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Successive Transitions in $\{N(CH_3)_4\}_2ZnCl_4$ and $\{N(CH_3)_4\}_2CoCl_4$

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Incommensurate-commensurate transitions and low temperature phases of ferroelectric $\{N(CH_3)_4\}_2ZnCl_4$ and $-CoCl_4$ were investigated by X-ray scattering. As the temperature decreases, the incommensurate phase transforms to the ferroelectric phase, in which the cell-dimension is fivefold along the *c*-axis. In the Zn-salt, the ferroelastic phase is realized below the ferroelectric phase. In the Co-salt, another incommensurate phase exists between the ferroelectric and ferroelastic phases. In these materials, the successive transitions are related to modes on the Λ_4 branch, while the incommensurate-commensurate transition in K_2SeO_4 is related to the Λ_2 branch. A model free energy that explains the successive transitions is proposed.

Recently ferroelectricity, incommensurate phases, and successive transitions were found in $\{N(CH_3)_4\}_2ZnCl_4$ and $\{N(CH_3)_4\}_2CoCl_4$ (abbreviated hereafter TMATC-Zn and -Co, respectively) by Sawada *et al.*[1] The pressure-temperature phase diagram of these materials were determined by Shimizu *et al.*[2] Ultrasound propagation in TMATC-Zn has also been investigated.[3] At room temperature (the phase I), TMATC-Zn and -Co have been reported to be isomorphous to each other[4] and belong to the space group *Pmcn*.*

By means of X-ray scattering, we have determined the space groups of the commensurate phases of TMATC-Zn.[5] We have also reported preliminarily that the incommensurate phase of TMATC-Zn transforms to the commensurate ferroelectric phase in which the cell-dimension along the *c*-axis is not three- but fivefold.[6] The former is the case of K_2SeO_4,[7] and the latter is also realized in TMATC-Co.[8]

In Table I, phases, space groups and the wave numbers of TMATC-Zn and -Co at 1 atm are summerized. The space groups of the commensurate phases are induced from the space group *Pmcn* of the phase I and are related to the Λ_4 representation.[5] The phase II′ of TMATC-Co also takes the incommensurate structure characterized by the wave number $k_z=\frac{2}{5}-\delta$.[8]

In this report, we will present the results of the detailed X-ray diffraction study on TMATC-Zn and -Co and explain the successive transitions in the frame of the Landau theory.

Table I. Phases, space groups and wave numbers of the satellite reflections of TMATC-Zn and -Co at 1 atm.

	TMATC-Zn	TMATC-Co	
I	*Pmcn*		I
	23.6°C	20.6°C	
II	Incommensurate	$k_z=\frac{2}{5}+\delta$	II
	7.0	8.0	
III	$P2_1cn$ Ferroelectric	$k_z=2/5$	III
		6.3	
	2.3	Inc. $k_z=\frac{2}{5}-\delta$	II′
		4.5	
IV	$P112_1/n$ Ferroelastic	$k_z=1/3$	IV
	−105	(−81)	
V	$P12_1/c1$		V
	−118	(−151)	
VI	$P2_12_12_1$	$k_z=1/3$	VI

The satellite reflections $(h\ k\ l\pm\zeta)$ with $\zeta=\frac{2}{5}+\delta$ were recognized at 10°C by Weissenberg photographs. Intense satellite reflections exist at $(2\ 0\ \zeta)$ and $(2\ 0\ 2\text{-}\zeta)$. The majority of scans were made along the c^*-direction between (2 0 0) and (2 0 2) with a two-circle diffractometer.

From the distribution of the superstructure reflections and the extinction rules observed in Weissenberg photographs, we determined the space groups of low temperature phases as shown in Table I. Here we mention ferroelasticity of the monoclinic phase IV of TMATC-Zn. The monoclinic domains were observed under a polarizing microscope in the

* The crystallographic axes are taken as ref. 1 ($b\simeq\sqrt{3}a$, c: pseudo-hexagonal axis).

samples of the c-plate of TMATC-Zn. The difference 2ϕ between the extinction position of two neighbouring domains is about 8° at 0°C and increases monotonically with decreasing the temperature. Two kinds of domain boundaries (bc-plane and ac-plane) were observed. By applying external stresses the area of domains can be changed very easily; this implies that the phase is ferroelastic.

