ESR and Dielectric Studies of the Incommensurate Commensurate Phase Transition in $\{N(CH_3)_4\}_2ZnCl_4$

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The incommensurate phase in $\{N(CH_3)_4\}_2ZnCl_4$ crystal was studied by ESR and Dielectric measurements.

Two damaged centers $N(CH_3)_3^+$ and $ZnCl_3^-$ were produced in γ-irradiated samples at room temperature. Ferrielectric loops are also examined near IC-C phase transition temperature.

Introduction

In the point of incommensurate-commensurate (IC-C) phase transitions, many investigators have paid attentions to $(NH_4)_2SO_4$ type ferroelectrics, because of the structural simplicity of the crystal. Successive phase transitions and ferroelectrity in tetramethylammonium tetrachlorozincate $\{N(CH_3)_4\}_2ZnCl_4$ have been reported by S. Sawada et al.,(1) which has very similar chemical properties to $(NH_4)_2SO_4$. The crystal $\{N(CH_3)_4\}_2ZnCl_4$; $[(TMA)_2ZnCl_4]$ is regarded as the menber of Rb_2ZnCl_4 group.(2)

At room temperature, $(TMA)_2ZnCl_4$ belongs to the space group D_{2h}^{16}-Pmcn, in which $a=8.946\pm0.007$, $b=15.515\pm0.012$, $c=12.268\pm0.007$A and $Z=4$.(3) On cooling this crystal shows successive phase transitions from I to VI phase. Phase II is known as incommensurate phase which has a wave number of $q_c=(1-\delta)c^*/3$, where c^* is a reciprocal vector.(3)(4) The dielectric constant ε_a shows a jump and a maximum at 4.4 and 8.0°C on heating respectively. The dielectric constants have different values between on heating and cooling pass. Phase III is regarded as ferroelectric. Ferroelectric 50Hz hysteresis loop in the temperature range of phase III along a axis was observed by S. Sawada.(1) However, he suggested that the phase III shoud be ferrielectric since the observed hysteresis loops are ferrielectric ones just below the transition temperature.(5)

In our earlier ESR study of γ-irradiated $(NH_4)_2SO_4$ crystals we analysed the phase transition machanism of the crystal by the damaged centers.16) For the investigations of the phase transitions by ESR measurements, the doping method of the transition metals to the sample is very powerful, then we planed to study the ESR spectra by the method. However, in this paper, we report the ESR spectra of the damaged conters of γ-irradiated samples. We will report the ESR results of Mn^{2+} and Cr^{3+} doping of $(TMA)_2ZnCl_4$ at another place.

For study of the incommensurate phase of the crystal, NMR investigations of Rb_2ZnCl_4 have been done in two groups.7,8) They showed the broadening of the resonance lines at the phase correponding to the incommensurate phase.

In this paper we show the results of the dielectric and ESR lines of the crystal at the incommensurate phase.

Incommensurate phase transition

Structural phase transition in incommensurate (INC) phases are of growing interest. General features of INC phases have been recently described with the Landau theory by Levanyuk and Sanikov.9) The phase transition from the highly symmetric phase into the INC phase is continuous, and at lower temperature the modulation of the wave vector is of domain structure.

In the Landau theory of the second order phase transitions the Lifshitz condition is one of the most important conditions, when the lifshitz invariant of the form $r\left(\frac{\partial s}{\partial z}\right)-s\left(\frac{\partial r}{\partial z}\right)$ can be constructed from the basis functions r and s of irredusible representation, where z represents a vector component. Ishibashi and Dvořák showed the numerical solutions of the incommensurate phase under the existence of the Lifshitz invariant.[10] They took the following thermodynamic potential

$$f(x)=\frac{\alpha}{2}(p^2+q^2)+\frac{\beta}{4}(p^4+q^4)+\frac{\gamma}{2}p^2q^2 +\delta\left(p\frac{dq}{dx}-q\frac{dp}{dx}\right)+\frac{k}{2}\left[\left(\frac{dp}{dx}\right)^2 +\left(\frac{dq}{dx}\right)^2, \qquad (1)$$

where α is assumed to be $\alpha=\alpha_0(T-T_0)$, and p, q are transition parameters belonging to a two-dimensional representation, which is applicable to the phase transitions of $(NH_4)_2BeF_4$. The Euler equations are numerically solved to minimize the thermodynamic potential

$$F=\int_{-L}^{L} f(x)\,dx, \qquad (2)$$

where Euler equation of the general function of $f(x)$ is given by[11]

$$\frac{\partial f}{\partial y}-\frac{d}{dx}\,\frac{\partial f}{\partial y_x}. \qquad (3)$$

