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Incommensurate-Ferroelastic (Commensurate) Phase Transition in $\{N(CH_3)_4\}_2CuCl_4$

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Incommensurate (IC)-monoclinic (ferroelastic) phase transition in $\{N(CH_3)_4\}_2CuCl_4$ crystal has been studied by means of dielectric and ultrasonic methods. The elastic constant c_{55} has been found to show a remarkable softening in the IC phase towards the IC-monoclinic transition temperature T_2. The result is discussed on the basis of a thermodynamic theory, and the distinctions between the IC-ferroelastic transition and the IC-ferroelectric transition are pointed out.

§1. Introduction

Much attention has been paid to various crystals having the β-K_2SO_4 structure from the view point of the incommensurate (IC)-commensurate (C) phase transition. Very recently it was found by our group[1)] and by Gesi and Iizumi[2)] that $\{N(CH_3)_4\}_2CuCl_4$ crystal undergoes the successive phase transitions from the normal phase ($D_{2h}^{16}-Pmcn$, $Z=4$) to the IC phase at $T_1=24$°C, and then at $T_2=18$°C to the monoclinic commensurate phase ($C_{2h}^5-P12_1/c1$, $Z=12$) with the lattice parameter tripled along the c_H-axis compared with that of the normal phase. The C phase in $\{N(CH_3)_4\}_2CuCl_4$ is shown to be ferroelastic.[1)] This IC-ferroelastic transition makes a contrast with the wellknown IC-ferroelectric transition. On further cooling $\{N(CH_3)_4\}_2CuCl_4$ crystal undergoes the third phase transition at $T_3=-10$°C and changes into another monoclinic phase ($C_{2h}^5-P112_1/m$, $Z=4$), which has no superlattice structure (Table I).

The purpose of the present paper is to report the detailed studies of dielectric and ultrasonic properties in $\{N(CH_3)_4\}_2CuCl_4$ crystal with special attention to the normal-IC transition at T_1 and the IC-C transition at T_2.

§2. Experimental Results

Single crystals of $\{N(CH_3)_4\}_2CuCl_4$ were grown by the slow evaporation at 30°C from aqueous solution which contained stoichiometric molar ratio of $N(CH_3)_4Cl$ and $CuCl_2 \cdot 2H_2O$. Grown crystals are transparent, orange and of hexagonal prism in form.

The dielectric constant was measured at 1 KHz by using a high-precision capacitance bridge. Sample plates were polished with ethanol, and carbon paste (Dotite XC-12) was painted on their faces as electrodes. The dielectric constant ε_{aH} along the a_H axis shows slight but clear changes of slope both at the normal-IC transition temperature T_1 and at the IC-C (ferroelastic) transition temperature T_2 (Fig. 1). At T_3, the dielectric constant ε_{aH} decreases discontinuously.

The measurement of sound velocity was made by the pulse-echo method. PZT transducers ($f=3.3$ MHz) were bonded to speci-

Table I. Phase sequence in $\{N(CH_3)_4\}_2CuCl_4$

	$T_3=-10$		$T_2=18$		$T_1=24$ (°C)	
IV		III		II		I
Ferroelastic $C_{2h}^5-P112_1/n$ ($Z=4$)		Ferroelastic $C_{2h}^5-P12_1/c1$ ($Z=12$) Commensurate		Paraelastic $c\approx 3c_H$ Incommensurate		Paraelastic $D_{2h}^{16}-Pmcn$ ($Z=4$) Prototype

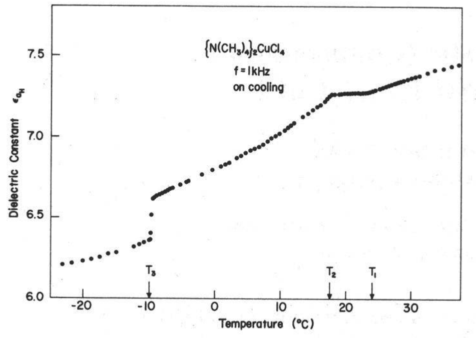

Fig. 1. Temperature dependence of the dielectric constant ε_{aH} in $\{N(CH_3)_4\}_2CuCl_4$.

mens with resin. In order to obtain the shear elastic constant c_{55}, a transverse ultrasonic wave propagating along the a_H axis with its polarization along the c_H axis was studied. The temperature dependence of the elastic constant c_{55} of $\{N(CH_3)_4\}_2CuCl_4$ is shown in Fig. 2, where the value of crystal density $\rho=1.38$ g/cm^3 is used. The elastic constant c_{55} shows a clear change in slope at T_1, and decreases rapidly and then tends to vanish towards the IC-C (monoclinic) transition temperature T_2 in the IC phase. In the C phase between T_2 and T_3 no echos could be observed, probably due to the appearance of ferroelastic domains. In the phase IV below T_3 ultrasonic echos were again observed.

