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Inelastic neutron scattering investigation of low temperature phase transition in Rb_2ZnCl_4 and K_2ZnCl_4

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Résumé. — Des mesures de diffusion inélastique des neutrons ont mis en évidence l'existence d'un mode optique mou au point $T \left(\frac{1}{2} (\mathbf{b}^* + \mathbf{c}^*) \right)$ de la zone de Brillouin responsable de la transition de la phase ferroélectrique vers la phase basse température dans les deux composés Rb_2ZnCl_4 and K_2ZnCl_4 . Pour K_2ZnCl_4 on montre que la branche optique molle présente un minimum au voisinage de T dans la direction $\left(\mu \mathbf{b}^* + \frac{1}{2} \mathbf{c}^* \right)$, ce qui confirme l'existence de la nouvelle phase incommensurable récemment trouvée par Gesi. L'origine de cette phase est discutée sur la base d'un modèle phénoménologique dont on dérive aussi les formules des constantes élastiques et leur comportement au voisinage de la transition vers la phase incommensurable.

Abstract. — Inelastic scattering of neutrons has revealed soft optic modes at the T point $\frac{1}{2} (\mathbf{b}^* + \mathbf{c}^*)$ of the Brillouin zone both in Rb_2ZnCl_4 and K_2ZnCl_4 which are responsible for the phase transition from the ferroelectric to the lowest temperature phase of these materials. Moreover, in K_2ZnCl_4 near the T point a minimum on the soft optic branch in the direction $\left(\mu \mathbf{b}^* + \frac{1}{2} \mathbf{c}^* \right)$ has been found which confirms the existence of a new incommensurate phase recently discovered by Gesi. The origin of this incommensurate phase is discussed from a phenomenological point of view and formulae for elastic constants are derived describing their behaviour near the transition into the incommensurate phase.

1. Introduction.

It has been proposed [1] that a most natural way how to describe the whole phase sequence observed in A_2BX_4 -type crystals is to start with the prototypic hexagonal phase $\text{P6}_3/\text{mmc}$. Then the high-temperature orthorhombic phase I of Pnma symmetry can be looked upon as resulting from this prototype *via* small distortions associated with one of the triply degenerate

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soft modes, e.g. that with the wave vector $\frac{1}{2}\mathbf{b}_1^H$. It is well-known that in Rb_2ZnCl_4 , K_2ZnCl_4 when lowering the temperature below the phase I an incommensurate (IC) phase II sets in and is modulated along the x -axis (— in what follows we shall use the coordinate axis x, y, z parallel to the basic vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ of the orthorhombic unit cell —). This IC is followed by the ferroelectric lock in phase III of $\text{Pn}2_1$ symmetry. At still lower temperatures a phase IV exists the symmetry of which is not yet well established. It has been suggested [1] that the phase IV is due to the softening of the remaining two still degenerate modes of the hexagonal prototype. The corresponding wavevector $\mathbf{q}_c$ in the orthorhombic phase is equal to $\frac{1}{2}(\mathbf{b}^* + \mathbf{c}^*)$ (T-point of the Brillouin zone). Recently this hypothesis has been confirmed independently by Gesi [2] and in this paper. Moreover, it seems likely that a new IC phase modulated along the y -axis exists in K_2ZnCl_4 [2] before the phase IV sets in (see Sect. 4).

The present paper is organised as follow. In section 2 experimental details are given. In sections 3 and 4 we report on results of coherent inelastic neutron scattering studies performed on Rb_2ZnCl_4 and K_2ZnCl_4 , respectively. Based on available experimental data and symmetry analysis of normal modes we propose in section 5 a picture of dispersion curves in the direction $\xi(\mathbf{b}^* + \mathbf{c}^*)$ of the Brillouin zone. In section 6 we discuss within Landau theory the nature of the new IC phase discovered in K_2ZnCl_4 and how its existence would manifest in elastic and dielectric properties.

2. Experimental.

We have grown single crystals of Rb_2ZnCl_4 and K_2ZnCl_4 by slow evaporation of a saturated solution. Inelastic neutron scattering measurements have been carried out on 0.5 cm^3 samples mounted in a displax closed cycle cryostat and data were taken as function of temperature with a 0.05 K stability. These experiments have been performed on a three axis spectrometer located on a cold source at the Orphée Reactor (LLB-CEN-Saclay, France). We have worked mainly with the plane $(\mathbf{b}^*, \mathbf{c}^*)$ as scattering plane. Energy scans were done with fixed incident neutron k_i of $2.662\text{ \AA}^{-1}$ and $1.55\text{ \AA}^{-1}$.

3. Rb_2ZnCl_4 .

In the low temperature phase IV below $T_0 = 74\text{ K}$ we observed superstructure reflections located at $\left(0, k + \frac{1}{2}, l + \frac{1}{2}\right)$. They have a weak intensity. We have chosen the most intense ones : $(0, 4.5, 1.5)$, $(0, 0.5, 4.5)$, $(0, 2.5, 1.5)$ and $(0, 4.5, 0.5)$ to collect our neutron data.

