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The Behavior of Complex Heat Capacity Near the First Order Phase Transition

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We have measured complex heat capacity in potassium dihydrogen phosphate (KH_2PO_4, KDP), thiourea ($SC(NH_4)_2$, TU), ammonium sulfate ($(NH_4)_2SO_4$, AS) and triglycine sulfate ($(NH_2CH_2COOH)_3H_2SO_4$, TGS) using an ac calorimetry. The crystals, KDP, TU and AS, have been known to undergo the first order phase transition. They showed the anomaly in the imaginary part of the complex heat capacity in narrow temperature region around the transition points. On the other hand, TGS which undergoes the second order phase transition showed no anomaly in the imaginary part at the phase transition point. The imaginary part of the complex heat capacity may reflect the dynamic behavior of the two-phase coexistence region.

I. INTRODUCTION

Traditionally, heat capacity has been considered to be a static and an equilibrium quantity. Recently, however, many works have been reported where the heat capacity is treated as a dynamic quantity. [1,2]

Suppose that a periodic heat flow is applied to a sample as a stimulus, one can expect that a corresponding periodic temperature variation is induced in the sample as a response. According to the general definition of susceptibility, we can introduce a quantity, complex heat capacity, defined by using such stimulus and response.

Thus the complex heat capacity can be considered to closely connect to the dynamic nature of the thermal state of materials. In fact, heat capacity involves, in general for a static environment, the contribution due to all the internal degree of freedom. Thus the complex heat capacity must be a more general quantity by which to study the dynamic structure of materials than other susceptibilities such as complex dielectric constant.

In this paper, we study dynamic behavior of the heat capacity near phase transition temperature in some dielectrics using the ac calorimetric technique. The materials studied here are mainly single crystals having the first order phase transition point. These are potassium dihydrogen phosphate (KH_2PO_4, KDP), thiourea ($SC(NH_4)_2$, TU) and ammonium sulfate ($(NH_4)_2SO_4$, AS) . Triglycine sulfate ($(NH_2CH_2COOH)_3H_2SO_4$, TGS), which shows the second order phase transition, was also studied to see the difference of the behavior of the complex heat capacity between the two types of the phase transition.

II. EXPERIMENTAL

1. Measurement system

In this study, the complex heat capacity has been evaluated with an ac calorimetry. This is a method in which one obtains the heat capacity by measuring the temperature amplitude of the periodic temperature variation caused by the applied periodic heat flow to the sample. The temperature of the sample changes in time at the same frequency as that of the heat flow.

In the case of this experimental setup described above, the temperature of the sample as a function of time t, $T(t)$, can be written as follows;

$$T(t) = T_b + T_{dc} + T_{ac}(t) \qquad (1)$$

where T_b is the temperature of a heat bath, T_{dc} is the time independent temperature which is the average rise from the bath temperature, and $T_{ac}(t)$ is the time-dependent temperature.

When we consider the dynamic behavior of the heat capacity, we should not mix up the thermal relaxation and the relaxation of the internal degree of freedom. The former is caused by the thermal diffusion inside the sample. Therefore, this relaxation, which is characterized by the relaxation time denoted by τ_1, depends on the sample size. By contrast, the latter proceeds even after the sample has reached at the thermal equilibrium and does

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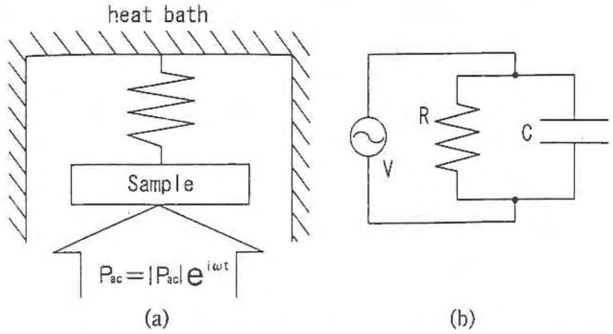

Fig. 1. (a) Thermal system of ac calorimetry, (b) Equivalent electrical circuit for thermal system

not depend on the sample size.

The thermal system of the ac calorimetry used in this study is schematically shown in Fig. 1(a). The sample is thermally linked to a heat bath and the link, which is composed of the thermocouples attached to the sample and also of the helium atmosphere gas surrounding the sample, is represented by R. As seen in this figure, the sinusoidal heat flow, $P_{ac} = |P_{ac}|\exp(i\omega t)$, is supplied to the sample. In the case where the flow being applied is a square wave as will be mentioned below, this sinusoidal heat flow corresponds to the fundamental component of the Fourier series for the square wave.