Now we describe the X-ray scattering experiments. The temperature dependence of the intensity of the primary satellite reflection $(2\,0\,\zeta)$ and the modulation wave number $k_z=\zeta$ are shown in Fig. 1. The integrated intensity $I(2\,0\,\zeta)$ follows the relation $I\propto(T_c-T)^{2\beta}$ with $2\beta=0.74\pm0.03$ (TMATC-Zn) and 0.76 ± 0.03 (TMATC-Co). The change of the intensity is clear at the III-IV or II′-IV transition. The modulation wave number ζ decreases monotonically with decreasing the temperature. The simultaneous observation of the X-ray scattering and the D-E hysteresis loop with samples of platelet form revealed that ζ stays at 2/5 in the ferroelectric phase III. In TMATC-Co, ζ changes almost continuously from phase II to III and to II′. In the ferroelastic phase IV, ζ stays at 1/3. Shimizu *et al.*[2] have found that the ferroelectric phase III becomes narrow and finally merges in the incommensurate phase with increasing the pressure. In our X-ray study, the only difference between the phase II and II′ exists in the modulation wave number. It seems that the incommensurate phase locks into the ferroelastic phase IV and that the ferroelectric phase III is realized in this cource. The incommensurate-ferroelastic (commensurate) phase transition has been found in $\{N(CH_3)_4\}_2CuCl_4$ recently,[9] but this material has different transition sequences from those of TMATC-Zn and -Co.

Figure 2 shows the temperature dependences of the satellite reflections, the monoclinic angle γ and the extinction angle 2ϕ in TMATC-Zn. In the ferroelastic phase IV, the intensity $I(2\,0\,\frac{2}{3})$ and γ increase almost linearly with decreasing the temperature. On the other hand, the intensity of the primary satellite $I(2\,0\,\frac{1}{3})$ and 2ϕ increase as $\sim(5-T)^{0.4\pm0.1}$. This fact suggests that the order parameter is a mode with $k_z=1/3$ on the Λ_4 branch and that the strain x_6 is induced by the frozening of the order parameter. Next we consider a model free energy which explains the successive transitions of TMATC-Zn and -Co.

We consider the following free energy:[10]

$$
\begin{aligned}
F=\sum_k \Bigg\{ & \sum_{m=1}^{5} \frac{1}{2m}\alpha_{2m}|Q_k|^{2m}+\frac{1}{2}\alpha_2'|R_k|^2 \\
&+\frac{1}{2}\alpha_2''|P_k|^2+\frac{1}{2}\beta_2(Q_k^3R_{3k-1}^*+c.c.) \\
&+\frac{1}{2}\beta_3(Q_k^2R_{3k-1}P_{5k-2}^*+c.c.) \\
&+\beta_8|Q_k|^2(Q_{1/3}^6+Q_{1/3}^{*6})\Bigg\} \\
&+\frac{1}{2}c_6x_6^2+\frac{1}{2}c_5x_5^2+\frac{1}{2}dS^2 \\
&+\beta_4(Q_{1/3}^3+Q_{1/3}^{*3})x_6-i\beta_5(Q_0-Q_0^*)x_5 \\
&-i\beta_6(Q_{1/3}^3-Q_{1/3}^{*3})S,
\end{aligned}
$$

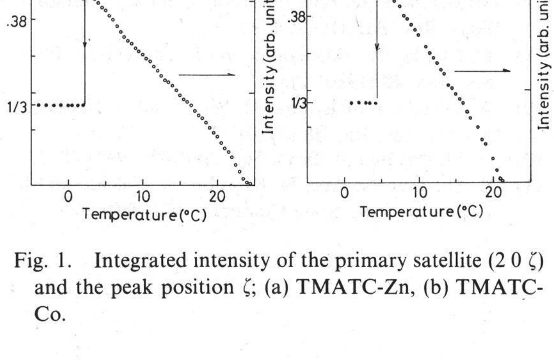

Fig. 1. Integrated intensity of the primary satellite $(2\,0\,\zeta)$ and the peak position ζ; (a) TMATC-Zn, (b) TMATC-Co.

