Incommensurate phases in a mixed system $[(CH_3)_4N]_2CuBr_xCl_{4-x}$

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Two incommensurate (I) phases in a rich phase diagram of the solid solution $[(CH_3)_4N]_2CuBr_xCl_{4-x}$ are investigated for multicritical points. The x-ray diffraction shows that on the Cl-rich side the I part of the wave vector changes sign at $x = 0.4$; still the lock-in transition occurs only 6 K below the N-I transition. On the Br-rich side the x-ray diffraction, the differential scanning calorimetry, and the dielectric-constant measurements show the shrinking I phase. Again the multicritical point is not reached due to the remaining intermediate phase, for which an explanation is given in terms of the random modulated structure.

I. INTRODUCTION

Incommensurate (I) structures in dielectrics have been investigated intensively in the past fifteen years.[1] Typically, in I phases the amplitude and the wavelength of the structural modulation vary with the temperature T. In order to explore the possibility of multicritical points in the phase diagrams of I dielectric structures the influence of additional parameters like hydrostatic pressure[2] and external electric field[3] has been investigated. Of particular interest are the multicritical points where the modulation disappears continuously, as is the case near the Lifshitz point.[3,4] In mixed I systems the composition parameter x plays a role of an additional variable. This allows to search for a suppression of the I phase in the x-T phase diagram and to examine the behavior near these particular points in the phase diagram. So far few mixed systems with an I phase have been investigated through a wide parameter range.[5] The solid solution $[(CH_3)_4N]_2CuBr_xCl_{4-x}$,[6] belonging to the most extensively studied structural family of K_2SeO_4, offers this possibility and is the subject of our analysis.

In spite of some experimental and theoretical studies[5-7] of I structures in mixed systems, the question of possible phase diagrams is not settled. Within phenomenological theories of I dielectrics[8] the mixed system can be simulated by the concentration dependence of parameters in the Landau-type free-energy functional. The most important role is played by the driving (Lifshitz) term of the I phase. A concentration-induced change of the sign of the Lifshitz term can thus lead to a multicritical point. On the other hand mixed systems have inherent quenched disorder, which can essentially influence the existence and the properties of the I phase.[9]

In the vast majority of cases in the K_2SeO_4 family the modulation forms along the pseudohexagonal **a** axis of the crystal and so it does in $[(CH_3)_4N]_2CuCl_4$.[10,11] As an exception the isomorphous $[(CH_3)_4N]_2CuBr_4$ displays an I phase[12,13] modulated along the **c** axis. The x-T phase diagram of the solid solution $[(CH_3)_4N]_2CuBr_xCl_{4-x}$ may therefore contain new multicritical points[6] involving I phases.

In this paper we will examine the system by differential scanning calorimetry (DSC), x-ray diffraction, and dielectric susceptibility measurements, concentrating mainly on the (near) disappearance of the I phase and on the multicritical (Lifshitz-like) point on the Cl-rich side. Experimental results are presented in Sec. II Section III is devoted to the theoretical description of experimental results in terms of phenomenological models and also to the discussion of the possible origin of the remaining intermediate I-like phase.

II. EXPERIMENTS AND RESULTS

Mixed crystals of $[(CH_3)_4N]_2CuBr_xCl_{4-x}$ were grown from equilibrated mixed solutions for 53 different compositions.[6] The x-T phase diagram (Fig. 1) was established by DSC using a Perkin-Elmer differential scanning calorimeter (DSC-2). The sample size was between 20 and 30 mg and the temperature was changed at a rate of 20 K/min in order to obtain a sufficient DSC signal. The shape and the T hysteresis of the DSC peaks allow for an approximate distinction between first-order and second-order phase transitions (Fig. 2). According to the DSC curves the first phase transition on cooling down from the common high-temperature phase A is of the second order. All subsequent transitions occurring in the phase diagram appear to be first order. It should be pointed out, however, that using DSC it is quite difficult to distinguish between discontinuous (first-order) and continuous soliton-dominated incommensurate-commensurate (C) transitions in I systems.[8,14,15] This problem applies in our case, e.g., to the transition between phases B and C.
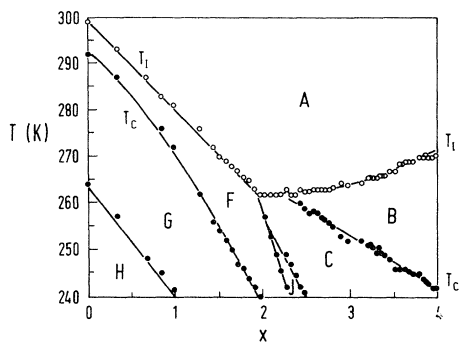
LIECHTI, KIND, PRELOVŠEK, FILIPIČ, AND LEVSTIK

FIG. 1. Phase diagram of $[(CH_3)_4N]_2CuBr_xCl2_{4-x}$ as obtained by DSC. Open and full dots denote second-order and first-order transitions, respectively.