We shall show that observed pretransitional effects in this compound are of displacive type. At 295 K Rb_2ZnCl_4 is in the IC phase II. Figure 1 reports measurements of the lowest optic modes and the acoustic modes which propagate along the t direction, together with a sketch of the expected dispersion curves (see also part 5). In this scattering geometry only the quasi longitudinal and quasi-shear acoustic modes which are polarised in the $(\mathbf{b}^*, \mathbf{c}^*)$ plane can be measured. The optic branch has a sizeable structure factor in the $(0, 0.5 \rightarrow 0, 0.5, 4.5)$ zone. The (005) Bragg peak being silent, acoustic modes are not observed in this scattering geometry. We did not detect any intensity anomaly for this optic mode which could be related to an anticrossing effect with the lowest t_1 acoustic mode. Energy scans (constant $k_i = 2.662\text{ \AA}^{-1}$, energy resolution $\Delta\omega = 0.31\text{ THz}$) have been systematically fitted with a damped harmonic oscillator (D.H.O.) taking into account resolution effects.

When decreasing the temperature the optic branch is clearly seen to soften at the zone boundary $T = \frac{1}{2}(\mathbf{b}^* + \mathbf{c}^*)$ (cf. Fig. 2).

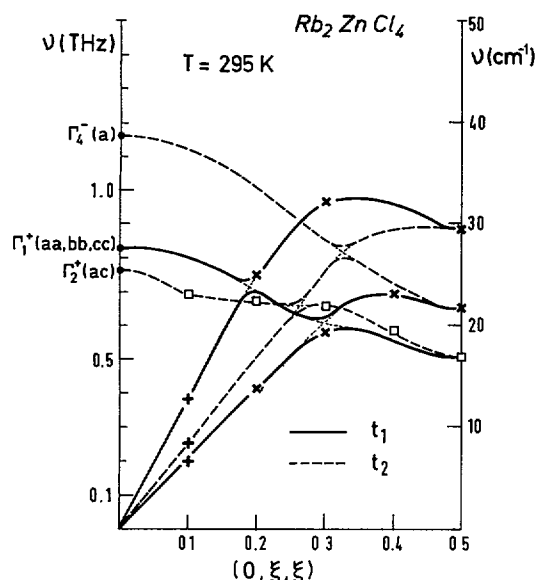


Fig. 1.

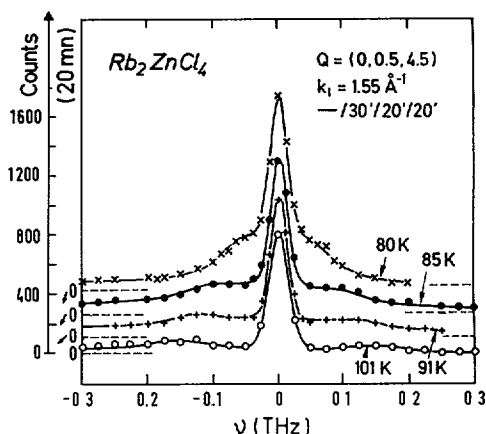


Fig. 2.

Fig. 1. — Dispersion curves for Rb_2ZnCl_4 at 295 K in the $(b^* + c^*)$ direction. (See section 5 for detailed discussion). (x) and (□) are neutron data points for the acoustic and optic modes, respectively. (+) are calculated values obtained from the Brillouin study in reference [3], (●) experimental Raman and IR points from references [4, 5]. Solid lines are just a guide for eyes.

Fig. 2. — Constant Q scans at $(0, 0.5, 4.5)$ for different temperatures which show the softening of the optic mode in Rb_2ZnCl_4 ($\nu = 0$ signal is the elastic incoherent response of the crystal) (O) experimental points. Solid lines are results of fitting with a DHO.

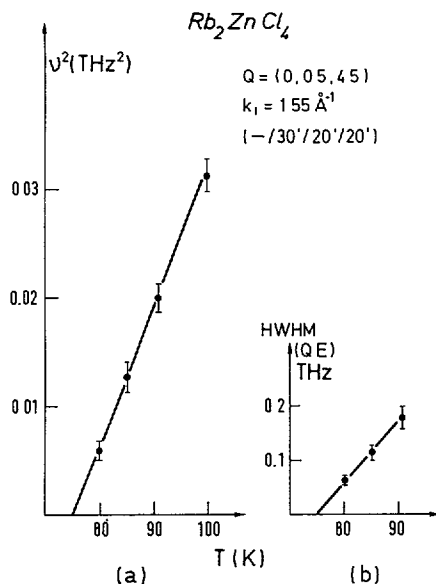


Fig. 3. — a) Square of the frequency of the soft optic mode at the T point as a function of temperature. (●) Results from a fit to a DHO. b) Temperature dependence of the half width at half maximum (HWHM) of the quasielastic response which is much weaker than the incoherent elastic response.

