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Dielectric Constants of RS-ARS Mixed Crystal System

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Complex dielectric constants of Rochelle salt(RS)–ammonium Rochelle salt(ARS) mixed crystal system have been investigated with a conventional LCR-meter at temperatures from 20K to 295K at 10kHz. The obtained data have been plotted on the ϵ'–ϵ'' plane, and they show a fairly continuous locus. They show considerable difference among the region I($0 < x < 0.025$), the region II($0.025 < x < 0.18$) and the region III($0.18 < x < 0.92$). The temperature where the ϵ'' is maximum is in the region of the ferroelectric phase in the region I and the region III. In the region II, the maximum point of the ϵ'' is the higher temperature side than the temperature where the ϵ' is maximum.

I. INTRODUCTION

As is well known, Rochelle salt(RS) undergoes successive phase transition as temperature decreases. With decreasing temperature, the paraelectric phase turns into the ferroelectric one at 297K with a prominent dielectric anomaly, and the paraelectric phase appears again at 255K. [1] The polar axis of the ferroelectric phase is the *a*-axis. On the other hand, ammonium Rochelle salt(ARS) has a polar phase below 110K, and the polar axis is parallel to the *b*-axis. [2] Structures of the two crystals are isomorphous in their paraelectric phases and it is possible to obtain mixed crystals RS_{1-x}–ARS_x of the whole range of x.

The phase diagram of the mixed crystal system has been investigated by Makita and Takagi. [3] They have divided the concentration into four regions according to their dielectric property; region I($0.00 < x < 0.025$), region II($0.025 < x < 0.18$), region III($0.18 < x < 0.92$), and region IV($0.89 < x < 1.00$). Essentially this classification is due to the concentration x of ARS.

In the region III, Horioka *et al.* reported dielectric relaxation in the frequency region between 3.8MHz and 24GHz at various x. [4] According to them, in the small x region, the character of the relaxation is almost the Debye type, however, in the large x region, the relaxation shows non-Debye type character. The static dielectric constants estimated from Cole-Cole plot show good agreement with the Curie-Weiss law. Elastic compliance, s(X-45°), has been also investigated for the crystals with x = 0.20,0.23,0.48,0.87 in the region III by Maeda and Ikeda. [5] They show that a sharp anomaly arises at T_c, and the anomaly of x=0.48 crystal has been explained as a phenomena accompanied with the first order phase transition. On the other hand, Ivanov *et al.* have argued the phase transition in the region III is of the second order from the studies on birefringence, dielectric permitivity(1kHz,ac-field=500V/m), piezomodulus and spontaneous polarization. The dielectric permitivity and piezomodulus d_{14} obey the Curie-Weiss law. [6] The specific heat of the mixed crystal have studied in the region III by Noda *et al.*. [7] It has been showed that the anomalies in the thermal quantities at the phase transition are very small in the whole regin III.

In this paper, the anomalous behavior of complex dielectric constants of the mixed crystals (x = 0.0,0.11,0.22,0.34,0.48,0.68,0.72) is studied. The constants are precisely measured by a conventional LCR meter, and temperature dependence of the real part ϵ' and the imaginary part ϵ'' are obtained. A trial plot is made on the ϵ'–ϵ'' plane and a discussion of them is made.

II. EXPERIMENTAL AND RESULTS

The mixed crystals were grown by slow evaporation from mixed aqueous solutions of Na-tartrate, K-tartrate and NH_4-tartrate. For dielectric measurements, plates perpendicular to the *a*-axis were prepared from the crystals, and the typical dimension of the sample crystals was 5 × 5 mm^2 and 0.5mm in thickness.

Temperature of the sample was controlled using a closed-cycle helium type refrigerator with a controller over the temperature range from 295K to 20K. Cooling rate was kept to be 0.1K/min during the measurements. All the measurements were performed with an LCR meter [HP4284A] by the four-terminal method, where each line were separately protected by electrostatic shield to prevent electric noises. The ac-field frequency for the measurement was 10kHz and the amplitude was kept below 25V/m.