TABLE I. Classification of phases.

Phase	Space group	Wave vector
A	$Pnma$	
B	$inc.c$	$q_c = \frac{1}{2} + q$
C	$P2_1ca$	$q_c = \frac{1}{2}$
F	$inc.a$	$q_a = \frac{1}{3} + q$
G	$P112_1/a$	$q_a = \frac{1}{3}$
H	$P2_1/n11$	$q_a = 1$
J	Unknown	

Most of the phase regions found in the phase diagram can be extrapolated from the known pure end members and are characterized as presented in Table I. Apparently, there is no region in the diagram where I modulations both along a and c are present simultaneously. The stability range of the I phase B is clearly reduced on substitution of Br by Cl and the DSC results would indicate on the existence of the triple point at $x \sim 2.3$ and $T = 262$ K, joining phases A, B, and C. At first sight this point would be a candidate for a Lifshitz point[4] since the (first-order) I-C phase transition line $T_c(x)$ merges with a second-order line $T_I(x)$, both existing for $x < 2.3$, and continues as a second-order direct transition $T_c(x)$ to the ferroelectric C phase for $2 < x < 2.3$. However, theory does not allow for such a point in systems with allowed Lifshitz invariants (without external fields[3]) and moreover more detailed dielectric measurements, presented below, are consistent with an intermediate phase even for $x < 2.3$.

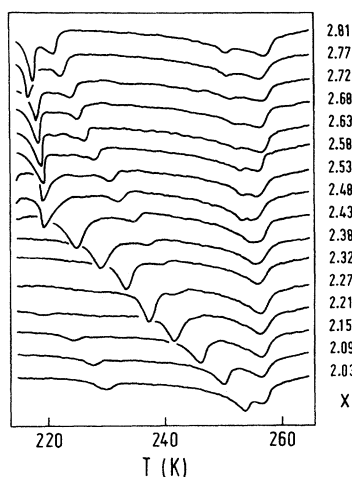On the Cl-rich side of the phase diagram latent heat peaks at $T_c(x)$ are too small to be detected by our DSC

for $x < 0.8$. The transitions are therefore obtained from the x-ray diffraction. Close to $x = 0.4$ the stability range T_I-T_c of the I phase F shows a minimum of 6 K. The latent heat of various transitions is evaluated from the area under peaks in the DSC curves (Fig. 2). Along the first-order-like transition line between the phases F and G a reduction of the latent heat at $T_c(x)$ accompanies the shrinking of the range $T_I - T_c$ of the I phase when the composition $x = 0.4$ is approached. Similarly, the latent heat at $T_c(x)$ vanishes linearly on approaching $x \sim 2.3$ from the Br-rich side.

In the $x - T$ phase diagram the space groups (see Table I) expected from the known pure end members are checked by means of x-ray precession photographs (Cu $K\alpha$ radiation). The characteristic Bragg peaks of the I phases as well as of the C low-temperature phases confirm the expected groups. In order to study the I phases B and F in more detail single crystals of different compositions were examined on a four-circle x-ray diffractometer Syntex P21 using Mo $K\alpha$ radiation. At $T = 295$ K the lattice constants prove to be linear functions of the crystal composition x, showing on a complete miscibility of two pure components. The relative increase of lattice constants on complete substitution is different for three crystal axes and amounts to 4.18% for c, 3.77% for a, and 2.88% for b. The major changes occur in the plane (a, c) out of which the I modulations develop. In the I phases the diffraction vector was varied in 50 steps of 0.002 reciprocal lattice units to scan an I reflection along the direction of modulation. The position and the intensity

FIG. 2. Typical DSC heating curves in vicinity of the multicritical point between the phases A, B, and C.
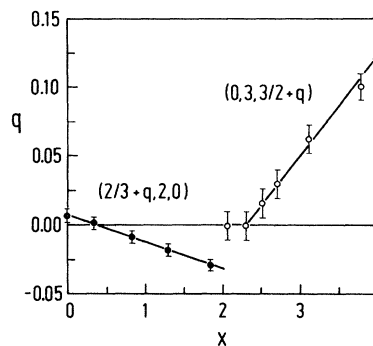

FIG. 3. Wave vector q at the onset T_I of the incommensurate phases B and F.

of the I satellite reflections are recorded simultaneously. Here the temperature of the samples was varied by means of a regulated nitrogen gas flow and stabilized to ± 0.05 K.

