Metastable chaotic state and the soliton density in incommensurate Rb_2ZnCl_4

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The temperature dependence of the soliton density n_s derived from the dielectric data in Rb_2ZnCl_4 is compared with the one obtained from nuclear-magnetic-resonance measurements and x-ray scattering data. The finite value of n_s at the "lock-in" transition T_c and the nonzero value of n_s below T_c demonstrate that on cooling through T_c a metastable chaotic state with randomly pinned solitons is reached.

I. INTRODUCTION

Recent dielectric constant measurements[1,2] have shown the existence of a large thermal hysteresis in Rb_2ZnCl_4 both above and below the "lock-in" transition T_c. The dielectric constant is finite[3] at the incommensurate (I)-commensurate (C) transition T_c and—on cooling from above—exhibits an anomalously high value below T_c. The incommensurate satellite x-ray reflections[4–6] are anomalously broadened in the neighborhood of T_c and show similar hysteresis phenomena as the dielectric constant.

The above phenomena and the apparent lack of long-range order have been interpreted in terms of the destruction of the multisoliton lattice due to random-phase pinning. A metastable chaotic state with randomly spaced pinned solitons[7,8] has been indeed predicted to exist intermediate between the I and C phases. Randomly pinned solitons may occur as metastable entities even in the C phase below T_c where the soliton formation energy becomes positive.

In this Rapid Communciation we introduce a theoretical model for these effects and present some quantitative information for the magnitude of the pinned soliton density in Rb_2ZnCl_4 as derived from dielectric constant and x-ray broadening data, and checked by ^{87}Rb nuclear magnetic resonance measurements.

II. THEORY

The classical Landau theory of the I-C transition in Rb_2ZnCl_4 predicts[3,9,10] that the dielectric susceptibility exhibits a Curie-Weiss law on approaching T_c from above

$$\chi = \chi_0 + \frac{C}{T - T_c}, \quad T > T_c \ , \tag{1}$$

whereas it should abruptly drop to χ_0 below T_c in the C phase:

$$\chi = \chi_0, \quad T < T_c \ . \tag{2}$$

χ is rather low as long as the incommensurate modulation wave can be described by a plane wave. It strongly increases with decreasing soliton density in the multisoliton lattice limit on approaching T_c. The soliton density

$$n_s = d_0/x_0 \ , \tag{3}$$

where d_0 is the soliton width and x_0 the intersoliton spacing, is here given by

$$n_s = \frac{\pi/2}{K(k)} \ , \tag{4}$$

where the parameter k is within the constant amplitude approximation determined from the condition

$$\frac{E(k)}{k} = \frac{\pi\delta}{4A_0^2} \frac{1}{(\kappa\bar{\gamma})^{1/2}} \ . \tag{5}$$

The temperature T enters expressions (4) and (5) through the amplitude of the complex order parameter $A_0^2 = \alpha_0(T_I - T)/\beta$. $E(k)$ and $K(k)$ are complete elliptic integrals while the parameters δ, κ, and $\bar{\gamma}$ are defined in Refs. 3 and 9. From expression (4) it follows that $n_s \to 0$ as $T \to T_c^+$ in view of the divergence of the intersoliton distance x_0.

In the vicinity of the I-C transition impurities and discrete lattice effects[7] become important. They induce a chaotic state with randomly spaced pinned solitons. Here we introduce a simple one-dimensional model which simulates the effect of impurities in destroying the periodicity of the multisoliton lattice. We consider a sequence of phase solitons with the single soliton formation free energy F_s and the nearest-neighbor interaction falling off exponentially with the intersoliton distance. The effect of impurities is described by an electric field which varies spatially in a random way and acts on the polarization pattern (see Fig. 1).