When the thermal gradient inside the sample is negligible, i.e. when the measurement is carried out at the frequency where the condition $\omega\tau_i \ll 1$ is valid and the temperature of the sample is regarded as being uniform, the equivalent electrical circuit for this thermal system can be written as in Fig. 1(b). The alternating current power source V, the electric resistance R, the capacitance C and the potential difference across the capacitor correspond to, respectively, the supplying heat flow to the sample, the thermal resistance, the heat capacity and the temperature difference between the sample and the heat bath. In this case, the complex amplitude of the temperature oscillation of the sample, T_{ac} is given by

$$T_{ac} = \frac{P_{ac}}{R^{-1} + i\omega C} = \frac{P_{ac}}{i\omega C}\left[1 + \frac{1}{i\omega\tau_e}\right]^{-1} \tag{2}$$

where $\tau_e = RC$ is the characteristic time in which the heat escapes from the sample to the heat bath.

Now, we introduce the complex heat capacity as;

$$C^*(\omega) = C'(\omega) - iC''(\omega) \tag{3}$$

where $C'(\omega)$ and $C''(\omega)$ are the real and the imaginary parts, respectively. Combining Eqs.(2) and (3), we obtain the real and the imaginary parts of the complex heat capacity using the amplitude of T_{ac} denoted as $|T_{ac}|$ and the phase of T_{ac} against P_{ac} denoted as ϕ; [3]

$$C'(\omega) = -\frac{|P_{ac}|}{\omega|T_{ac}|}\sin\phi \tag{4}$$

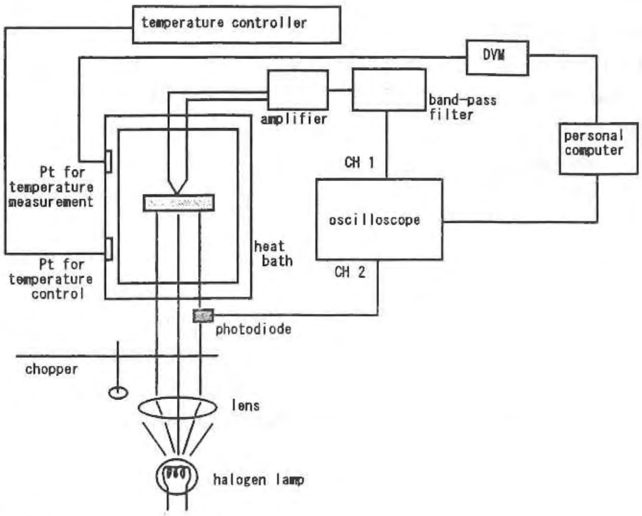

Fig. 2. Measurement system

$$C''(\omega) = \frac{|P_{ac}|}{\omega|T_{ac}|}\cos\phi - \frac{1}{\omega R} \tag{5}$$

The measurement system in this study is shown in Fig.2. Light of the halogen lamp has been used as the heat source. Chopping the light beam by the chopper, we can get a periodic square wave. This beam heats up the bottom side of the sample. The signals from the thermocouples attached to the upper side of the sample are amplified by a differential amplifier (NF Electronic Instrument, 5305). They are displayed on an oscilloscope (Hewlett Packard, HP54600B) after the noise reduction by using a dual channel programmable filter (NF Electronic Instrument, 3624). This filter has been employed as a band-pass filter with the central frequency being equal to the frequency of the chopping. The wave form displayed on the oscilloscope is transferred to a personal computer (NEC, PC9801ES). Using this computer, the Fourier transform is performed to obtain the values of $|T_{ac}|$ and ϕ.

In this study, we have calculated only the first term of the right hand of Eq.(5) for $C''(\omega)$ because it is impossible to evaluate the thermal resistance R, needed for precise calculation of the imaginary part $C''(\omega)$. For this reason, we have subtracted a constant value from the data of $C''(\omega)$ so that the value of $C''(\omega)$ at temperatures far from a transition point becomes zero. This procedure can be considered as a reasonable choice since the heat capacity is a real quantity, which is not depending on the measuring frequency, $C_{static} = C'(0)$, i.e. $C''(\omega)$ should be zero in such temperature region. The amplitude of the heat flow, $|P_{ac}|$, is also unknown, therefore we will discuss about the results using only the relative values, not the absolute ones.

2. Sample preparation

The samples used in this study are potassium dihydrogen phosphate (KH_2PO_4, KDP), thiourea ($SC(NH_4)_2$, TU), ammonium sulfate ($(NH_4)_2SO_4$, AS) and triglycine sulfate ($(NH_2CH_2COOH)_3H_2SO_4$, TGS). All of the sample crystals were grown from saturated solutions. As the solvents, methyl alcohol was used in the case of TU and water for the other samples. The slow evaporation method at room temperature was employed to grow the crystals. The typical sample size was about $1mm \times 1mm \times 0.1mm$. The type of the thermocouples used here was chromel-alumel. The thermocouples were attached to the sample using varnish. A small amount of dry graphite film lubricant was sprayed upon the side where the light beam from the halogen lamp was irradiated.