In the I phase B the intensity of the reflection $(0, 3, \frac{3}{2} + q)$ is found to follow the relation $I = I_0(T_I - T)^{2\beta}$, and the exponent $\beta = 0.33 \pm 0.02$ is approximately constant in the range $2 < x < 4$. The variation of the wave vector q at the onset T_I with the composition x is presented in Fig. 3. q goes linearly to zero on approaching $x \sim 2.3$ from the Br-rich side. Because of the width of satellite reflections and their vanishing intensity at T_I it is, however, impossible to determine the position of satellites at $x \lesssim 2.3$.

On the Cl-rich side the I wave vector q of the satellite reflection $(2/3 + q, 2, 0)$ also changes with x along the $T_I(x)$ line between phases A and F (Fig. 3). The I satellites in the F phase are sharper than the ones of phase B. Within the experimental resolution q varies linearly with x and changes sign for $x = 0.4$, where also the temperature range of the intermediate (I-like) phase is minimum, but still clearly measurable. The monoclinic angle characterizing the ferroelastic phase G appears below T_c. It is seen from a splitting of the I satellite due to the formation of domains. In the I phase the position q is almost independent of the temperature. In the ferroelastic phase G, however, the splitting of the reflection increases continuously with the decreasing temperature.

Since the phase C is a ferroelectric one, this allows the study of the sequence of A, B, C phases via quite sensitive dielectric susceptibility measurements. The dielectric measurements were performed by a Hewlett Packard 4284A Precision LCR meter at the frequency of 1 kHz. For $x > 1.97$ where the I modulation is along the c axis, the polarization is along the a axis, along which also all dielectric measurements were performed. The typical sample size used were $2.5 \times 5.0 \times 0.8$ mm^3, with the biggest surface cut perpendicular to the pseudohexagonal a axis.

Temperature dependence of the real part of the dielectric constant along the a axis ϵ_a is plotted in Fig. 4 for several x. The spontaneous polarization P_0 of the samples was measured by a Sawyer-Tower bridge at the frequency of 50 Hz under the electric-field amplitude of
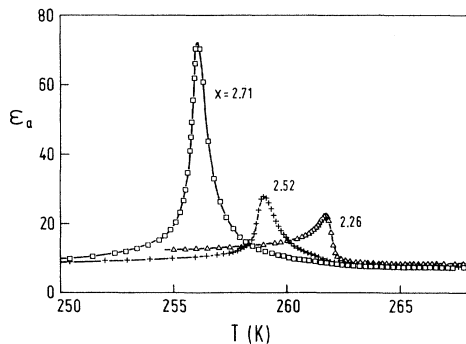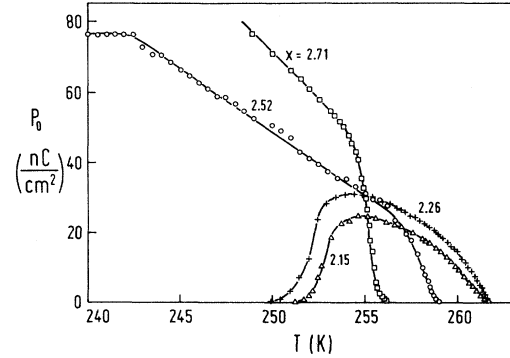

FIG. 5. Temperature dependence of the spontaneous polarization P_0 at various x.

14 kV/cm. Such an electric field should be sufficient to saturate the ferroelectric polarization loops,[12] which is clearly true for $x < 2.52$; for $x = 2.71$ the saturated polarization was, however, reached only in the temperature range $T_c - T < 8$ K. On the other hand, for smaller $x = 1.97, 2.03, 2.10$ as well as for $x = 3.41$ and $x = 4.0$ no hysteresis loops were observed along the a axis, in contrast to Ref. 12, where for $x = 4.0$ the temperature dependence of the spontaneous polarization was reported. Our results for the spontaneous polarization $P_0(T)$ at various x, measured at the frequency 50 Hz, are presented in Fig. 5.