The transition temperature from highsymmetric phase (prototypic phase; $p=q=0$) to the incommensurate phase is given as

$$T_1=T_0+\frac{\delta^2}{\alpha_0\kappa}. \qquad (4)$$

The transition parameters p and q are sinusoidal function of x as

$$p=\rho\sin\frac{|\delta|}{\kappa}x, \quad q=\rho\cos\frac{|\delta|}{\kappa}x, \qquad (5)$$

and the potential is

$$F_{INC}=-2L\frac{1}{3\beta+\gamma}\left(\alpha-\frac{\delta^2}{\kappa}\right)^2. \qquad (6)$$

The wavelength of the phaes modulation $k=\frac{|\delta|}{\kappa}$ is not a simple multiple of the lattice period of the prototypic phase, because numerical values of δ and κ have nothing to do with the lattice period. It is just *an Incommensurate* phase.

Experimental

Single crystals were grown by slow evaporation from aqueous solution of $\{N(CH_3)_4\}_2ZnCl_4$, which were synthesized by the chemical reaction of

$$2\{N(CH_3)_4\}Cl+ZnCl_2\rightarrow\{N(CH_3)_4\}_2ZnCl_4.$$

In this reactions, its *pH* was adjusted by adding various amount of H_2SO_4 to aqueous solution, and we got very transparent solutions.

Irradiation were made by ^{60}Co γ-rays about 4×10^5 r at RT. ESR measurements were made by X-band spectrometer with a variable temperature controller between liquid nitrgoen and RT. The g-and A-values of the center were determined by using the DPPH powder and Mn^{2+} in ZnO.

Dielectric constants with DC biasing fields were measured by a capacitance bridge (YHP 4270A) at various frequencies. The sample capacitances were plotted automatically on X-Y recorder.

Pyroelectric charge and current are also measured by electrometer (Keithley 610C).

D-E hysteresis loops at 60Hz were measured by *pepinsky* bridge.

Results

(1) ESR spectra

At low microwave power there is a large single central line which saturates at high power about 20mW. Thus it is easy to separate the two damaged centers which are shown in figure 1. The central line is almost isotropic with a g value of 2.004. Since no *hfs* on this line was observed, this central line is probably caused by $ZnCl_3^-$. In the measurement on $(NH_4)_2SO_4$, the central line was identified to SO_3^-

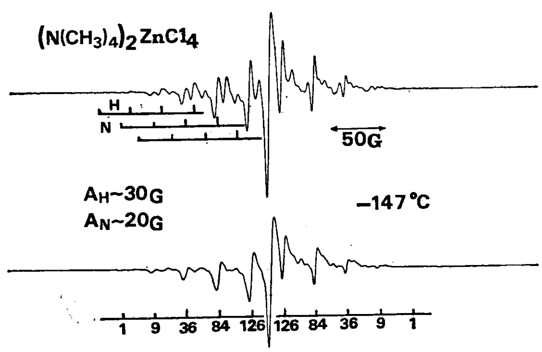

Fig. 1 Typical spectra of the $N(CH_3)_3^+$ center. The stick diagrams indicate the *hfs* of the center. The numerical values indicate the intensity ratio of this radical.

radical.[6]

Figure 1 shows ESR spectra taken with applied magnetic field to the a-axis. There are many lines for this center. For analysis of this center, ESR spectra were obtained every 5° of rotation about the three perpedicular crystalline axes. The spectra show that there are two types of centers which have different orientations in general orientation of the crystal. Type I center is almost isotropic and has strong intensity. We identified these centers to $N(CH_3)_3^+$ radicals, analogous to the NH_3^+ radicals in $(NH_4)_2SO_4$ crystal which we have reported on ESR studies of the irradiated $(NH_4)_2SO_4$ crystals.[6] The analysis of these spectra are shown in Fig. 2. For this orientation, the *hfs* constants are almost equal so that the resulting spectra should be ten lines spetra with intensity ratio of 1:9:36:84: 126:126:84: 36:9:1 as shown in Fig. 2. The *hfs* constants of nitrogen and protons are $A_N \cong 20$ G and $A_H \cong 30$ G, respectively at -147°C.