3. Light axis correction

As mentioned above, the measurement frequency should be chosen so as to make the τ_i effect negligible. Therefore, at first, we measured the frequency dependence of the phase ϕ at the vicinity of the phase transition temperature to find the appropriate frequency region. By solving the thermal equation, which takes account of the temperature gradient inside the sample, the phase ϕ is estimated as follows; [4]

$$\phi \simeq -\frac{\pi}{2} + \tan^{-1}\left(\frac{1}{\omega\tau_e} - \frac{\sqrt{10}}{2}\omega\tau_i\right) \qquad (6)$$

As seen in Fig.2, in our measurement system, the reference signal comes from a photodiode which is located just beside the beam axis. Therefore, we must take account of a phase shift angle ϑ caused by the difference of the position between the photodiode and the sample. Thus, the value of ϑ is given as;

$$\phi \simeq -\frac{\pi}{2} + \tan^{-1}\left(\frac{1}{\omega\tau_e} - \frac{\sqrt{10}}{2}\omega\tau_i\right) + \vartheta \qquad (7)$$

or,

$$\tan\left(\phi + \frac{\pi}{2} - \vartheta\right) = \frac{1}{2\pi\tau_e}\cdot\frac{1}{f} - \frac{\pi\sqrt{10}\tau_i}{1/f} \qquad (8)$$

where $f = \omega/2\pi$ is the measuring frequency. From Eq.(8), it is found that, in the plot of $\tan(\phi + \pi/2 - \vartheta)$ versus $1/f$, the τ_i effect contributes to the deviation from a straight line. Figure 3 shows the result of the measurement at 221.3K for the sample of AS which is close to the phase transition temperature. Those solid line in this figure is the result of a fit by employing a non-linear least squares fitting procedure. For this fit, the optimum parameter values were $\vartheta = -0.525$ [rad], $\tau_i = 4.54$ [msec], and $\tau_e = 0.339$ [sec]. In the case of this sample, it is found that the τ_i effect can be neglected at 1.0Hz. Similar measurements were carried out for the other samples and the τ_i effect can be neglected at 1.0Hz for all materials used in this study.

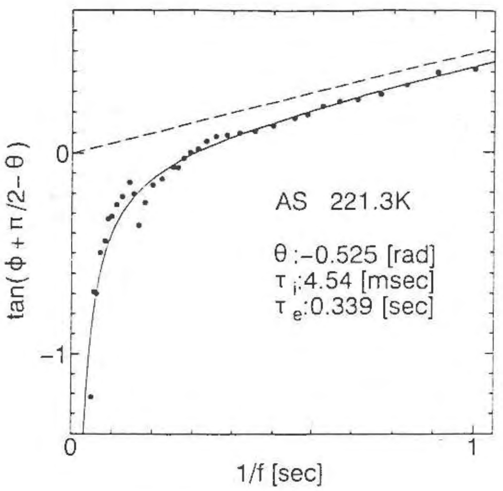

Fig. 3. $1/f$ plot of AS at 221.3K

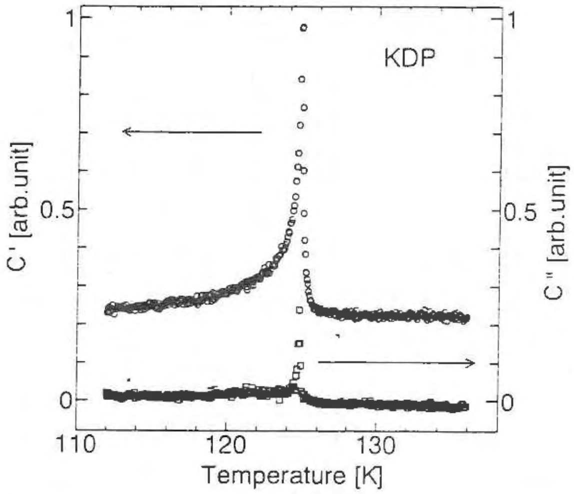

Fig. 4. Temperature dependence of $C'(\omega)$ and $C''(\omega)$ in KDP

In this measurements, the amplitude of the temperature oscillation, $|T_{ac}|$, is about 0.2K and the rate of the bath temperature variation is 1~5K/h around the phase transition temperature.

III. RESULTS AND DISCUSSION

Figures 4~6 show the results for the samples KDP, TU and AS , respectively. It has been known that these dielectrics undergo the first order phase transition. [5–7] As seen in these figures, there are sharp anomalies at each transition points. It should be noted that the temperature range, where the anomaly in $C''(\omega)$ is observed, is much narrow compared to that for $C'(\omega)$. On the other hand, Fig.7 shows the result of TGS which has been known as material undergoing the second order phase transition. [8] In this case, there is no anomaly in $C''(\omega)$.

