Heat capacity measurements with a.c. microcalorimetry

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Abstract - An ac microcalorimetric technique is applied to studies on precise heat capacity measurements of a small piece of solid samples and a small quantity of liquid samples. For this purpose a light-irradiation type ac microcalorimetric method is useful and especially is applied to the measurements of detailed temperature dependence of heat capacity in a very small solid sample at phase transitions. The heat capacity measurements under various conditions are also possible. For a small quantity of liquid samples, the absolute value of heat capacity is determined with a high accuracy. Recently, this is extended to a trial measuring heat capacity as a function of frequency. From the measurement of ac temperature of condensed materials at the surface, one can obtain the product of heat capacity and thermal conductivity in a wide frequency range and therefore, get knowledge for dynamic heat capacity.

1. INTRODUCTION

I have devoted more than twenty years to carrying ac microcalorimetric measurements. A light-irradiation type ac calorimetric method is successfully applied to the measurement of anomalous heat capacity at phase transitions of ferroelectrics, ferromagnets, liquid crystals, binary alloys, etc. It should be stressed that this method requires only a very small sample. Therefore, the measurement can be performed for a selected sample, for instance, a piece of qualified single crystals. This point is important to consider behavior of heat capacity at phase transition precisely. I have also developed a light-irradiation type ac microcalorimetric method for a small quantity of liquids or materials suspended in liquid. In this case, the absolute value is determined within an accuracy of 1%. Dynamic heat capacity is one of the subjects which have been interested from theoretical point of view for a long time. From the ac calorimetric measurement of the frequency dependence of the product of heat capacity and thermal conductivity, knowledge for dynamic heat capacity is obtainable because thermal conductivity is expected to be weakly frequency-dependent. In this article, to show the best use of an ac microcalorimetric method, several topics will be discussed.

2. PRINCIPLE OF AN AC MICROCALORIMETRIC METHOD

The ac microcalorimetric methods may be characterized by the ac heat sources; In one method, the ac heat is applied to a sample by irradiation of alternatively chopped light and in another method, by Joule-heating of electrical resistance attached to a sample. For the heat capacity measurement of a very small sample, the former method has an advantage since the additional contribution caused by the attachement of heater is excluded. Then, in the present consideration, we will focus our attention mainly to an ac microcalorimetric method of light-irradiation type(ref. 1).

Let us consider a sample with the thickness of L. Light chopped at a frequency of f irradiates the front face of the sample as shown schematically in Fig. 1. The chopped light works as a source of ac heat flux Q.
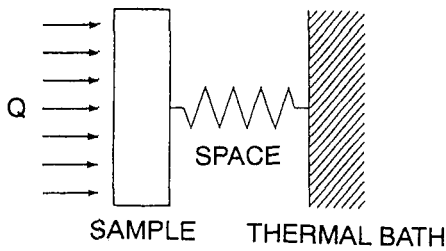
Fig. 1. Schematic view of a light-irradiation type ac microcalorimeter.

The ac temperature at the rear face, T_{ac}, is detected by a small sensor. The application of the chopped light causes not only the ac temperature but also the dc temperature rise T_{dc} beyond the temperature of the thermal bath. In our method, a halogen lamp was used as a source of light irradiation and to detect T_{ac} and T_{dc}, two pairs of fine chromel-alumel thermocouple wires were attached to the rear face of the sample with a small quantity of adhesive. The system is composed of chopped light, a sample, space and a thermal bath, which are arranged in one-dimensional way as shown in Fig. 1. In the space an appropriate gas is filled to allow heat exchange between the sample and the thermal bath to retain T_{ac} at a steady temperature.

Under a certain measuring condition, T_{ac} is inversely proportional to the heat capacity C of a sample per unit area. Deviation from such an ideal relationship is considered in terms of two relaxation times.(1) When a step-like heat is applied to the sample, T_{dc} increases with an external relaxation time τ_e. The external relaxation time is given by the heat capacity of the sample per unit area times thermal resistance per unit area between the sample and the thermal bath. (2) An internal relaxation time τ_i is related to the time which is required to get a uniform temperature in the sample. Let us define τ_i by $L^2/\sqrt{90D}$, where D is the thermal diffusivity of the sample. Using the two relaxation times, in the range of frequency of $1/\tau_e < \omega < 1/\tau_i$ where $\omega = 2\pi f$, the relation between T_{ac} and C is approximately given by

$$T_{ac} = \frac{Q}{\omega C}\left[1 + \frac{1}{\omega^2 \tau_e^2} + \omega^2 \tau_i^2 + \sqrt{40}\frac{\tau_i}{\tau_e}\right]^{-1/2} e^{-i\theta},$$