In our study of γ-irradiated $(NH_4)_2SO_4$ crystals, we found that the NH_3^+ center decays so fast that we could not observe the spectra at a few days later of the irradiation. This center also shows the rapid decay.

(2) Temperature dependes of ESR spectra

Down to the normal paraelectric-incommensurate phase transition temperature, and also to incommensurate-commensurate phase transition temperature, we could not observe any change of the spectrum. the intensity of the spectrum becomes stronger than the RT spectrum at lowering the temperature (Fig.2).

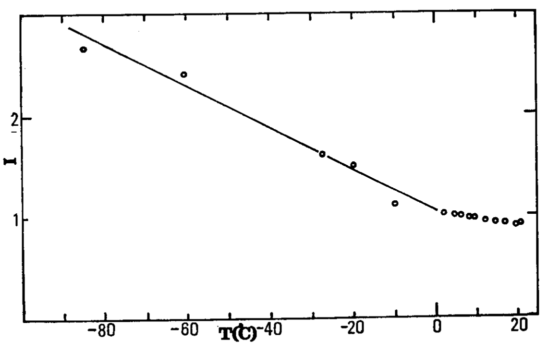

Fig. 2 Temperature dependence of the ESR spectra intensities.

The change of the spectra should be refered to the symmetry change of the crystals. Mashiyama et al. reported that the symmetry group at lower temperature is monoclinic space group.[4]

The protons of $N(CH_3)_3^+$ are all equivalent at the liquid nitrogen temperature, because no different of A_H tensors are observed. It seems that the $\{N(CH_3)_4\}^{2+}$ ion makes hindered rotation about the nitrogen atom even at low temperature. The angular dependence of the spectra shows the ion of $\{N(CH_3)_4\}^{2+}$ takes different orientations at low temperature. Figure 3 shows the temperature dependences of ESR spectra. This change of the orientration of the ceter is reversible to the temperature.

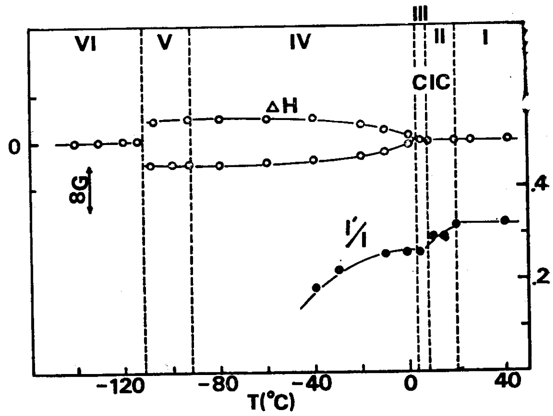

Fig. 3 Temperature dependence of the center. ΔH shows the line splittings by the symmetry change of the crystal. I'/I means the intensity change of the Type II to Type I of the $N(CH_3)_3^+$ radical.

Moskalev et al. have been reported the ^{35}Cl NQR spectra.[7~8] They pointed that the line broadening at the incommensurate phase because of the construction of the domain-like layers. The broadening of the line determined by the width of the "domain wall". However, our ESR spectra shows no such anomalous broadening. It will suggest that the damaged centers have a particular orientation (high symmetric position) and not be effected by surrounding molecules. Really the spectra are almost isotropic.

The paramagnetic ions doped in the crystal should be effected more than the damaged centers. Moreover, we could not observe line splittings corresponding to the superstructure of the crystal.