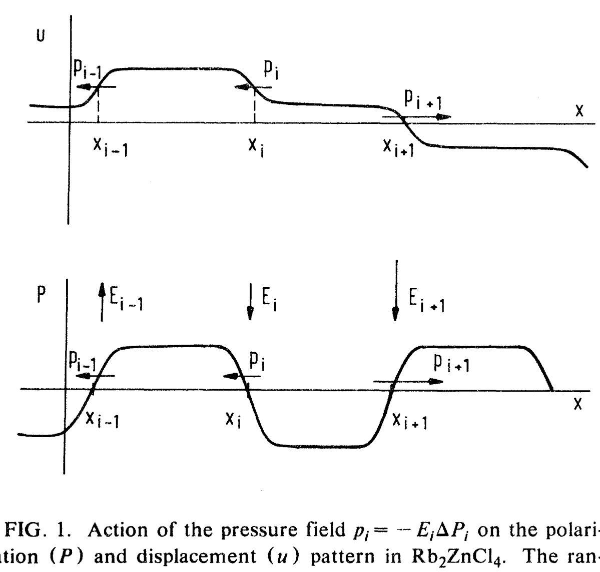

FIG. 1. Action of the pressure field $p_i = -E_i \Delta P_i$ on the polarization (P) and displacement (u) pattern in Rb_2ZnCl_4. The random internal electric field E_i simulates the effective impurities. ΔP_i represents the change of the polarization over the phase soliton.

Since in incommensurate ferroelectrics the solitons separate C regions of opposite polarizations, the fields, described by their values E_i at the soliton positions, would exhibit additional pressure fields p_i on the solitons. Since the impurities are distributed at random we assume a Gaussian distribution for E_i characterized by a width σ_E.

Within the I phase the random fields destroy the long-range order of the multisoliton lattice. On the other hand, below T_c a chaotic state with randomly spaced metastable solitons is obtained on cooling. The dielectric susceptibility will be thus anomalously high in the C phase:[11]

$$\chi = \chi_0 + \frac{P_c}{\pi\sigma_E} n_s, \quad T < T_c \ . \tag{6}$$

Here, $P_c = 0.12\ \mu C/cm^2$ is the spontaneous polarization in Rb_2ZnCl_4 just below T_c and $\sigma_E \sim 1$ kV/cm as estimated from the maximum of $\epsilon \sim 160$ at $T \sim T_c$.

The NMR frequency distribution[12] measures the soliton density and is close to T_c not affected by the destruction of long-range order. It is in the constant amplitude approximation obtained from

$$f(\nu) = \frac{\text{const}}{(d\nu/dx)} \tag{7}$$

as[11]

$$f(\nu) = \frac{\text{const}}{|\sin\phi|\{\Delta^2 + \cos^2[\frac{1}{2}n(\phi-\phi_0)]\}^{1/2}|d\nu/du|} \ , \tag{8}$$

where $\phi = \phi(x)$ is the phase of the incommensurate modulation wave $u = A_0\cos\phi(x)$ which is determined from the sine-Gordon equation,[12] $n = 6$ is the number of topologically different C domains, ϕ_0 is the initial phase which is determined by the position of the investigated nucleus in the commensurate unit cell, and Δ^2 is a constant which is related to the soliton density,[12] Eq. (5), by

$$k = 1/(1+\Delta^2)^{1/2} \ . \tag{9}$$

The value of n_s is 1 when $\Delta^2 >> 1$, whereas $n_s \to 0$ when $\Delta^2 << 1$. A fit of the theoretical and experimental NMR line shapes $f(\nu)$ yields Δ^2 and thus n_s, which can be compared with the soliton density derived from the dielectric constant data via the Landau theory as given by expressions (1)–(6).

Due to random fields the long-range order of the multisoliton lattice is destroyed resulting in a distribution of intersoliton distances and an anomalous broadening of the incommensurate x-ray satellites. In the random-field model the satellite line shape will be Gaussian with a half-width δq which follows a Curie-Weiss law[11] on approaching the transition from above:

$$\frac{\delta q}{q} \propto \frac{\delta x_0}{x_0} \propto \epsilon - \epsilon_\infty \propto \frac{1}{T - T_c} \ , \tag{10}$$

reflecting the increase in the half-width of the distribution of intersoliton distances δx_0. δq reaches its maximum values at $T_c^x \sim T_c$, where the spread in the intersoliton distances δx_0 becomes comparable with x_0.