Below 100 K energy scans were performed with constant $k_i = 1.55 \text{ \AA}^{-1}$ and a better energy resolution ($\Delta\omega = 0.052 \text{ THz}$). Figure 3a evidences that the squared energy of this mode decreases linearly to zero at T_0 . This soft phonon remains underdamped until 80 K ; this has also been noticed below T_0 in the Raman study [6].

Our results show that a weak quasielastic response also coexists with the soft phonon. Our data were fitted using a DHO for the phonon and a Lorentzian function for the quasielastic contribution the width of which is presented in figure 3b (half width at half maximum = HWHM).

4. K_2ZnCl_4 .

4.1 ELASTIC RESULTS. — Like in Rb_2ZnCl_4 superstructure reflection peaks appear in the low temperature phase at the expected positions $\left(0, k + \frac{1}{2}, l + \frac{1}{2}\right)$ in the reciprocal space. They have a very weak intensity (one or two order of magnitude less than main Bragg reflections) except for four of them, namely $(0, 3.5, 4.5)$, $(0, 2.5, 1.5)$, $(0, 0.5, 4.5)$ and $(0, 1.5, 3.5)$.

We have looked for possible systematic extinction rules in this $(\mathbf{b}^*, \mathbf{c}^*)$ reciprocal plane. In the room temperature ferroelectric phase III we have the conditions : $0, k, l, k + l = 2n$, $0, k, 0, k = 2n$, $0, 0, l, l = 2n$ for possible reflections.

Forbidden reflection peaks in this latter phase remain very weak peaks below T_0 with an intensity weaker than the one of superstructure peaks. Our observations in this plane are compatible with the space group $A11a$ proposed by Dvořák *et al.* [1].

Unexpectedly in this material we observed a temperature dependent diffuse scattering. At 200 K a weak signal starts to develop around the superstructure peak positions of the low temperature phase. This diffuse scattering has an intensity which increases as the temperature decreases. It has also an unexpected Q distribution. As shown in figure 4, Q scans ($\omega = 0 \text{ THz}$) along the $\mathbf{b}^*$ direction have a profile which is well fitted with two Lorentzian scattering functions. These two components are located at $Q = \left(k + \frac{1}{2} \pm \delta\right) \mathbf{b}^* + \left(l + \frac{1}{2}\right) \mathbf{c}^*$.

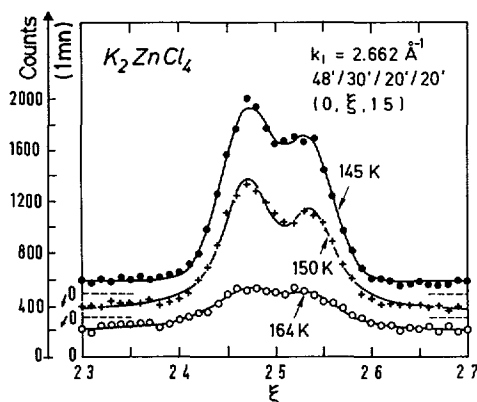


Fig. 4. — $E = 0$ scattering scans along the $\mathbf{b}^*$ direction at three temperatures above the IC-phase in K_2ZnCl_4 . Solid lines are results of fit with two Lorentzian scattering functions.

During the fitting procedure we have chosen to impose the same width to both components. In figure 5a this width is shown to decrease linearly when the temperature is lowered and to reach the instrumental resolution at 144 K. In the same temperature range (200 K $\rightarrow$ 144 K), the IC parameter δ decreases also linearly (cf. Fig. 5b). At 140 K the two satellites merge into a single peak giving a unique superstructure peak with an intensity two orders of magnitude greater than that of the satellite. Along the c^* direction the diffuse scattering has a line width which does not depend on the temperature and which has a value comparable to the instrumental resolution. Following Gesi [2] we propose to analyze the diffuse scattering as the precursor of an IC phase which stabilizes above T_0 between 140 K and 144 K.

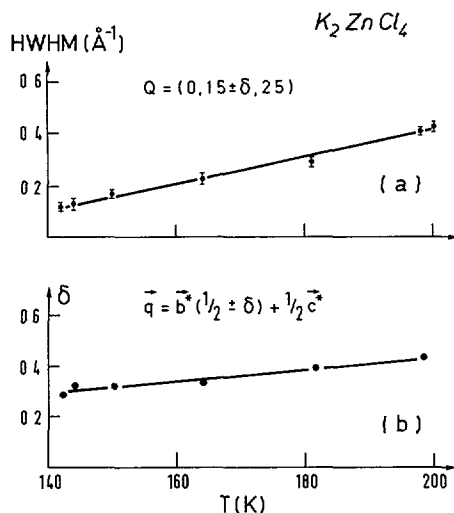


Fig. 5. — a) Temperature dependence of the HWHM ($\text{\AA}^{-1}$) of each Lorentzian component which describes the diffuse scattering above the IC phase in K_2ZnCl_4 . b) Variation with temperature of the IC parameter δ in K_2ZnCl_4 .