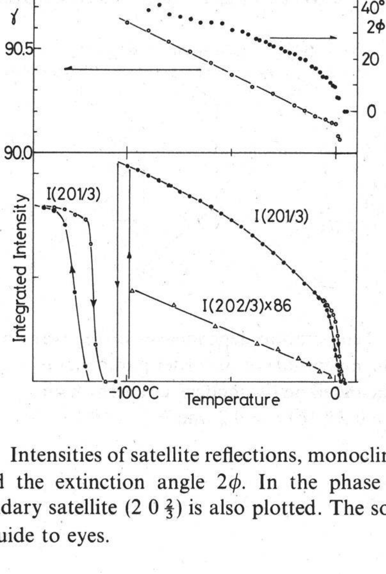

Fig. 2. Intensities of satellite reflections, monoclinic angle γ and the extinction angle 2ϕ. In the phase IV, the secondary satellite $(2\,0\,\frac{2}{3})$ is also plotted. The solid lines are guide to eyes.

where a primary order parameter Q_k belongs to the Λ_4 representation of $Pmcn$. A secondary parameter R_k belongs to the Λ_2 representation and the polarization P, strains x_6 and x_5 and a quantity S belong to the representation Γ_4, Γ_5, Γ_7 and Γ_2, respectively. We assume that $\alpha_2 = \alpha_0(T-T_0)+\gamma_0(|k|-k_0)^2$, $\alpha_2'=c+\gamma_r k^2$ and $\alpha_2''=\frac{1}{\chi}+\gamma_p k^2$. The β_2 term represents the lock-in mechanism to the ferroelastic phase IV and the β_3 term to the ferroelectric phase III. In the phase V, the strain x_5 is nonvanishing and the quantity S is nonzero in the phase VI.

Let's put the coefficients as followings: $\alpha_4=1$, $\alpha_6=2$, $\alpha_8=1.5$, $\alpha_{10}=0.2$, $\beta_2=\beta_4=\beta_6=1/3$, $\beta_3=1$, $\beta_5=1/2$, $\beta_8=0.3$, $\gamma_0=\gamma_p=\gamma_r=2$, $k_0=0.42$, $\chi=0.2$, $d=0.8$, $c_5=3.7$, $c_6=0.2$, and $c=0.2$. Then the transition temperature are $\hat{T}_{\text{I-II}}=0$, $\hat{T}_{\text{II-III}}=-0.143$, $\hat{T}_{\text{III-IV}}=-0.170$, $\hat{T}_{\text{IV-V}}=-1.119$, and $\hat{T}_{\text{V-VI}}=-1.246$, where $\hat{T}=\alpha_0(T-T_0)$. In Fig. 3, the temperature dependence of the primary order parameter $q=|Q_k|$ and the wave number k is shown for three different value of c. When $c=0.25$, the incommensurate phase transforms to the ferroelastic phase directly and the ferroelectric phase is not realized. When $c=0.2$, the phases II, III and IV appear successively (TMATC-Zn type). If $c=0.15$, the incommensurate phase appears again below the ferroelectric phase and then the ferroelastic phase appears (TMATC-Co type).

Figure 4 shows the transition temperature when the additional term $\frac{1}{630}\beta_{10}(Q_{2/5}{}^{10}+Q_{2/5}{}^{*10})$ is added to the free enegy F with $c=0.18$ and other coefficients given above. If $\beta_{10}=0$, the TMATC-Zn type transitions take place. If $\beta_{10}=200$, for example, the successive transitions II-III-II-IV take place, and for $\beta_{10}>220$, the ferroelectric phase III disappears.

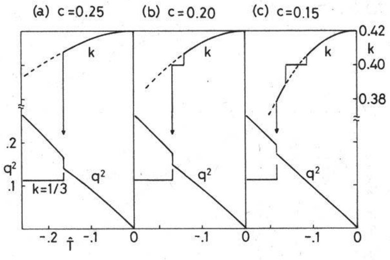

Fig. 3. Temperature dependences of the wave number k and the magnitude of the order parameter $q=|Q_k|$. They are calculated on the model free energy with $c_6=0.2$ and (a) $c=0.25$, (b) $c=0.2$ and (c) $c=0.15$.

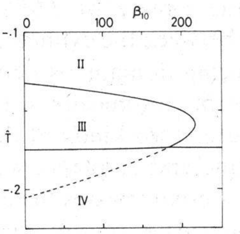

Fig. 4. Transition temperature when the β_{10} term is added. With increasing β_{10}, the ferroelectric phase III become narrower and finally merges into the incommensurate phase II.

It has been found recently that the phases of four salts, $\{N(CH_3)_4\}_2MCl_4$ (M:Zn, Co, Fe and Mn), can be classified by arranging them in a single pressure-temperature phase diagram.[11] The model free energy can explain the diagram qualitatively if the coefficients of the free energy depend on the pressure in a proper manner.

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