Below T_c^x, δq can be related[11] to the pinned soliton density as

$$\delta q = \frac{\pi}{2}\frac{q_0}{\sqrt{n}} n_s \ . \tag{11}$$

III. RESULTS AND DISCUSSION

The temperature dependence of the static dielectric constant of Rb_2ZnCl_4 around the I-C transition is presented in Fig. 1 both for a cooling and for a heating run. The measurements were performed along the direction of the ferroelectric axis. The data show—in agreement with Ref. 3—that on approaching T_c^+ from above the temperature dependence of the dielectric constant follows Eq. (1) with $C \approx 80$ K up to ~ 0.1–$1\,^\circ$C. In this interval, which depends on the quality of the crystal, a deviation from the Curie-Weiss law takes place and χ attains a finite maximum value which decreases with increasing impurity content. On cooling into the C phase, χ slowly decreases with a rather long tail and attains χ_0 only below $-120\,^\circ$C. This means that Eq. (2) is fulfilled only $\sim 40\,^\circ$C below T_c and not immediately below T_c. On heating from $-130\,^\circ$C, χ is practically temperature independent up to T_c^- where the dielectric constant abruptly increases to ~ 160 and then decreases on further heating into the I phase. The difference between T_c^+ and T_c^- in the investigated crystal (Fig. 2) amounted to $\sim 2\,^\circ$C.

The temperature dependence of the soliton density as derived from the dielectric data is shown in Fig. 2. It should be noted that the dielectric constant is sensitive to the soliton density only in the vicinity of T_c, where we get from Eqs. (4) and (5)

$$\chi - \chi_0 = \frac{Cn_s}{4\pi(T_I - T_c)} e^{\pi/n_s}, \quad T > T_c \ . \tag{12}$$

The pinned soliton density can also be determined below T_c from Eq. (6). The n_s values for $T >> T_c$ represent an extrapolation with the help of the Landau theory. To check on that we as well plotted the n_s values derived from the fitting of the experimental and theoretical ^{87}Rb $\frac{1}{2} \to -\frac{1}{2}$ NMR line shapes.[13] The n_s values derived from the dielectric and NMR data[13] agree rather well.

As it can be seen from Fig. 3 the value of n_s, which mea-

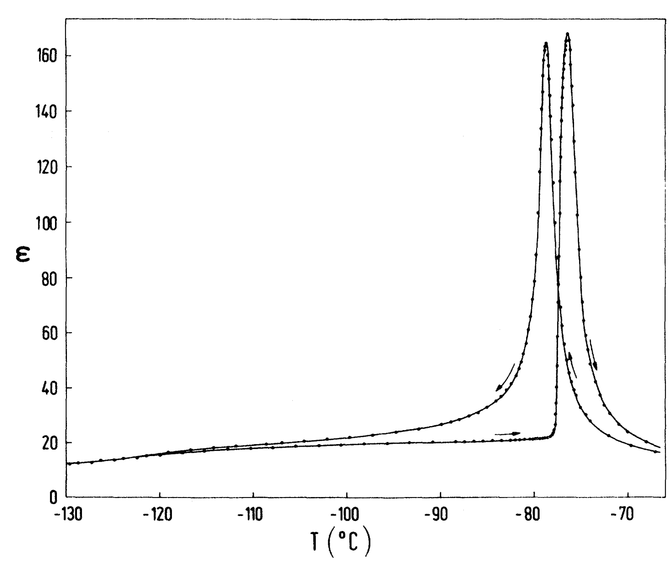

FIG. 2. Temperature dependence of the dielectric constant in Rb_2ZnCl_4 around T_c in the direction of the ferroelectric axis.

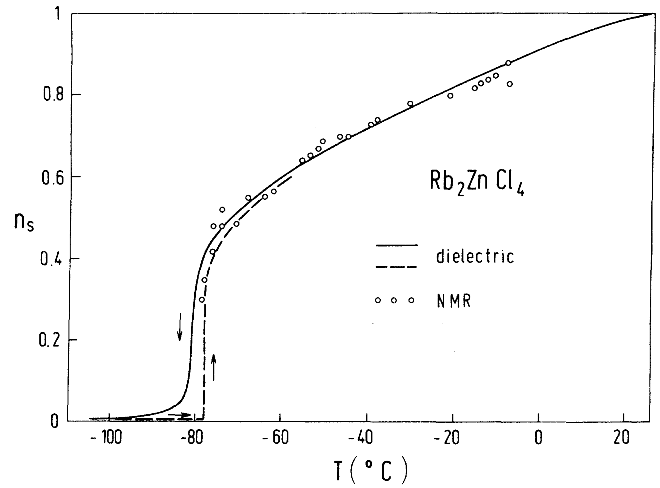

FIG. 3. Temperature dependence of the soliton density n_s in Rb_2ZnCl_4 as derived from the dielectric data in cooling and heating runs with the help of the Landau theory. The circles show the soliton density, derived from the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ nuclear magnetic resonance line shapes (Ref. 13).