4.2 INELASTIC RESULTS. — The figure 6 shows for $T = 295$ K the measured dispersion curves along the $(0, 1, 1)$ direction for the three acoustic modes (the pure transverse one has been obtained in the $(a^*, b^* + c^*)$ scattering plane) and for the lowest optic mode. In this compound the inelastic structure factor of the phonons are weak. The optic branch has been obtained near the $(0, 3, 5)$ weak Bragg peak (energy scans with constant $k_i = 2.662 \text{ \AA}^{-1}$) where the acoustic modes were not visible. We may suppose that it has the same symmetry as the corresponding mode in Rb_2ZnCl_4 even though this weak intensity precludes any definite conclusion relative to the crossing with the lowest t_1 acoustic mode. All the data have been systematically fitted as already explained. For $q = 0.1 \text{ \AA}^{-1}$ the slopes of the three acoustic branches are in good agreement with the sound velocities measured in the Brillouin experiment [8].

We have studied the behaviour with decreasing temperature of the modes which are polarized in the (b^*, c^*) plane. Eventhough below 200 K the fitting procedure was not easy because of the Bragg like contamination due to the presence of the diffuse scattering we were able to demonstrate that the optic mode softens at the zone boundary (T point). In this case we do not obtain a frequency temperature dependence comparable to what has been observed

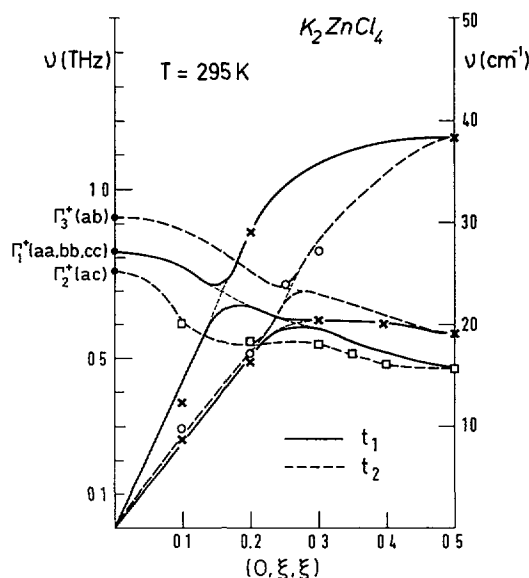


Fig. 6. — Dispersion curves for K_2ZnCl_4 at 295 K along the $(b^* + c^*)$ direction: (x) and (□) are neutron data for the acoustic and optic modes, respectively which are polarized in the (b^*, c^*) plane, (O) neutron data points for the pure transverse acoustic mode polarized along the a^* direction. (•) Experiment Raman points from reference [7]. Solid lines are just a guide to the eyes.

in Rb_2ZnCl_4 . At the zone boundary and for temperature lower than 150 K, the frequency of this optic mode seems to stabilize at about 0.25 THz (cf. Fig. 7). At 160 K we have performed energy scans (constant $k_1 = 1.55 \text{ \AA}^{-1}$, energy resolution $\Delta\omega = 0.035 \text{ THz}$) at various distances (q values) from the zone boundary in the b^* direction.

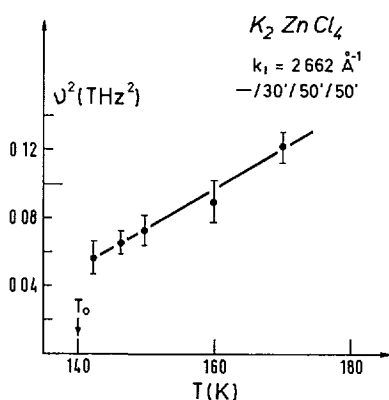


Fig. 7.

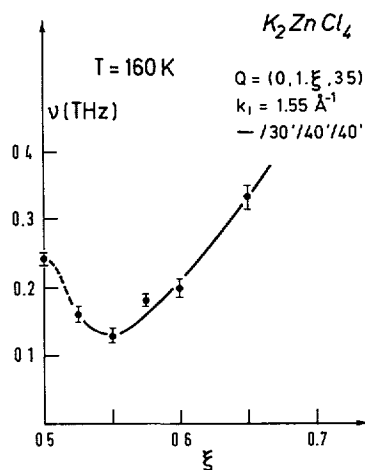


Fig. 8.

Fig. 7. Square of the soft optic mode frequency at the T point in K_2ZnCl_4 as a function of temperature

Fig. 8. — Dispersion relation of the soft optic branch in the b^* -direction at 160 K, for K_2ZnCl_4 .

Each energy scan was fitted with a DHO for the phonon mode plus a Lorentzian function to describe the signal at $\omega = 0$. (The elastic incoherent response of the crystal is a delta function). Neither an overdamped oscillator alone, nor a Lorentzian scattering alone would give a good fit of the data. As shown in figure 8, this fitting procedure gives a minimum ($\omega = 0.10$ THz) of the phonon branch located at $(0, 1.54, 3.5)$. This point corresponds to the position of the maximum of the quasielastic diffuse scattering. Further experiments with a better energy resolution are nevertheless necessary to study the behaviour of the quasielastic response when approaching the transition temperature to the IC phase.