Near the presumable multicritical point $x \sim 2.3$ the dielectric measurements allow for a more detailed investigation of the phase diagram, as presented in Fig. 6. As usual the T_I transition from the paraelectric to the I phase is determined as the highest temperature above which the dielectric constants on cooling and on heating runs coincide.[12] Below T_I, ϵ_a obtained on cooling or on heating differ substantially. At T_I the dielectric constant shows also a kink on cooling runs.[10,12,16] T_c is fixed as the temperature where ϵ_a has the maximum value. So determined T_c coincide within 0.05 K on cooling and on heating, they as well agree with the onset of the spontaneous polarization.

FIG. 4. Temperature dependence of the dielectric constant ϵ_a for crystals with various x.
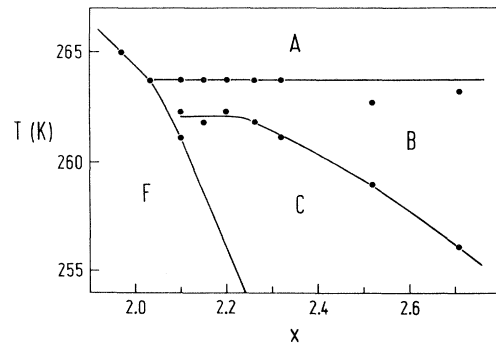

FIG. 6. Phase diagram determined by dielectric measurements. Lines serve as the guide to the eye.

Measurements of the dielectric measurements clearly indicate the existence of an intermediate phase even below $x \sim 2.3$, i.e., for our samples with $x = 2.26, 2.2, 2.15$, with a pronounced anomaly of ϵ_a approximately 2 K below the appearance of this phase at T_I. On the other hand, for $x = 1.97$ and 2.03 no hysteresis loops were observed and also $\epsilon_a(T)$ variation is *clearly different* than for the higher concentrations. In the latter two cases we observe only one maximum in the dielectric constant which is by value almost two orders of magnitude weaker than for higher x. This observation is consistent with a quite different character of the phase F.

III. PHENOMENOLOGICAL MODELS

The properties of both I phases, B and F, can be discussed within the same phenomenological framework, appropriate for I ferroelectric and ferroelastic dielectrics of the A_2BX_4 class.[1,8] We will mainly concentrate on the phase sequence A-B-C with the doubling of the unit cell along the c axis. In this case the free-energy density can be expressed in terms of the complex order parameter $Q(z)$, associated with the two-dimensional irreducible representation of the space group $Pnma$ on the Λ line, coupled to the polarization $P(z)$, both varying along the direction z,[3,8]

$$
f = \frac{\alpha}{2}|Q|^2 + \frac{\beta}{4}|Q|^4 - \frac{\delta}{2}\left(Q\frac{dQ^*}{dz} - Q^*\frac{dQ}{dz}\right)
$$
$$
- \frac{\gamma}{2}(Q^n + Q^{*n}) + \frac{\kappa}{2}\left|\frac{dQ}{dz}\right|^2 + \zeta P(Q^p + Q^{*p})
$$
$$
+ \frac{1}{\chi_0}P^2 - PE, \tag{3.1}
$$

where at fixed concentration x we assume $\alpha = \alpha_0(T - T_0)$, while $\beta, \gamma, \delta, \kappa, \zeta, \chi_0$ are taken to be T independent. For the Br-rich $[(CH_3)_4N]_2CuBr_xCl_{4-x}$ the doubling of the unit cell is characteristic for the C phase,[12] hence $p = 2$ and $n = 2p = 4$. The phase sequence and properties at a given x are therefore expected to be isomorphous to more extensively studied dielectric $(NH_4)_2BeF_4$.[3] It should be mentioned that an analogous treatment is appropriate for the description of the sequence A, F, G, with the reference C phase characterized by tripling of the unit cell, i.e., $p = 3$ and $n = 6$, while the role of the secondary order parameter, P in Eq. (3.1), is taken over by the homogeneous strain.[1,10]

The simplest approach to a mixed system is to allow a variation of parameters with x. Since the I (or intermediate) phase nearly disappears at particular x, it is most natural to assume that the crucial concentration dependence is in the Lifshitz (δ) term, driving the para-I transition. Hence, we will in the following test the hypothesis that the observed phenomena on the Br-rich side can be explained by a linear variation of δ, i.e., $\delta = \delta_0(x - x_0)$ with $x_0 \sim 2.3$. It is evident that an analogous assumption would explain the changing of the sign on the Cl-rich side at $x \sim 0.4$.