§3. Discussions

As is shown in the above, one of the characteristic features of the IC-ferroelastic phase transition in $\{N(CH_3)_4\}_2CuCl_4$ is that the elastic constant c_{55} tends to vanish towards the IC-ferroelastic transition temperature. This fact can be understood on the basis of the thermodynamic theory as follows.

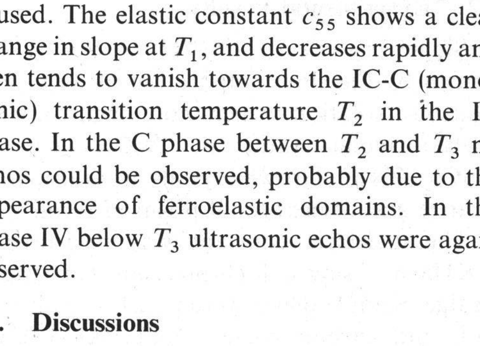

Fig. 2. Temperature dependence of the elastic constant c_{55} in $\{N(CH_3)_4\}_2CuCl_4$.

Let us assume that the free energy in the IC phase can be written as

$$\begin{aligned}F_{\rm IC}=&\omega_k^2 Q_k Q_k^* +\frac{1}{4}\beta(Q_kQ_k^*)^2+\frac{1}{36}\gamma(Q_kQ_k^*)^3\\&+b_K P_K P_K^* +\frac{1}{6}f_1(Q_k^3 P_K+Q_k^{*3}P_K^*)\\&+c_K x_K x_K^* +\frac{1}{6}g_1(Q_k^3 x_K-Q_k^{*3}x_K^*)\\&+\frac{1}{2}b_0 P_0^2+\frac{1}{2}f_2 Q_k Q_k^* P_0^2\\&+\frac{1}{2}c_0 x_0^2+\frac{1}{2}g_2 Q_k Q_k^* x_0^2,\end{aligned}\qquad(3)$$

where Q_k is the primary order parameter belonging to the Σ_2 irreducible representation, and the polarization wave P_K and strain wave x_K with the wave vector $K=3(k_c-k)$ are included as the secondary order parameters. P_0 is the homogeneous polarization along the a_H axis, and x_0 is the homogeneous strain corresponding to shear strain x_5.

From eq. (3) we can expect that at the normal-IC transition temperature T_1 the dielectric constant ε_{aH} and the elastic constant c_{55} should show kinks as expressed by

$$\begin{aligned}\Delta\varepsilon_{aH}&\propto f_2<Q_{k_i}>^2,\\ \Delta c_{55}&\propto g_2<Q_{k_i}>^2,\end{aligned}\qquad(4)$$

where k_i is the wave vector of the frozen-in mode. This is in agreement with the experimental results (Figs. 1 and 2).

When the temperature is slightly lowered from T_1, we can expect by following the procedures adopted by Dvorak and Petzelt,[4] that the elastic constant $c_{55}(T)$ should be written in the harmonic approximation as

$$c_{55}(T)=c_0-\frac{g_1^2}{4}<Q_{k_i}>^4\left(\frac{1}{\Omega_{\rm p}^2(K_{\rm i})}+\frac{1}{\Omega_{\rm A}^2(K_{\rm i})}\right),\qquad(5)$$

where $\Omega_{\rm p}^2(K_{\rm i})$ and $\Omega_{\rm A}^2(K_{\rm i})$ are the frequencies of the phase mode and amplitude mode with the wave vector $K_{\rm i}=3(k_c-k_{\rm i})$, respectively. It is seen from eq. (5) that the elastic constant $c_{55}(T)$ should decrease, as the phason frequency $\Omega_{\rm p}^2(K_{\rm i})$ tends to decrease as T_2 is approached. Thus the elastic softening associated with the IC-ferroelastic transition can in this approximation be understood as a result of the coupling of the elastic strain x_0 mainly with the phason mode with the wave vector K_i.

Near the IC-ferroelastic transition point T_2 the crystal is considered to become a domain-like structure having both positive and negative strain regions which are separated by so-called discommensuration. It can be expected that the elastic constant in such state may be small, since the change of the domain width takes place easily under external stress near T_2.

In summary, we have presented in this paper the evidence of elastic softening associated with the IC-ferroelastic transition, corresponding to dielectric softening in the case of the IC-ferroelectric transition.

References

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