5. Dispersion curves.

Let us now discuss the symmetry of modes in the t direction and the B direction $\mu\mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$. There are two nondegenerate symmetry species in the t direction: t_1 and t_2 compatible at the Γ point with Γ_1^+ (aa, bb, cc), Γ_4^+ (bc), Γ_2^- (b), Γ_3^- (c) and Γ_1^- (abc), Γ_4^- (a), Γ_2^+ (ac), Γ_3^+ (ab), respectively. We remind that in the ferroelectric phase (Γ_1^+ , Γ_2^-) change into Γ_1 , (Γ_1^-, Γ_2^+) $\rightarrow \Gamma_3$, (Γ_3^+, Γ_4^-) $\rightarrow \Gamma_4$, (Γ_3^-, Γ_4^+) $\rightarrow \Gamma_2$. At the T point the t_1 and t_2 modes become degenerate (there are two different symmetry species at this point in the parent phase Pnma (cf. Tab. I) but just one in the ferroelectric phase Pn2₁a). This double degeneracy persists in the B direction (one symmetry species only). This symmetry analysis and the available infrared [5], Raman [4, 7, 9] and our neutron inelastic scattering data make possible to suggest the form of dispersion curves along the t direction (cf. Figs. 1, 6) both for Rb_2ZnCl_4 and K_2ZnCl_4 . For this purpose we have to determine the symmetry of the soft branch. Experimental results suggest that it is polarised in the $(\mathbf{b}, \mathbf{c})$ plane. Unfortunately the symmetry does not impose any restrictions on eigenvectors of normal modes propagating in the t direction (including the T point) with respect to this plane. (The acoustic modes near the Γ point are exceptions: one mode of t_2 symmetry is purely transverse and two modes of t_1 symmetry are polarized in the $(\mathbf{b}, \mathbf{c})$ plane). Since no anticrossing effects between the lowest acoustic branch of t_1 symmetry and the soft branch have been observed at least for Rb_2ZnCl_4 (see Sect. 3, 4) we propose that the symmetry of the latter is t_2 . Actually a branch of this symmetry is compatible at the Γ point with the lowest frequency mode Γ_2^+ (ac) observed in Rb_2ZnCl_4 and K_2ZnCl_4 .

When analysing the experimental data we have to eliminate those modes which occur at the Γ point due to incommensurate modulation or the tripling of the a period; these modes have nothing to do with the branches in the t direction. There is no problem of this kind with Rb_2ZnCl_4 since experimental data in the parent phase are available. This, however, is not the case of K_2ZnCl_4 . A temperature independent Γ_3^+ (ab) mode at 0.6 THz (20 cm^{-1}) has been observed in the Raman spectra at room temperature [7, 9]. Since there is no analogous mode

Table I. — The irreducible representations $T_{\pm}$ of the space group Pnma at the point T, $\mathbf{q}_c = \frac{1}{2}(\mathbf{b}^* + \mathbf{c}^*)$.

$\{e\}$	$\{2_y 0 \frac{1}{2} 0\}$	$\{m_x \frac{1}{2} \frac{1}{2} \frac{1}{2}\}$	$\{m_z \frac{1}{2} 0 \frac{1}{2}\}$	$\{I\}$	$\{2_x \frac{1}{2} \frac{1}{2} \frac{1}{2}\}$	$\{2_z \frac{1}{2} 0 \frac{1}{2}\}$	$\{m_y 0 \frac{1}{2} 0\}$
$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\pm \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\pm \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\pm \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$	$\pm \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$

in this frequency range neither in Rb_2ZnCl_4 [4] nor in K_2SeO_4 [10] we suggest that this mode is in fact induced by the frozen mode responsible for the ferroelectric phase; indeed, by symmetry arguments it can be shown that the transverse acoustic mode at $\mathbf{q} = \frac{1}{3}\mathbf{a}^*$ polarised in the c -direction might be seen in the ab spectrum. From the Brillouin scattering data [8] we have calculated its frequency (neglecting dispersion) as 0.58 THz (19 cm^{-1}). Finally it should be pointed out that we have considered the lowest frequency modes only necessary for satisfying the compatibility relations at the T point.

The dispersion of the highest ι_2 branch near the Γ point seems to be rather steep in Rb_2ZnCl_4 (cf. Fig. 1). Actually this branch could terminate, as in K_2ZnCl_4 , at the Γ_1^- point which correspond to the Γ point of the soft branch in the $\mathbf{a}^*$ direction. Unfortunately this frequency is unknown but it could be well below (in K_2SeO_4 it is 0.6 THz at 130 K [11]) the frequency of the Γ_4^- mode.

6. Landau theory of the new IC phase in K_2ZnCl_4 .

As it will be seen it is useful to describe the phase transition into the phase IV by means of the free-energy density f_0 corresponding to the orthorhombic phase I. There are two irreducible representations (cf. Tab. I) of Pnma at the point T of interest. Both of them lead to the same form of f_0 as well as to the same symmetry of the phase IV.

