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Metastability of ferroelectric domains over a wide temperature range in the incommensurate phase of K_2ZnCl_4

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Abstract. The commensurate (C)–incommensurate (INC)–normal (N) sequence of phase transitions in K_2ZnCl_4 has been investigated through Raman scattering (external and internal modes), x-ray diffraction and DSC experiments. A low-frequency mode, observed in the $b(ac)a$ orientation, is assigned to the pseudo-phase mode. It is anomalously active up to 50 K above the C–INC phase transition temperature ($T_L = 403$ K) though with a weak intensity. The conservation of a splitting of an internal vibrational mode is also observed up to 453 K. From x-ray diffraction the lineshape of the $(-4\ -1\ 0\ -1)$ satellite exhibits a pinning in the superstructure position which remains observable more than 100 K above T_L. This could be connected with the existence of ferroelectric domains in a wide temperature range in the INC phase. Such a hypothesis seems to be confirmed by DSC experiments.

1. Introduction

Many crystals have been found to present incommensurate (INC) phases over fairly large ranges of temperature. Among these, considerable attention has been devoted to the A_2BX_4 dielectric compounds. These compounds have an orthorhombic high-temperature phase. At lower temperatures they present different sequences of modulated phases among which an INC phase is often found. Description of this family including a mutual comparison of the symmetries and structures of its members on the basis of semimicroscopic models have been given by Hogervorst [1], by Janssen [2] and by Fabry and Pérez-Mato [3]. Other descriptions in the framework of the average space group of Landau's theory have been published by Plesko *et al* [4] and by Muralt *et al* [5]. De Wolff [6] and Janner and Janssen [7] have introduced the very useful concept of superspace groups in order to describe the symmetry of INC modulated structures in terms of space groups of more than three dimensions.

The present study is concerned with K_2ZnCl_4. In the high-temperature normal (N) phase, this crystal exhibits $Pmcn$ symmetry with four molecules per unit cell [8, 9]. At $T_I = 553$ K, it undergoes a structural transition to an INC phase characterized by a wavevector $q\delta = [\frac{1}{3} - \delta(T)]c^*$. The modulation is mainly due to rotations of the $ZnCl_4$ tetrahedra around the pseudo-hexagonal c axis and also to smaller rotations around the b direction [10]. In the commensurate (C) phase, below $T_L = 403$ K, the space group becomes $P2_1cn$ and the wavevector is locked at the C value $q\delta = \frac{1}{3}c^*$ [11]. The lock-in transition is of the first-order type and it exhibits some hysteresis correlated with the defects of crystal growth as usual for these compounds [12]. Further studies in the low-temperature range have shown new phase transitions [13, 14].

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The purpose of the present paper is to obtain a better insight into the INC phase first in K_2ZnCl_4 in the vicinity of T_L and then more generally in A_2ZnX_4 compounds from complementary studies made on Rb_2ZnCl_4. The existence of a multisoliton lattice in the low-temperature part of the INC phase is now well established [15–18]. Nearly C regions are separated by discommensurations (DCs) where the phase of the order parameter changes rapidly [19, 20]. Nucleation and annihilation of pairs of dislocations (DLs) made up of six DCs and their motions along the *c* plane play an important role in the transition process.

In the present work, the influence of DCs and defects have been studied via investigations in the N–INC–C phase transition sequences by Raman scattering (external (10–80 cm^{-1}) and stretching internal (250–350 cm^{-1}) modes), x-ray diffraction and differential scanning calorimetry (DSC) experiments on single crystals. The results are presented and discussed in the following sections.

2. Experimental procedures

All the single crystals of K_2ZnCl_4 used in our experiments were grown by the slow evaporation method from an aqueous solution of KCl and $ZnCl_2$. The single crystals grown are transparent.

For Raman scattering experiments the sample was illuminated by the light beam of an Ar^+ laser with a constant output of 100 mW at 4880 Å. The scattered light was analysed by using a Coderg T800 triple monochromator with an instrumental resolution of about 1 cm^{-1}. The output signal was counted with a photon counter (Princeton Applied Research 1109) and recorded.

DSC measurements were made using a Perkin-Elmer DSC 7 differential scanning calorimeter. The calorimeter was calibrated from indium which has a melting point of 429.15 K, i.e. in the range of temperatures studied here. The crystal was encapsulated in a metallic cell containing 45 mg. The calorimeter operated between 300 and 600 K with rates of temperature changes of $\pm(5 - 80)$ K min^{-1}.

X-ray experiments were performed on a four-circle diffractometer using Mo Kα radiation.