(1)

$$\theta = \arcsin\left[\frac{1 - \dfrac{4\omega^2\tau_i^2}{3} + \sqrt{10}\dfrac{\tau_i}{\tau_e}}{1 + \dfrac{1}{\omega^2\tau_e^2} + \omega^2\tau_i^2 + \sqrt{40}\dfrac{\tau_i}{\tau_e}}\right].$$

(2)

Under the both conditions that **A**. $\omega\tau_e \gg 1$, and **B**. $\omega\tau_i \ll 1$, eqn 1 tends to

$$T_{ac} = \frac{Q}{i\omega C}.$$

(3)

The condition **A** corresponds to a usual adiabatic condition. In the ac microcalorimetry, when ω is far larger than $1/\tau_e$, a cycle of heat oscillation happens without accompanying ac heat loss. If the space between the sample and the thermal bath is evacuated, τ_e becomes long and therefore, the condition **A** is reached easily but T_{dc} becomes large. On the other hand, the condition **B** is satisfied by putting L thin. From this point of view, the sample thinner, easier to satisfy the condition **B**. As a result, the ac microcalorimetry of light-irradiation type is compatible with the measurements for a very small sample.

In addition to the above fact, one can observe a small change of heat capacity by use of a lock-in amplifier. Owing to high sensitivity of a lock-in-amplifier the amplitude of ac temperature which is usually dealt with is a few mK. Then, the data points can be taken every 10mK.

3. APPLICATION OF AC MICROCALORIMETRY

3.1 Characteristics of ac microcalorimetry

As pointed out above, this method is applied to the measurements of the detailed temperature dependence of anomalous heat capacity at phase transitions for a very small sample, for instance, in the case of a high-temperature superconductor only a small quantity of a good single crystal is obtainable and therefore, the ac calorimetric measurement has been carried out for the crystal with a mass less than 1 mg in order to observed the precise critical behavior(ref. 2). Because of a small plate-like sample the measurement can be performed under the various conditions, i.e., electric field(ref. 3), magnetic field(ref. 4) and pressure(ref. 5,6) and also makes possible simultaneously the other measurements, for instance, the measurement of dielectric constant(ref. 7). As an example of a very small sample, very recently the heat capacity measurement has been preformed for thin free-standing liquid crystal films composed of a few molecular layers(ref. 8).

In the measurement of a liquid sample, the absolute value of heat capacity of the sample is determined by adopting a cell composed of a fine tube. From the measurement of the ac temperatures of a vacant cell, a cell filled with a standard material and a cell filled with a sample, we can determine the absolute value of heat capacity with a high accuracy.

Recently the ac microcalorimetry is extended to the measurement of frequency dependence of heat capacity. Generally heat capacity possesses frequency spectrum. Owing to the frequency limitation in the measurements it is not easy to observe the spectrum in a general case, however the preliminary measurement has been examined at the glass transition(ref. 9).

3.2 First-order phase transition

According to Gibbs' phase rule, when free energies of two adjacent phases intersect at a temperature under a certain pressure, it results in the coexistence of the two phases. The temperature is called a first-order transition temperature. However, the anomalous heat capacity associated with latent heat has more or less a certain width in the temperature axis in actual cases. This is due to defects, impurities, etc. To detect the behavior of typical latent heat we need to measure for a sample with good quality.

We have carried out the ac microcalorimetric measurement for a small sample of $BaTiO_3$, which is grown by a top-seeded solution technique(ref. 10). The dimension of the sample is 2x2x0.1 mm. The temperature dependence of heat capacity is given in Fig. 2 in the narrow temperature range of 407.5 and 409.0K. A distinct sharp anomaly takes place at the first-order transition temperature. The arrow pointing upward means that the signal of ac temperature goes to extremely small due to the contribution of latent heat.
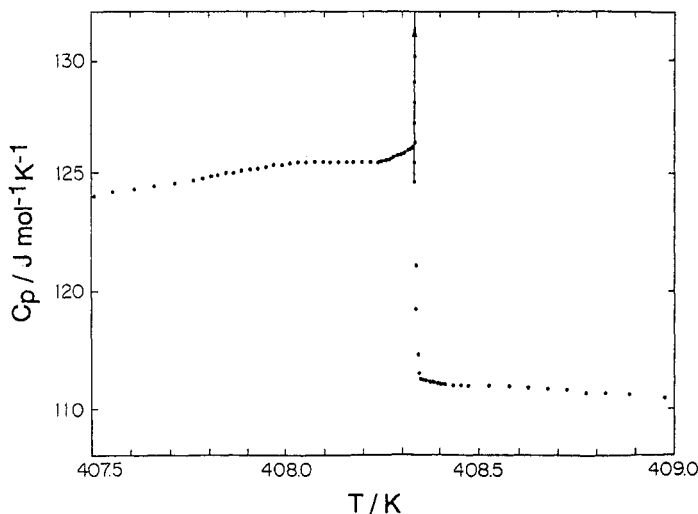

Fig. 2. Temperature dependence of heat capacity at the first-order phase transition temperature of a $BaTiO_3$ single crystal (ref. 10).