Note that in the ferroelectric phase III these representations become identical. It is easy to show that at the point there is no Lifshitz invariant. Therefore the origin of an IC phase, if any, might be due to the existence of a pseudo-Lifshitz invariant in which order parameters of different symmetries might be involved [12]. Let us denote the two-dimensional basis corresponding to the representation $+$ and $-$ as p_+ , q_+ and p_- , q_- , respectively. The following pseudo-Lifshitz invariants can be constructed:

$$\left(\frac{dp_+}{dy} p_- - p_+ \frac{dp_-}{dy} + \frac{dq_+}{dy} q_- - q_+ \frac{dq_-}{dy} \right),$$

$$\left(\frac{dp_+}{dz} p_- - p_+ \frac{dp_-}{dz} - \frac{dq_+}{dz} q_- + q_+ \frac{dq_-}{dz} \right)$$

and

$$(Q^3 + Q^{*3}) \left(\frac{dp_+}{dx} q_- - p_+ \frac{dq_-}{dx} + \frac{dq_+}{dx} p_- - q_+ \frac{dp_-}{dx} \right)$$

where Q is the order parameter (with $\mathbf{q} = \frac{1}{3}\mathbf{a}^*$) which induces the phase III. Obviously, the last invariant is of higher-order than the first two, a fact which becomes apparent only if we consider f_0 of the phase I. In terms of normal lattice modes the pseudo-Lifshitz invariant describes a repulsion of two different branches which under some favorable quantitative circumstances (and not always as in the case of a Lifshitz invariant) may produce a minimum near q_c on the lowest of the two branches involved [12]. The experimental facts suggest that this is not the case of Rb_2ZnCl_4 but in K_2ZnCl_4 it happens along the q_y -direction (cf. Fig. 8). It should be pointed out that our pseudo-Lifshitz invariants are constructed with two doubly degenerate modes, i.e. four modes are involved, and not just with two non-degenerate modes as in the case of NaNO_2 or thiourea, for example. We are not aware of any qualitatively new consequence of this slightly generalized form of a pseudo-Lifshitz invariant. As we have mentioned already the $+$ and $-$ modes are in the phase III of the same symmetry which causes a repulsion between them described by the term

$$(Q^3 + Q^{*3})(p_+ p_- + q_+ q_-).$$

Finally it should be pointed out that the + and - branches remain doubly degenerate at a point B, i.e. in the TZ direction parallel to the k_y -axis, even in the phase III.

Instead of taking into account the pseudo-Lifshitz invariant explicitly we shall use an equivalent procedure, i.e. we shall consider just one doubly degenerate branch of p, q modes and assume that a minimum has developed on it near in the q_y -direction. In analogy with the non-degenerate case [13] we shall describe this situation by introducing appropriate derivatives of the order parameters p, q with respect to y . Then f_0 reads :

$$f_0 = \frac{1}{2} \alpha_0 (T - T_0) (p^2 + q^2) + \frac{1}{4} \beta (p^4 + q^4) + \frac{1}{2} \beta_1 p^2 q^2 + \frac{\gamma}{2} \left[\left(\frac{dp}{dy} \right)^2 + \left(\frac{dq}{dy} \right)^2 \right] + \frac{\lambda}{2} \left[\left(\frac{d^2 p}{dy^2} \right)^2 + \left(\frac{d^2 q}{dy^2} \right)^2 \right] \quad (1)$$

with $\alpha_0, \beta, \lambda > 0$ but $\gamma < 0$.

The corresponding Lagrange-Euler equations have well-known homogeneous solutions (phase IV) and non-homogeneous ones which cannot be found analytically. The homogeneous solutions are :

$$1) \beta_1 > \beta ; p_s^2 = \frac{\alpha_0 (T_0 - T)}{\beta}, q_s = 0 \text{ (or vice versa)}$$

which leads to the symmetry Pcl1.

$$2) |\beta_1| < \beta ; p_s^2 = q_s^2 = \frac{\alpha_0 (T_0 - T)}{\beta + \beta_1} ; A11a.$$

The space-group symmetry of the monoclinic phase IV of K_2ZnCl_4 is not exactly known so far but it seems likely that it is A11a (see Sect. 4). Recently the same conclusion was drawn in [14]. Near the phase transition temperature T_1 from the phase III into the C phase the non-homogeneous approximative solution can be taken in the form of single harmonics, e.g. $p_s = P \cos q_1 y$, $q_s = Q \sin q_1 y$, provided $\beta_1 > 0$ which we assume hereafter. Minimizing the free energy $F_0 = \frac{1}{L} \int_0^L f_0(y) dy$ ($L = 2\pi/q_1$) with respect to q_1, P, Q we get

$$q_1^2 = -\frac{\gamma}{2\lambda}, \quad T_1 = T_0 + \frac{\gamma^2}{4\alpha_0\lambda}$$

and

$$P^2 = \frac{4\alpha_0(T_1 - T)}{\beta}, \quad Q = 0 \quad \text{if } \beta_1 > \beta \quad \text{and} \\ P^2 = Q^2 = \frac{4\alpha_0(T_1 - T)}{\beta + \beta_1} \quad \text{if } \beta_1 < \beta. \quad (2)$$