Raman scattering experiments and X-ray diffraction studies have been carried out up to high temperatures. These experiments were performed in a heating process with a compressed hot-airstream system.

3. Experimental results

3.1. Raman measurements

3.1.1. External modes. In a symmetrical scattering geometry $b(cc)a$ in which the amplitude mode is Raman active [21], the data show a damped phonon with a frequency varying from 29 to 25 cm^{-1} as the temperature increases from 300 to 533 K (i.e. $T_I - 20$ K). Two other modes are Raman active in the C and INC phases. One of these remains active in the N phase. Although it has a very weak intensity, its frequency could be fairly accurately defined to be 47.0 ± 0.3 cm^{-1} at 600 K.

For the antisymmetrical scattering orientation $b(ac)a$ (B_2 symmetry), a correct fit of the experimental spectra required two modes in the C phase at room temperature. Their frequencies are 19.6 ± 0.1 cm^{-1} and 47.2 ± 1.5 cm^{-1}. The latter is always poorly defined from 300 up to 600 K; so the temperature dependence of its frequency will no longer

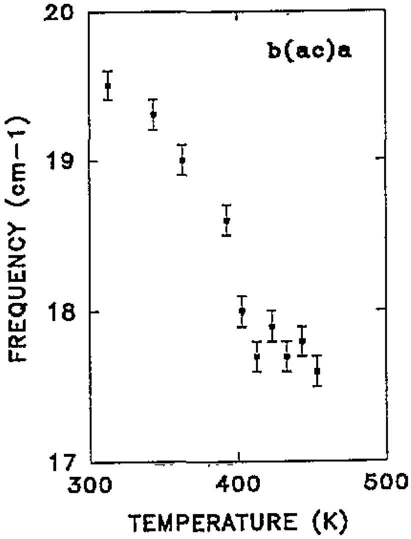

Figure 1. Temperature dependence of the phase mode frequency in K_2ZnCl_4 observed in the $b(ac)a$ scattering geometry.

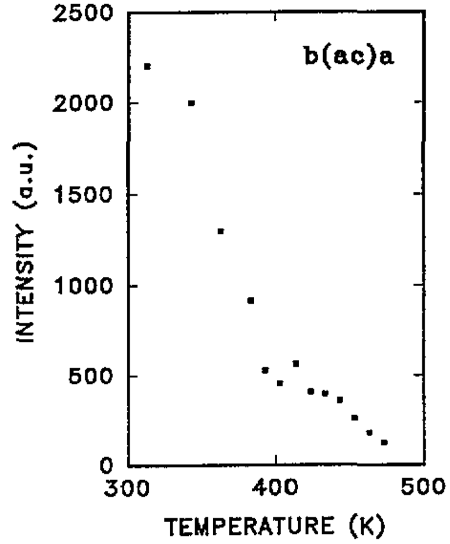

Figure 2. Integrated intensity of the phase mode as a function of temperature (a.u., arbitrary units).

be considered in the following (figure 1). The sharp phonon peak that is observed at 19.6 cm^{-1} at room temperature and that is active in an antisymmetrical configuration is attributed to the pseudo-phase mode [22, 23]. The width of this mode corresponds to the experimental resolution (1 cm^{-1}) contrary to the other phonon peaks observed in all Raman spectra, which are much broader. Its frequency shows a linear dependence upon temperature (-0.015 ± 0.001 cm^{-1} K^{-1}) below 403 K (T_L) while it becomes constant above T_L (figure 1). This pseudo-phase mode has an anomalous behaviour since it is found to be active up to 50 K above T_L with a very weak intensity (figure 2). Just above the lock-in transition, the INC phase is described in terms of domains with a C structure separated by DCs. In this range of temperatures the phase mode frequency is different from zero because of the associated localized states and because of the presence of ferroelectric domains [24]. Far above T_L, the ferroelectric domains can be observed via the behaviour of the pseudo-phase mode.

Table 1. The correlation between the free-ion tetrahedral symmetry T_d and the symmetry of the ferroelectric phase (C phase) C_{2v} through the symmetry site C_1.