The obtained relations ϵ' vs. temperature T of the mixed crystals show good agreement with those of the previous paper. [3] However the peak value of ϵ' at the lower transition point for RS is smaller than that reported in the previous paper. It may be possibly con-

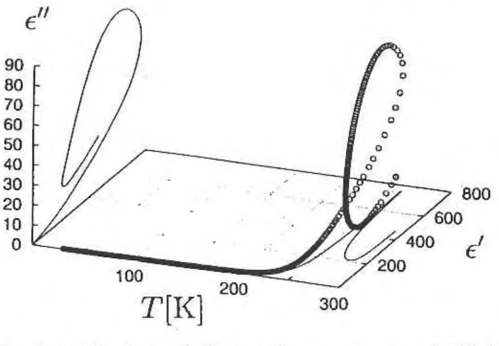

Fig. 1. A trial plot of dielectric constants of RS in three dimensional space of ϵ'-ϵ''-T(circles). Projections of it on T-ϵ' and ϵ'-ϵ'' planes are shown too(thin lines).

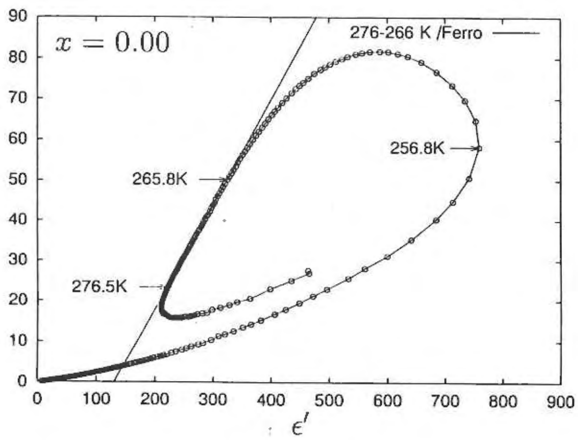

Fig. 2. The projection of dielectric constans of RS on the ϵ'-ϵ'' plane. The thin line is a guide line showing that there is a linear part in the projected locus.

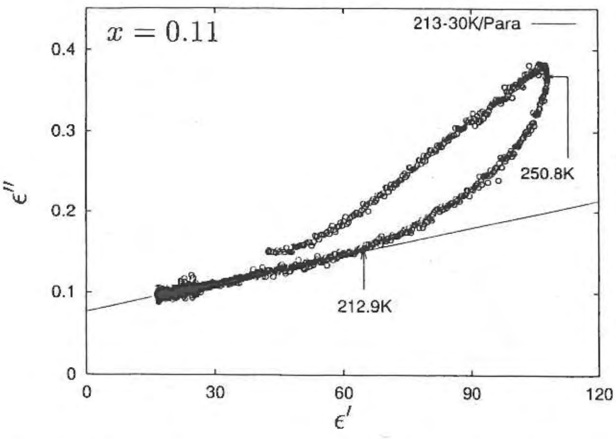

Fig. 3. The projection on the ϵ'-ϵ'' plane of x =0.11.

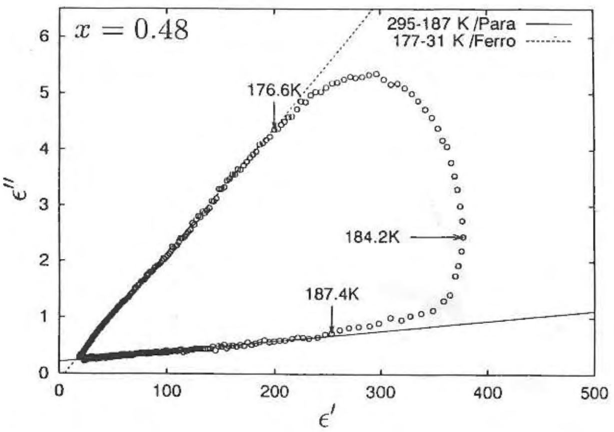

Fig. 4. The projection on the ϵ'-ϵ'' plane of x =0.48.

sidered that the difference in the the ac-field amplitude due to the different measurement method; a capacitance bridge was used in the previous paper. [3] A trial plotting of the measured dielectric constants in the region I is made in a three dimensional space with the axes of T, ϵ' and ϵ''. The plotting gives a smooth locus in whole temperature region. In Fig. 1, the data points with connected lines are shown. In Fig. 2, the projection on the ϵ'-ϵ'' plane of the plot is shown. In the lower paraelectric phase, the locus on the ϵ'-ϵ'' plane have no region displaying linear relation between ϵ' and ϵ''. The gradient of the locus varies with temperature. However in the ferroelectric phase, the locus have a linear region from 269K to 279K. The gradient in the low temperature phase is smaller at any temperature than that of the linear part in the ferroelectric phase.

From the measurements of the complex dielectric constants in the region II and III, the similar trial plots can be obtained. In the projection of the loci on the ϵ'-ϵ'' plane in the region II($x = 0.11$), the gradient of the locus diverges to infinity around the maximum of ϵ'.