Let us discuss elastic properties governed by coupling terms :

$$\frac{1}{2} (p^2 + q^2) (a_x u_{xx} + a_y u_{yy} + a_z u_{zz}), \frac{1}{2} a (p^2 - q^2) u_{yz}, \\ \frac{1}{2} \left[\left(\frac{dp}{dy} \right)^2 + \left(\frac{dq}{dy} \right)^2 \right] (l_x u_{xx} + l_y u_{yy} + l_z u_{zz}), b (Q^3 + Q^{*3}) pq \cdot u_{xy}, \\ b_1 (Q^3 + Q^{*3}) pq \cdot (p^2 - q^2) u_{xz} \quad (3)$$

where $u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right)$ denotes a strain component. Since the structure is modulated in

the y -direction we take the displacement field $\mathbf{u}$ in the form :

$$u_i = f_i(y) + \alpha_{ix}x + \alpha_{iy}y + \alpha_{iz}z \quad (i = x, y, z; \alpha_{ik} = \alpha_{ki}) \quad (4)$$

where α_{ik} are homogeneous strain components. We shall discard the last two coupling terms as higher order effects. Adding now the coupling terms and the elastic energy to (1) we get the total free-energy density f from which we can calculate external stress components σ_{ik} as :

$$\sigma_{ik} = \frac{1}{L} \int_0^L \frac{\partial f}{\partial u_{ik}} dy. \quad (5)$$

Using this formula and solving Lagrange-Euler equations for u_i (and not for u_{ik} !) with the ansatz (4) we get for the spontaneous strains :

$$\begin{aligned} u_{yy}^s &= -\frac{1}{2c_{22}} \left[a_y(p_s^2 + q_s^2) + l_y \left(\left[\frac{dp_s}{dy} \right]^2 + \left[\frac{dq_s}{dy} \right]^2 \right) \right], \\ u_{yz}^s &= -\frac{a}{2c_{44}} (p_s^2 - q_s^2), \\ u_{jj}^s &= -\frac{1}{2c_{jj}} \left[a_j \frac{1}{L} \int_0^L (p_s^2 + q_s^2) dy + l_j \frac{1}{L} \int_0^L \left(\left[\frac{dp_s}{dy} \right]^2 + \left[\frac{dq_s}{dy} \right]^2 \right) dy \right] \\ &= -\frac{1}{4c_{jj}} (a_j + q_1^2 l_j) (P^2 + Q^2), \quad (j = x, z \text{ or } 1, 3). \end{aligned}$$

Note that u_{yy}^s and u_{yz}^s are non-homogeneous since they are locally determined by the order parameters and their derivatives. On the other hand u_{jj}^s are homogeneous. In fact an homogeneous part of u_{yy}^s is missing because for simplicity we put the non-diagonal elastic constants $c_{ik} = 0$. This simplification does not change qualitatively the formulae for elastic constants c'_{ik} in the IC phase. Now we put the expressions for u_{ik}^s into Lagrange-Euler equations for p, q . After linearising these equations we can calculate the change of p, q due an applied homogeneous stress and using the formula (5) we get :

1) $P \neq 0, Q = 0; \beta_1 > \beta$ (see the formulae (2))

$$c'_{ii} = c_{ii} - \frac{(a_i + l_i q_1^2)^2}{3\beta + 5\mu P^2} \quad (i = 1, 2, 3), \quad c'_{44} = c_{44} - \frac{a^2}{3\beta + 5\mu P^2}.$$

2) $P^2 = Q^2; \beta_1 < \beta$

$$c'_{ii} = c_{ii} - \frac{2(a_i + l_i q_1^2)^2}{3\beta + \beta_1 + 5\mu P^2}, \quad c'_{44} = c_{44} - \frac{2a^2}{3\beta - \beta_1 + 5\mu P^2}.$$

Obviously, if we put $q_1 = 0$ we recover the usual formulae for an improper ferroelastic. All constants exhibit a jump down at T_1 followed by an increase due to the sixth-order term $\frac{1}{6}\mu(p^6 + q^6)$ we have added to f . P^2 is determined by equations (2) in which β should be replaced by

$$\beta \rightarrow 3 \left[\beta - \frac{1}{2} \left(\frac{a^2}{c_{44}} + \frac{a_y^2}{c_{22}} \right) \right] - \sum_{i,3} \frac{(a_i + l_i q_1^2)^2}{c_{ii}}$$

and β_1 by

$$\beta_1 \rightarrow \beta_1 - \frac{1}{2} \left(\frac{a_y^2}{c_{22}} - \frac{a^2}{c_{44}} \right) - \sum_{i,3} \frac{(a_i + l_i q_1^2)^2}{c_{ii}}$$