The use of an homogeneous free-energy density with effective parameters for a mixed systems is, however, only a

virtual-crystal approximation (VCA). The randomly distributed (quenched) constituents in the solution would require an introduction of spatially varying parameters. Such approaches have been already introduced in the theories of hysteresis phenomena, of the disorder-induced phason gap, and in the consideration of the destroyed long-range order in I ferroelectrics.[9] As far as the phase diagram is concerned these aspects seem to become important only when the spatial average $\bar{\delta} \sim 0$, hence near possible multicritical points.

Within the VCA the I wave vector q at T_I follows from Eq. (3.1) as $q = \bar{\delta}/\kappa \propto (x - x_0)$, consistent with the x-ray results (Fig. 3), both in the Br- and in the Cl-rich phases. The para-I transition is determined by $\alpha = \bar{\delta}^2/\kappa$, hence

$$
T_I = T_0 + \frac{\bar{\delta}^2}{\alpha_0\kappa} = T_0 + \eta(x - x_0)^2. \tag{3.2}
$$

In general T_0 should be considered as an x-dependent quantity, although the phase diagram of the B phase would indicate nearly constant T_0 in the regime $x > 2.1$. Still the known variation of $T_I(x)$ is not enough to determine uniquely T_0.

The constant amplitude approximation (CAA) $Q = \rho_0 \exp(i\phi)$ is usually employed to describe the minimum energy configuration of (3.1) in the I phase for $T < T_I$. This yields approximately $\rho_0 \propto \sqrt{T_I - T}$, while the lock-in transition temperature T_c is determined by the vanishing of the free energy of a single discommensuration (phase soliton)[14,15]

$$
F_s = \frac{8}{n}\rho_0^{p+1}\sqrt{\kappa\bar{\gamma}} - \frac{2\pi\delta}{n}\rho_0^2 = \mu(T - T_c), \tag{3.3}
$$

with $\bar{\gamma} = \gamma + \chi_0\zeta^2$. For $p = 2$ it follows from Eq. (3.3) that $\rho_0 \propto \delta$ and

$$
T_I - T_c = \nu(T_I - T_0). \tag{3.4}
$$

Experiments do not allow us to fix $\nu \sim \beta/\bar{\gamma}$. Still dielectric measurements (at least for pure $[(CH_3)_4N]_2CuBr_4$) show a well-pronounced Curie law at $T > T_c$, characteristic for (nearly) continuous I-C lock-in transitions. This poses a limitation on the strength of the anisotropy γ. In particular, we get for the model (3.1) with $n = 4$ the requirement $\nu > 13$, as it follows from a more general analysis presented in Ref. 15. From Fig. 1 we see that this is impossible to achieve with x-independent T_0.

It has been shown for several I ferroelectric systems that the Landau phenomenological theory using Eq. (3.1) accounts very well for measured dielectric properties,[3,17] in particular for the temperature dependence of the dielectric constant $\epsilon(T)$ in the I phase as well as for the spontaneous polarization P_0 in the ferroelectric phase. For P_0 we get from Eq. (3.1)

$$
P_0 = \zeta\chi_0\rho_0^p \sim \frac{\zeta\chi_0\alpha_0}{\beta}(T_I - T). \tag{3.5}
$$

Looking at the measured polarization P_0 in the C phase (Fig. 5), we find a clear confirmation of the linear temperature dependence in Eq. (3.5), where the values and slopes are nearly independent of the concentration x. The only clear dependence on x enters via the variation

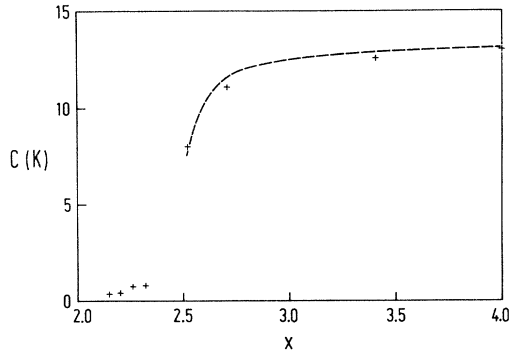FIG. 7. Composition dependence of the Curie constant C. The dashed line is calculated from Eq. (3.7) at measured points.

of the lock-in temperature $T_c(x)$.