T_d	C_1	C_{2v}
(ν_1) A_1		$12A_1$
	$3\times 4A$	$12A_2$
(ν_3) F_2		$12B_1$
		$12B_2$

3.1.2. Internal modes. The study of the stretching modes of the $ZnCl_4$ tetrahedra was performed in the $b(cc)a$ configuration from room temperature up to 600 K. In the C phase, three modes at 281, 295 and 300 cm^{-1} are observed from a numerical fitting using damped

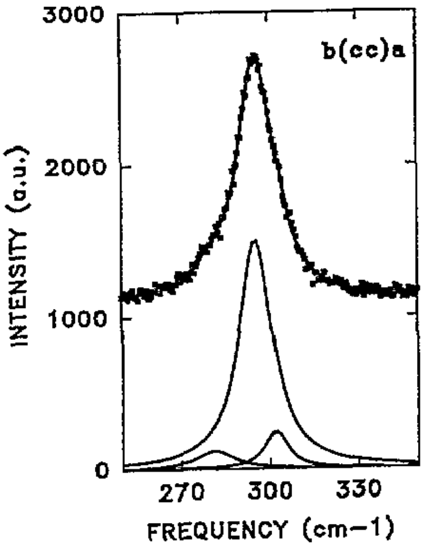

Figure 3. Raman spectra of the stretching modes of K_2ZnCl_4 in a symmetrical scattering geometry in the C phase (a.u., arbitrary units): ■, experimental data; ——, overall calculated spectrum and deconvoluted individual modes.

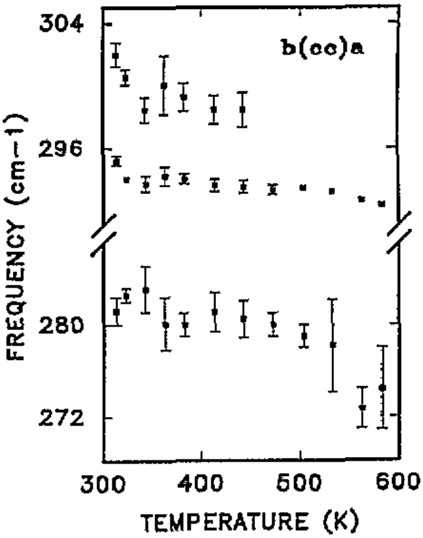

Figure 4. Temperature dependence of the stretching-mode frequencies of K_2ZnCl_4 observed in the $b(cc)a$ scattering geometry.

Table 2. Slopes of the temperature dependences of the symmetrical breathing ν_1 mode in the C and INC phases.

Phase	Frequency (cm^{-1})	$\partial\nu/\partial T$ (cm^{-1} K^{-1})
C	293.9 ± 0.1	-0.008 ± 0.001
INC	293.0 ± 0.1	-0.015 ± 0.001

Table 3. The correlation between the free-ion tetrahedral symmetry $\mathcal{T}_d$ and the symmetry of the normal phase $\mathcal{D}_{2h}$ through the symmetry site C_s.

$\mathcal{T}_d$	C_s	$\mathcal{D}_{2h}$
(ν_1) A_1		$6A_g$: $\nu_1\nu_2\nu_3\nu_3'\nu_4\nu_4'$
	6A′	$6B_{3g}$: $\nu_1\nu_2\nu_3\nu_3'\nu_4\nu_4'$
(ν_2) E		
	3A″	$3B_{1g}$: $\nu_2'\nu_3''\nu_4''$
(ν_3, ν_4) $2F_2$		$3B_{2g}$: $\nu_2'\nu_3''\nu_4''$

oscillators (figure 3) whereas 12 modes are expected from the correlation table for internal stretching modes (table 1). The missing lines could be either of too low intensity or they could be quasi-degenerate with the observed lines. For the 295 cm^{-1} mode a slope breaking (table 2) as well as a splitting (figure 4) are observed in the surstructure phase. This splitting remains up to 50 K above T_L instead of disappearing just at T_L as in all other configurations studied [13]. The change-over from two modes to a single mode can be interpreted by a different description of the C and INC phases. In the C phase, the modulation is characterized by only three tetrahedron configurations while in the INC phase it is described by a continuum of tetrahedron orientations. The fact that the conservation of this splitting at $T_L + 50$ K is found only in this configuration could indicate that the ferroelectric domains have a preferential orientation. Previous electron microscopy studies have revealed that the motion of the DLs are usually parallel to the c plane and those perpendicular to the c plane are scarce [16]. In the N phase, above T_I, two modes remain active: an intense fairly broad line (HWHM, about 8.0 ± 0.2 cm^{-1}) at about 292 cm^{-1} and a weak and broader line (HWHM, about 17.0 ± 3.0 cm^{-1}) at about 275 cm^{-1} since three A_g modes (ν_1, ν_3 and ν_3') are expected in this configuration. The most intense line corresponds to the symmetrical breathing ν_1 mode and the other is therefore assigned to one of the two ν_3 modes (table 3). The third is either too weak or overlapped.