The elastic constants c'_{ii} ($i = 1, 2, 3$) were measured by Brillouin scattering [15]. Near the phase transition into the phase IV c'_{11} and c'_{33} exhibit a small jump smeared by order-parameter fluctuations. On the other hand c'_{22} exhibits only a small continuous change of the slope. As it has been pointed out in [15], this suggests that the coefficient a_y is negligible. Consequently, there is no jump and practically no influence of fluctuations on the temperature behaviour of c'_{22} which is entirely determined by the higher-order term $h_y u_{yy}^2 (p^2 + q^2)$. As it follows from our formulae (6) the temperature dependence of c'_{ik} would be of the same type if the phase transition goes directly to the commensurate (C) phase IV or to a new IC phase. In the latter case, however, we could have a good reason why the coupling between the order parameters and u_{yy} is negligible, namely when a_y and l_y have opposite sign and $|a_y| \simeq |l_y q_1^2|$. This hypothesis could be checked by uniaxial-pressure experiments since, as it follows from the expressions (1), (2) and the coupling terms (see (3))

$$\frac{1}{2} \left\{ a_y (p^2 + q^2) + l_y \left[\left(\frac{dp}{dy} \right)^2 + \left(\frac{dq}{dy} \right)^2 \right] \right\} u_{yy},$$

an applied stress σ_{yy} will change T_1 and q_1 :

$$T_1(\sigma_{yy}) = T_1(0) - \frac{a_y s_{22}}{\alpha_0} \sigma_{yy},$$

$$q_1^2(\sigma_{yy}) = q_1^2(0) - \frac{l_y s_{22}}{2\lambda} \sigma_{yy},$$

where s_{22} denotes the elastic compliance. An elastic neutron scattering experiment for measuring the dependence of q_1 on the uniaxial pressure is under preparation.

If there were indeed a new IC phase in K_2ZnCl_4 it would be interesting to measure those quantities which should exhibit temperature anomalies near the lock-in transition T_c from the IC into the C phase IV. Depending on the symmetry of the phase IV such quantities (mechanical c_{ik} and dielectric χ_{ik} susceptibilities) are:

1) Pc11 ; c_{44} , χ_{33} ,

1) A11a ; c_{66} , χ_{11} .

All these susceptibilities correspond to variables (strain and polarisation components) the spontaneous values of which break the symmetry of the phase III. Actually the origin of anomalies is in a bilinear coupling of these variables with the phason whose frequency goes to zero at T_c [16]. The bilinear coupling in the IC phase comes from the coupling terms of the order parameters p , q with strain (3) and polarisation components P_i :

$$pq \cdot P_x; (Q^3 + Q^{*3})(p^2 - q^2) P_z.$$

One should expect that the anomaly of χ_{11} would be the strongest. It is easy to show [15] that the anomalous part of the susceptibilities is proportional to $\omega_{\text{ph}}^{-2}(2q_1)$ where the phason frequency ω_{ph} goes to zero at T_c as q_1 . It should be pointed out, however, that according to [2] the lock-in transition is of first order that could hide the anomalies.

7. Conclusions.

Our experimental results evidence that in the ferroelectric phase III of both Rb_2ZnCl_4 and K_2ZnCl_4 there are soft optic modes at the T point $\frac{1}{2}(\mathbf{b}^* + \mathbf{c}^*)$ of the Brillouin zone. This confirms the idea that the low temperature phase IV is due to softening of modes which were soft in the prototypic hexagonal phase already. We have shown that these soft modes are polarized in the $(\mathbf{b}, \mathbf{c})$ plane; in addition we confirm that in Rb_2ZnCl_4 it remains underdamped near the phase transition. In K_2ZnCl_4 , however, the situation is more complex: we have found a minimum near the T point on the soft branch in the direction $(\mu \mathbf{b}^* + \frac{1}{2} \mathbf{c}^*)$ which demonstrates the existence of a new IC phase modulated in the $\mathbf{b}$ direction prior to the phase IV. Moreover, we have detected a quasielastic component typical for K_2ZnCl_4 suggesting that an order-disorder mechanism of the ZnCl_4 groups is involved in the phase transition.

We have analyzed the symmetry of modes in the t direction $\xi(\mathbf{b}^* + \mathbf{c}^*)$ and using our neutron inelastic scattering data and available Raman, Brillouin and infrared data we have proposed the course of branches in this direction which, however, remains rather speculative. Since there is no Lifshitz invariant at the T point, the origin of the new IC phase in K_2ZnCl_4 is, from a phenomenological point of view, in the existence of the pseudo-Lifshitz invariant constructed from two doubly degenerate modes of different symmetries. We have predicted which dielectric and elastic constants should be anomalous near the lock-in phase transition and derived the formulae for elastic constants c_{ik} near the IC phase transition. We have proposed an explanation why the anomaly of c_{22} , i.e. in the direction of modulation, is weak. Experiments under uniaxial pressure are in preparation for testing this hypothesis.

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