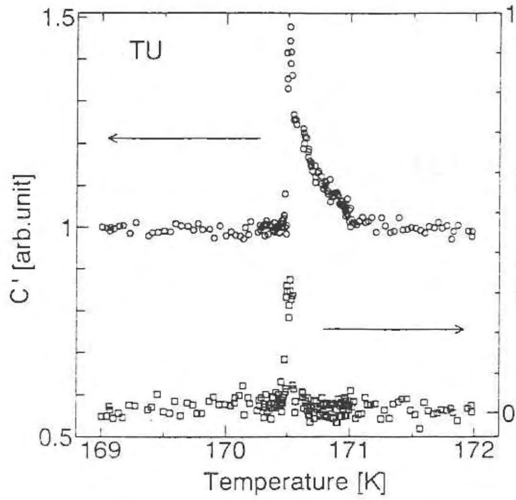

Fig. 5. Temperature dependence of $C'(\omega)$ and $C''(\omega)$ in TU

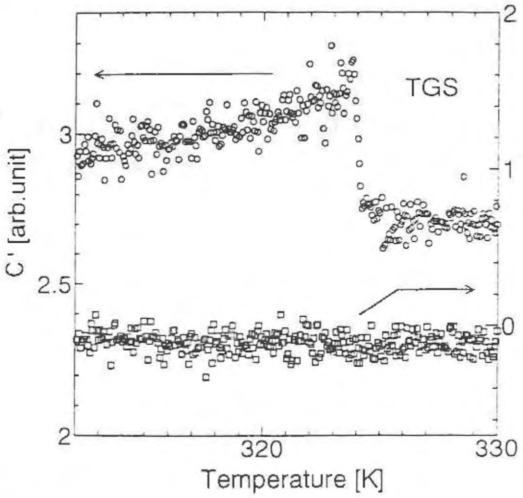

Fig. 7. Temperature dependence of $C'(\omega)$ and $C''(\omega)$ in TGS

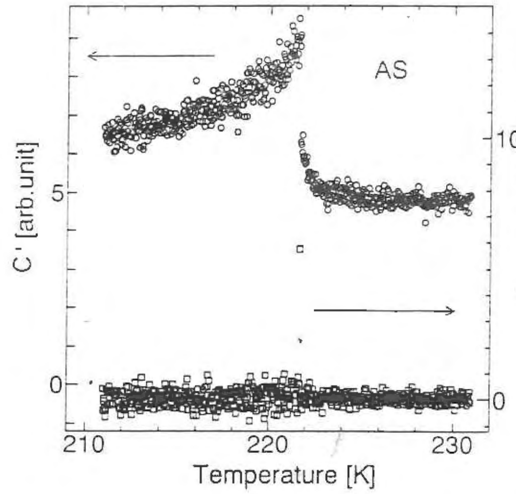

Fig. 6. Temperature dependence of $C'(\omega)$ and $C''(\omega)$ in AS

It has been reported by Ema *et.al.* that the phase lag is observed in the two-phase coexistence region for the Sm-C–Sm-C_2 transition, which is the first order phase transition, in DB_8ONO_2+$DB_{10}ONO_2$ liquid crystal mixture containing 51.22mol% of $DB_{10}ONO_2$. [9] In our case, the anomaly in $C''(\omega)$ also appears only in the narrow temperature range at the first order phase transition point and does not appear at the second order phase transition point. Therefore, it can be suggested that $C''(\omega)$ shows anomaly in the temperature region corresponding to the two-phase coexistence region belonging to the first order phase transition.

Although the physical background of $C''(\omega)$ is still not clear at present, it can be considered that $C''(\omega)$ reflects the dynamics of the two-phase coexistence region, something like the motion of the phase front, for example.

IV. CONCLUSIONS

We measured the temperature dependence of the complex heat capacity of potassium dihydrogen phosphate (KH_2PO_4, KDP), thiourea ($SC(NH_4)_2$, TU), ammonium sulfate ($(NH_4)_2SO_4$, AS), which undergo the first order phase transition, and triglycine sulfate ($(NH_2CH_2COOH)_3H_2SO_4$, TGS), which shows the second order phase transition, by employing an ac calorimeter at 1.0Hz. The imaginary part of the complex heat capacity shows a sharp anomaly in the very narrow temperature region only at the first order phase transition point. From this fact, it is conceivable to consider that $C''(\omega)$ is associated with the two-phase coexistence.

It should be noted, however, that this conclusion is restricted only at 1.0Hz chosen for this study. Further study with wider frequency range would bring deeper understanding about the dynamic behavior of $C''(\omega)$ at the first order phase transition.

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