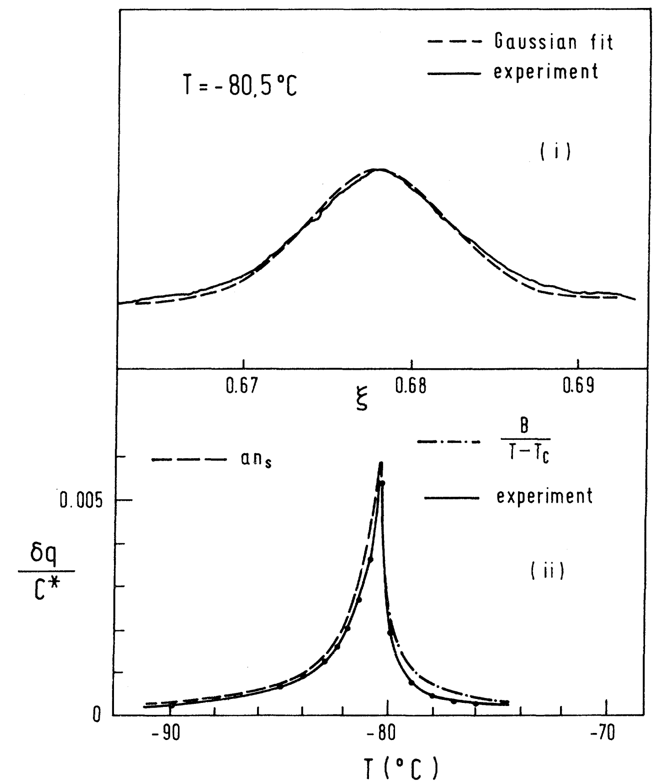

FIG. 4. (i) Comparison between the experimental and theoretical x-ray I satellite line shape in Rb_2ZnCl_4 at $T = -80\,°C$ assuming a Gaussian distribution of internal electric fields due to impurities. (ii) Comparison between the experimental and theoretical temperature dependences of the x-ray I satellite linewidth above T_c [Eq. (10)] and below T_c [Eq. (11)]. The temperature variation of n_s below T_c is taken from the dielectric data. The constant a equals 0.018, and the constant B equals 0.0018 K.

sures the volume fraction of the crystal occupied by the discommensurations, decreases from 1 at $T_I \simeq 27\,°C$ to about ~ 0.8 at $-26\,°C$ and reaches 0.6 at $-61\,°C$. The dielectric constant data show that n_s reaches a finite value of about 0.33 at T_c^+, whereas NMR data[12] yield a value ~ 0.30 in the same temperature range. Below T_c, n_s drops relatively fast from about 0.3 to 0.06 in a temperature interval of about 2 °C and then decreases rather slowly to zero with decreasing temperature. Twenty degrees below T_c, around $-100\,°C$, the soliton density is still more than 1%. This value is, however, so small that it is indistinguishable from zero for NMR techniques and can be seen only through dielectric data.

On heating from below n_s practically equals zero up to T_c^- where it abruptly jumps to about 0.33 and then slowly increases with increasing temperature.

The above temperature dependence of n_s agrees with the one deduced from the anomalous broadening of the x-ray satellites below T_c (Fig. 4). From the same figure we as well see that the x-ray line shape and temperature dependence above T_c follow the predictions of the random-field model.

The finite value of n_s at T_c, the hysteresis in n_s on cooling below T_c, and the anomalous x-ray satellite broadening represent strong additional evidence for the existence of a metastable chaotic state with randomly pinned solitons intermediate between the I and C phases.

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