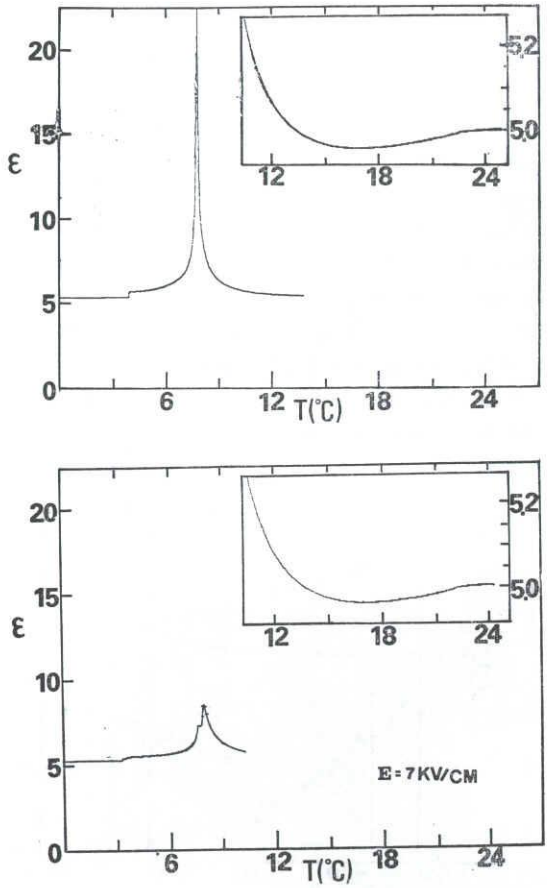

Fig. 4 Dependence of the dielectric constant *vs* temperature on DC biasing fields. (a) $E=0$kV/cm (b) $E=7$kV/cm.

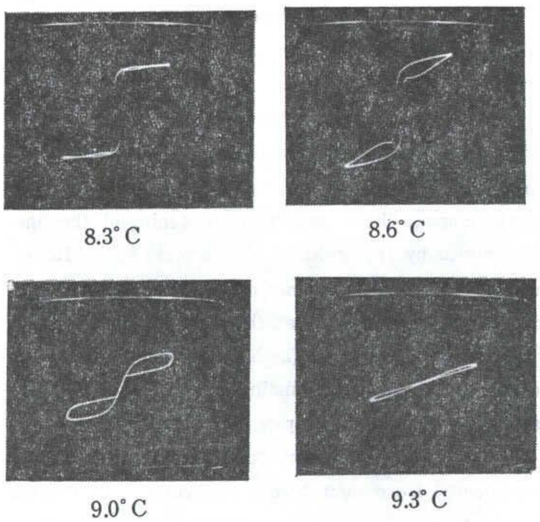

Fig. 5 Ferrielectric 60Hz *D–E* hysteresis loop along *a*-axis at IC–C phase transition point.

(3) **Dielectric and D–E hysteresis loop**

The dielectric constants have fairly large values than one reported by other investigators.[12] The dielectrc constants show the schrinkage and a new anomalous peak, when the electric biasing field is applied. It seems to correspond to a semipolar phase (Fig. 4).

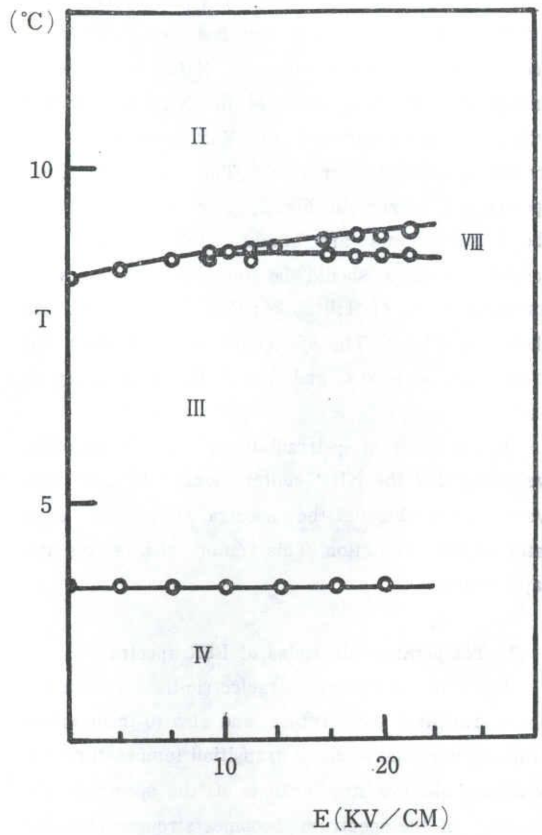

Fig. 6 Phase diagram *E vs T* of $\{N(CH_3)_4\}_2ZnCl_4$.