As a conclusion it can be said that Raman scattering experiments on external and internal modes exhibit the presence of ferroelectric domains far above T_L through observation of the phase mode plus a split ν_1 band until 453 K.

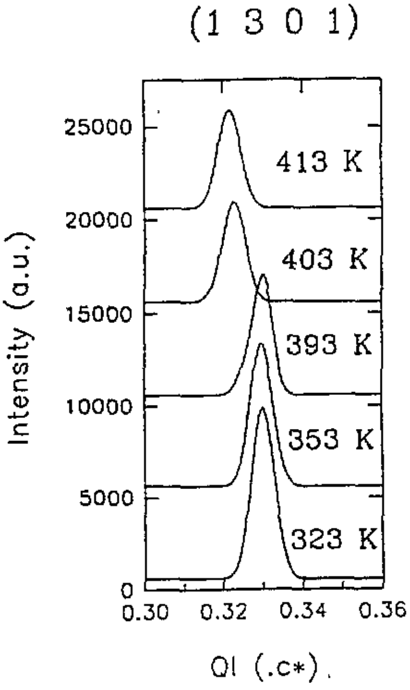

Figure 5. Q-scans of the (1 3 0 1) satellite line along c^* in the heating run for K_2ZnCl_4 (a.u., arbitrary units).

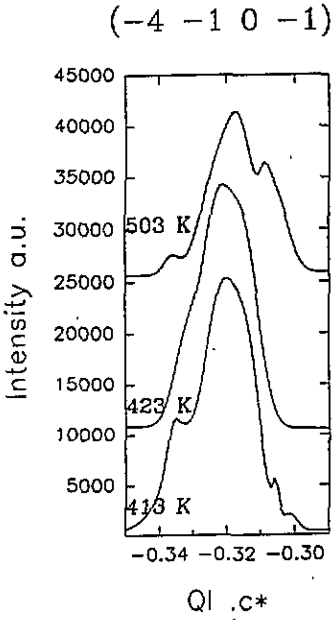

Figure 6. Q-scans of the $(-4 - 1\,0 - 1)$ satellite line along c^* in the heating run for K_2ZnCl_4 (a.u., arbitrary units).

3.2. Diffraction study

In this section the behaviour of two selected satellite lineshapes along c^* versus temperature is shown in figures 5 and 6. The $(h\,k\,l\,m)$ reflections correspond to satellites located in $Q = ha^* + kb^* + [l + m(\frac{1}{3} - \delta)]c^*$, δ being the misfit parameter.

The behaviour of the (1 3 0 1) satellite confirms that $T_L = 403$ K as expected (figure 5). This reflection is characterized by a low intensity and a noticeable sharpness. The low intensity of this satellite reflection is in agreement with the structural determination of

A_2BX_4 compounds because the atomic modulated displacements are very weak in the *b* direction. In this case the sharpness of this reflection reveals a long-range order in the direction corresponding to small modulated distortions.

From figure 6 the lineshape of the (−4 − 1 0 − 1) satellite exhibits a pinning in the superstructure position which is still observed more than 100 K above T_L. This observation confirms the existence of ferroelectric domains in this temperature range as suggested by Raman scattering studies.

The lack of long-range order corresponding to the anomalous broadening of a coexisting satellite reflection is certainly due to randomly spaced solitons. This regime can be interpreted as made up of metastable states extending over a wide temperature range in K_2ZnCl_4. It can be regarded as a multisoliton regime similar to that observed in Rb_2ZnCl_4 single crystals of high crystalline quality but only a few kelvins below T_L. It is noticeable that this satellite is more intense than the (1 3 0 1) satellite in agreement with the fact that the most important modulated displacements are observed along the *a* direction.

From this study of both satellites it can be assumed that metastable states induced by pinning of the superstructure reflections will be observed along directions which exhibit strong magnitude of the atomic amplitude modulation.

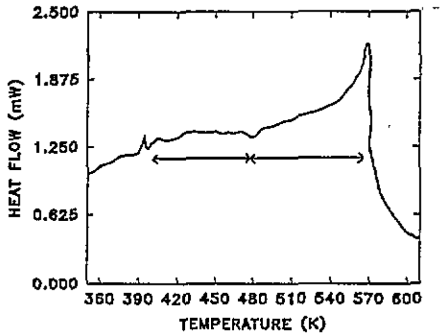

Figure 7. Thermogram of a K_2ZnCl_4 single crystal in a heating run. The scanning rate is 20 K min^{-1}.

3.3. Differential scanning calorimetry experiments

From heating runs in the INC phase the DSC experiments performed on single crystals seem to reveal the presence of those kinds of domain described in section 3.1. Accordingly the thermogram between 403 and 600 K can be shared in two regions (figure 7).