In the projection of the locus in the region III, there are two linear regions which are corresponding to the temperature range of the paraelectric and ferroelectric phases. The projected locus on the ϵ'-ϵ'' plane of the mixed crystal of $x = 0.48$ is shown in Fig. 4. The linear regions extend over 100K, and the gradient of the linear part corresponding to the ferroelectric temperature range is larger than that of the paraelectric temperature range. In the range around the phase transition temperature, the curve is rounded and this part of the curve connects the two linear parts. There is no sign to indicate the phase transition is of the first order. Figures 5 and 6 show the similar projected curves of the mixed crystals x = 0.68 and 0.72, respectively.

III. DISCUSSION

Our plots show the maximum point of the imaginary part ϵ''_{max} of the complex dielectric constant together with the maximum point of the real part ϵ'_{max}. In the cases of RS and the region III, the temperature where the imaginary part has the maximum value doesn't agree with the temperature where the real part has the maximum value. In the both cases, the temperature which gives the ϵ''_{max} is in the range of the ferroelectric phase.

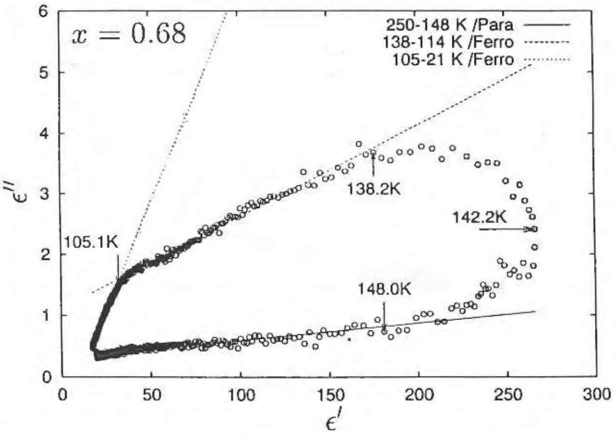

Fig. 5. The projection on the ϵ'–ϵ'' plane of x =0.68.

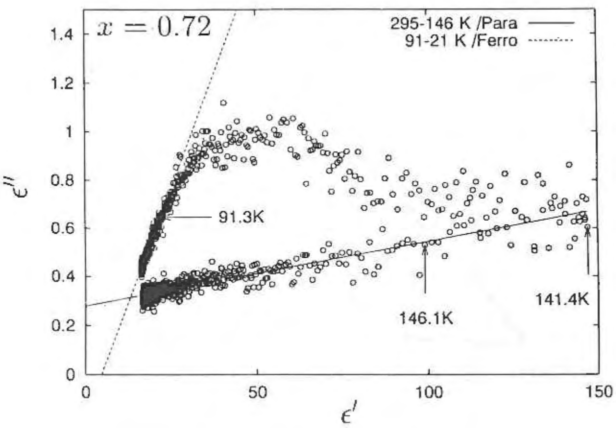

Fig. 6. The projection on the ϵ'–ϵ'' plane of x =0.72.

So that it is possibly considered that the character is related to the occurrence of the ferroelectric long range order, the formation of the domain structure and the correlation among ferroelectric dipoles. There is no phase transition in the region II. Even in the region there is temperature difference between the temperatures giving ϵ'_{max} and ϵ''_{max}. The short range interaction is possibly important in the region II.

A relation between ϵ' and ϵ'' is derived in the model of the Debye relaxation as below.

$$\epsilon''(\omega, T) = (\epsilon'(\omega, T) - \epsilon_\infty(T))\omega\tau_0(T) \qquad (1)$$

The value of $\tau_0(T)$ stands for the characteristic decay time and $\epsilon_\infty(T)$ is the high frequency limit of the dielectric constant. If ϵ_∞ and τ_0 have no temperature dependence, this equation gives a linear relation between ϵ' and ϵ''. It may be considered that these condition are satisfied in the temperature region with the linear locus of the ϵ'–ϵ'' plots. However it should be mentioned that, even in this case, the value of ϵ_∞ is negative some cases. This means that using Eq.(1) is not enough to evaluate the linear locus and that the obtained value of ϵ_∞ in Eq.(1) doesn't agree with the electronic polarization.

The mixed crystal system is a system where the orientation of RS dipole and that of ARS compete, so that a complex domain structure can be expected. To study the character by their dielectric properties, it will be required to study more precisely the region giving the linear relations between ϵ' and ϵ''.

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