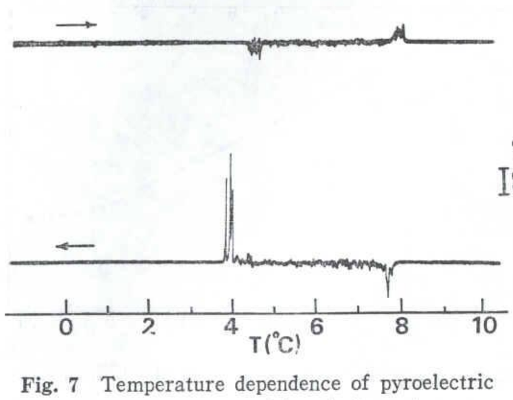

Fig. 7 Temperature dependence of pyroelectric current measured by electrometer.

Figure 5 shows a temperature dependence of 60Hz D–E hysteresis loop observed by *pepinsky* bridge. At near the temperature IC–C phase transition, hystseresis loops become triple (ferrielectric) and at almost double loops. The phase diagram of E–T is plotted in Fig. 6. We proposed a new phase (VIII) as a semipolar phase, because only in that phase we were able to observe the ferrielectric loops and which correspond to the anomalous dielectric peak with a biasing field.

Pyroecletric charge and currents are shown in Fig. 7. Anomalous noise have been observed at this commensurate phase in the pyrocurrent measurement.

S. Sawada et al.. concluded that the commensurate phase should be ferrielectric and no extra phase could not be observed in INC phase by the D–E loops.[5] Mashiyama et al. also got a same conclusion by precise x–ray diffraction studies with DC biasing.[13] However, on the contrary, we observed ferrielectric loops only just above the C–IC phase transition temperature (Fig. 5). Therefore, we dare to say that the new semipolar phase exist in incommensurate phase II (phase VIII). The phase VIII is not same as phase VII which induced by hydrostatic pressure.[14]

The transition temperature depends on the sample to sample. Really, no identical temperature are reported to IC–C transition in literatures. And moreover, this crystal shows a very high dielectric loss at IC–C transition temperature, then we are doubtful of the observed loops.

Conclusions

(1) Two damaged centers $N(CH_3)_3^+$ and $ZnCl_3^-$ are observed at γ–irradiated $\{N(CH_3)_4\}_2ZnCl_4$.

(2) No anomalous changes of the spectra are observed lowering the temperature in the prototypic, IC and C phases.

(3) At monoclinic phases (low temperature phases), spectra take different orientations from an orthorhombic phase.

(4) Ferrielectric loops are observed just above the IC–C transition temperature, which corresponds to a semipolar phase of the crystal with DC biasing fields.

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References

1) S. Sawada; J. Phys. Soc. Jpn **44** 687 (1978)
2) B. Morosin and E.C. Lingafelter; Acta Cryst. **12** 611 (1959)
3) K. Gesi and M. Iizumi; J. Phys. Soc. Jpn **48** 337 (1980)
4) S. Tanisaki and H. Mashiyama; J. Phys. Soc. Jpn **48** 339 (1980) Their conclusion about cell dimension of the IC–C phase is 5 *c* for the fundamental unit of the cell (X–ray diffraction).
5) S. Sawada et al.; J. Phys. Soc. Jpn **48** 1397 (1980)
6) I. Suzuki and R. Abe; J. Phys. Soc. Jpn **30** 586 (1971); N. Shibata, R. Abe and I. Suzuki; *ibid.* **41** 2011 (1976)
7) A.K. Moskalev et al.; phys. stat. sol. (a) **50** k157 (1978)
8) F. Milia; Phys. Letters **70A** 218 (1979)
9) A.P. Levanyuk and D.G. Sanikov; Soviet Phys.-Solid State **18** 245 (1976)
10) Y. Ishibashi and V. Dořák; J. Phys. Soc. Jpn **44** 32 (1978)
11) H. Margenau and G.W. Murphy; *The Mathematics of Physics and Chemistry; Nostrand Com.*
12) Gesi; private communication: He succeeded to growth better sample than ours. The dielectric constants of their samples show so much as high values as ours.
13) H. Mashiyama and S. Tanisaki; private communication.
14) H. Shimizu et al.; Solid State Commun. **29** 125 (1979)