If the I-C transition is continuous one expects at T_c a large increase of the dielectric constant ϵ_a, related to the softening of the soliton lattice,[17]

$$\epsilon_a = \epsilon_0 + \frac{C}{T - T_c}, \qquad (3.6)$$

with the Curie constant

$$C = \frac{P_0^2}{2\pi q \mu} \propto \frac{(T_I - T_c)^2}{\bar{\delta}^2}, \qquad (3.7)$$

where we have evaluated μ from Eq. (3.4), i.e., $\mu = \alpha_0 \pi \bar{\delta}/n\beta$. Inserting known values $T_I(x) - T_C(x)$ and $\bar{\delta} = \delta_0(x - x_0)$ with $x_0 = 2.27$ we obtain only a weakly x-dependent Curie constant (see Fig. 7), which is consistent with the measured one above $x > 2.3$. On the other hand, the Curie constant shows a clear drop at $x < 2.3$, indicating a qualitatively different intermediate phase.

A possible explanation of the intermediate phase at $x \lesssim 2.3$ (as well as for $x \sim 0.4$) can be given in terms of the phenomenological model Eq. (3.1), including the random spatially varying $\delta(\mathbf{r})$. Such models have already been discussed in the literature.[18] Still several important aspects relevant also for our system have not been clarified so far.

Although pure constituents at $x = 0$ and 4 would be characterized by quite different δ, it seems plausible that effective spatial variations are much weaker due to correlations between displacements in neighboring unit cells. Simplifying the analysis by assuming only the variation $\delta(z)$, we get at T_I that the modulation wave vector is determined by the average $\bar{\delta}$. On the other hand, within CAA the transition temperature to such inhomogeneous ordered phase is governed by $\overline{\delta^2}$, i.e.,

$$T_I = T_0 + \frac{\overline{\delta^2}}{\alpha_0 \kappa}. \qquad (3.8)$$

Hence, the transition appears above T_0 even if $\bar{\delta} = 0$, which could explain the observed phase diagram, Fig. 6.

The character of such intermediate ordered state is unclear. From the theoretical considerations of the proposed model with a random Lifshitz constant $\delta(\mathbf{r})$ one can conclude that the randomness always destroys the long-range order in the I phase (see the discussion in Ref. 9), in spite of some different conclusions.[18] Moreover, it seems plausible that at $\bar{\delta}$ the intermediate phase does not show any (even short-range) I modulation and is more of a spin-glass type with frozen-in local ordering. The onset of the C phase and the width of the intermediate phase are determined by the approximate criterion for T_c, i.e., $\overline{\delta^2}/\kappa \sim \gamma \rho_0^2$. Still the behavior of the disordered model Eq. (3.1) near T_c is not understood. In particular it is not clear if there exists some regime dominated by solitonlike objects, which would indicate the possible softening under the external field. This question is relevant in our case since the measured dielectric constant ϵ_a shows a pronounced anomaly near T_c (although with a much smaller Curie constant as seen in Fig. 7). It should, however, be admitted that present experimental results (together with open theoretical questions mentioned above) do not allow us to characterize more precisely the intermediate phase.

IV. CONCLUSIONS

Solid solutions $[(CH_3)_4N]_2CuBr_xCl_{4-x}$ are among a few systems, where possible additional multicritical points can be studied experimentally. Our investigations of the I phase B (as well as the phase F) indicate that they can be well modeled by a phenomenological Landau theory with a strongly composition-dependent strength δ of the Lifshitz invariant, changing sign at a nontrivial concentration x. This is a system where one can reach the point with the vanishing, although symmetry allowed, Lifshitz term.

We have studied experimentally in detail the vicinity of such presumable multicritical point in the B phase at $x \sim 2.3$. Measurements of the dielectric constant ϵ_a indicate the existence of the intermediate phase even at $\delta = 0$. The origin of this phase cannot be settled with certainty. It is clear on one hand that a system with $\delta = 0$ is very susceptible to any higher-order Lifshitz-like terms. In a homogeneous system they would reflect a more complicated modulation, measurable via the x-ray diffraction, etc. Since our observations so far are not confirming this possibility, we propose the interpretation in terms of the inhomogeneous glasslike phase. This one is allowed in a disordered system with a spatially random Lifshitz term, driving the intermediate phase. In contrast to some other systems where the disorder induces the phason gap, the thermal hysteresis, etc.,[7,9] in our system the randomness seems to become a predominant effect in the vicinity of multicritical points. Still further experimental and theoretical investigations are needed to confirm this hypothesis.

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