The first region (403–453 K), just above T_L, is characterized by an undulating baseline which could correspond to the transformation of the ferroelectric domains. One can assume that the temperature spread of the transformation of these domains is strongly dependent on the intensity of the corresponding superstructure lines. As a consequence these transformations are achieved at different temperatures above T_L, which causes the undulating shape of the baseline.

The second region (453–553 K), in which the thermogram appears to be much less spread than in the first, certainly corresponds to structural modifications resulting from the transition between the INC modulated structure and the N high-temperature phase.

However, in the cooling runs (figure 8), only one region is observed between T_I and T_L. On the other hand, when the scanning rate is increased, the very-low-energy peak corresponding to T_L is no longer observed (figure 8). These thermograms suggest that the INC phase can be interpreted as a structural modification which takes place from T_I and is

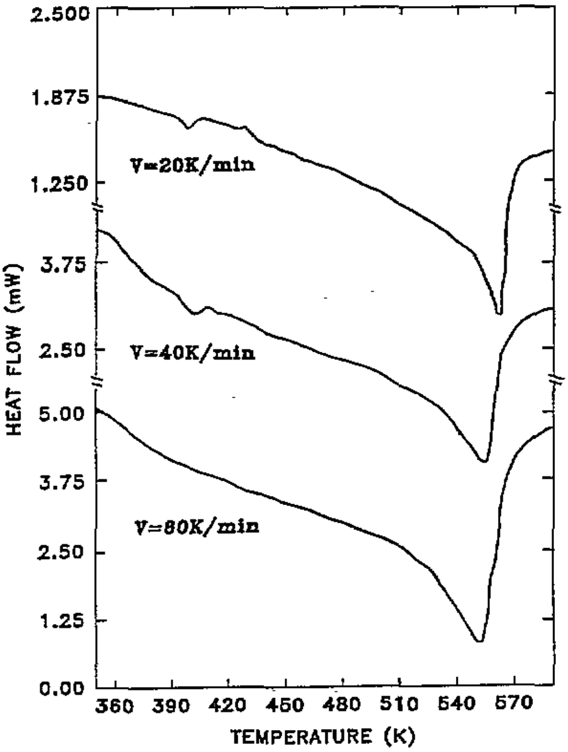

Figure 8. Evolution of thermograms, for K_2ZnCl_4, recorded in the cooling run for different scanning rates.

achieved at T_L for low scanning rates. Consequently, metastable states assigned, in heating runs, to ferroelectric domains above T_L are no longer observed in cooling runs. In the case of high scanning rates the structural transformation of the high-temperature phase is not complete either because the motion of the DLs is not achieved or their nucleation is prevented. In these cases, the experiments indicate the scale of time of the phenomenon which drives the lock-in transition.

4. Discussion

The most striking feature found in this study is the observation of certain superstructure lines above T_L. This phenomenon can result from interaction between modulation and crystal growth defects. A single crystal of K_2ZnCl_4 can be made of several growth sectors which undergo different phase transition sequences. The behaviour of the modulation versus temperature in a sector is certainly connected with the intensity of the superstructure lines and the crystal growth rate along the corresponding direction. From these considerations, one can assume that each sample is characterized by a special configuration between modulation and defects at room temperature. Such a hypothesis could explain the fact that the ferroelectric domains are observed at a lower temperature in Raman scattering studies than in x-ray experiments.

A previous x-ray study on Rb_2ZnCl_4 has shown that modulation–defect interaction causes pinning of the modulation to the defects and is certainly responsible for the hysteresis phenomenon around T_L. In extreme cases the lock-in transition was not observed [25]. As a consequence, in Rb_2ZnCl_4, defects play an important role in the INC phase.

To understand the influence of defects on the modulated phase transitions of A_2ZnX_4, we have to take into account the characteristics of the modulation at the growth temperature of the compounds. In Rb_2ZnCl_4 the defects lock the evolution of the modulation in the INC phase because of low amplitude and stability of modulation at the growth temperature. However, at room temperature, several configurations between defects and modulation coexist in K_2ZnCl_4 samples. This coexistence is observed via different kinds of superstructure lineshape along **c***. It could be explained by two complementary phenomena: the different growth rates along particular directions and the magnitude of modulated distortions along these directions. By increasing the temperature, the configuration between modulation and defects changes to reach a more stable equilibrium configuration. By decreasing the temperature, the coexistence of these configurations could cause the kinetic transformation observed in Raman scattering and DSC experiments [13].

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