (1), respectively. In Fig. 3 we present the variation of ϵ in the whole IC phase, measured with decreasing temperature, and compare the result with the theoretical prediction (8). Whereas $a = 1.102$ and $b = 0.45$ are essentially fixed the only adjustable parameter c is chosen as $c = 5.5$. The calculated $\epsilon(T)$ curve fits the data extremely well in the whole IC region and obeys the Curie-Weiss law in the multisoliton regime $0 < T - T_c < 4$ K that is consistent with the experimental result (Fig. 1). The same values of parameters can be used to calculate the temperature dependence of the incommensurability wave vector $\delta_0 \propto 1/x_0$. The result agrees well with neutron scattering data by Gesi and Iizumi,[3] which also reveal a continuous variation of δ_0 with temperature near T_c.

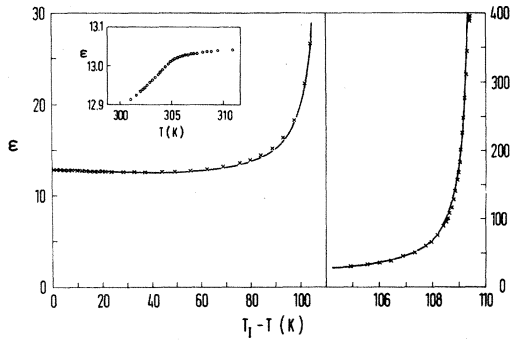

FIG. 3. Dielectric constant ϵ vs $T_I - T$ ($T_I = 304.24$ K) in the incommensurate phase of Rb_2ZnCl_4. Crosses represent experimental results while the full curve is the theoretical result, Eq. (8), where the adjustable parameter c is chosen as $c = 5.5$. The insert of Fig. 3 shows a kink in ϵ at T_I.

Finally, in view of the agreement between the presented theory and experimental results, we should comment on the approximations in our theoretical treatment. We have not used a strict minimization procedure for the calculation of ρ_0, since it would yield a first-order IC-C phase transition.[6,13] Whereas this is experimentally clearly not the case, our theoretical argument is as follows: Going beyond the constant amplitude approximation we should allow also variations of $\rho(x)$. Near T_c, $\rho(x)$ would, however, vary appreciably only within phase solitons. Nevertheless, within a Landau-type theory solitons would still behave as well-defined particles with an exponential interparticle interaction,[14] which is already incorporated in the $\rho(x) = \rho_0$ approximation. The effect of fluctuations has been neglected in our calculation. At $T \lesssim T_I$, fluctuations are known to lead to nonclassical critical exponents for ρ_0 (Refs. 15 and 16) in a broad temperature range. Due to a weak dependence on ρ_0 these deviations do not show up in ϵ near T_I. At the IC-C transition ρ_0 is nearly constant, hence it does not influence the critical behavior of ϵ. On the other hand, there exists no definite answer to the influence of phase fluctuations[2,17] on the IC-C transition. From the present work we could conclude that the phenomenological Landau-

type theory accounts very well also for this critical behavior. It should be pointed out that large values of $\epsilon >> \epsilon_0$ near T_c indicate that we are in a narrow soliton regime, which coincides with the region of the validity of Curie-Weiss law.

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