The heat capacities below and above the transition temperature shows a distinct jump. This behavior is explained in terms of a classical theory on phase transitions. The sharp jump of Fig. 2 appears in a single crystal grown by a top-seeded solution technique and however, a gradual change of the heat capacity above the transition temperature takes place in a crystal grown by a flux method. This fact is reasonably understood by taking into account that in the latter crystal the dispersion of the transition temperature arises from the impurities which are usually fluorine of up to 0.3%, etc. Therefore, on observing the detailed behavior of heat capacity at the phase transition temperature we should use a good single crystal.

3.3 Critical phenomena

To determine critical exponents and critical amplitudes is important to understand the nature of second order phase transition.

We have measured the heat capacity at the phase transition temperature of a series of the two-dimensional anisotropic Heisenberg antiferromagnets of K_2NiF_4 family (ref. 11). In the antiferromagnets only two-dimensional critical behavior is observed, since the three-dimensional critical region is too narrow to be detected. The spin Hamiltonian is consequently expressed as

$$H = 2 J \sum_{i,j} [(1-\Delta)(S_i^x S_j^x + S_i^y S_j^y) + S_i^z S_j^z], \tag{4}$$

where J is exchange energy, the summation runs over all pairs of nearest neighbor spins S_i and S_j on the simple square lattice, and Δ is an anisotropy parameter, for the pure Ising case $\Delta=1$ and for the Heisenberg case $\Delta=0$. According to universality hypothesis, if Δ has a positive, even small, value, the system expressed by eqn 4 should exhibit two-dimensional Ising-like critical behavior. In the ac microcalorimetric experiments for $A.K_2CoF_4(\Delta=0.49)$, $B.Ba_2MnF_6(\Delta=0.03)$, $C.Rb_2NiF_4(\Delta=0.0084)$, $D.K_2MnF_4(\Delta=0.0039)$, and $E.K_2NiF_4(\Delta=0.0020)$, all of the heat capacities show a longarithmic divergency at the Néel temperatures, T_N, in consistent with universality hypothesis. Therefore, the heat capacities are expressed by

$$C = A\|\ln|t\|\| + B + Et, \tag{5}$$

where $T=(T - T_N)/T_N$, A is critical amplitude, and B and E are constants. The critical amplitudes observed below and above T_N have the same values as expected from universality hypothesis. In our analysis, attention is focused on the change of critical amplitude which is expected by varying Δ. In order to show the relation between A and Δ, a double logalithmic plot of A ln 2/[Rln(2S+1)] vs Δ is plotted by open circles in Fig. 3 denoted by A to E, where ln2/ln(2S+1) is a normalization factor to compare the critical amplitudes among the antiferromagnets with different spin numbers. The closed circle denoted by I shows the point for the exact solution in the pure two-dimensional Ising system. As seen in Fig. 3, all of the results including
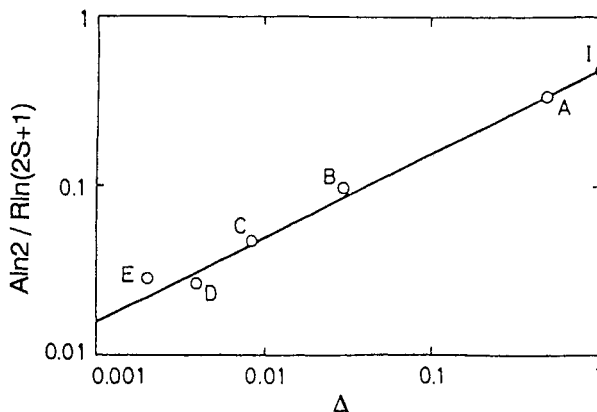

Fig. 3. Double logarithmic plots of the critical amplitude of heat capacity vs Ising anisotropy parameter in a two-dimensional anisotropic Heisenberg system for A to E and I, see text(ref. 11).

the exact solution are expressed by a straight line with the slope of 1/2, which is given by

$$A/R = F\Delta^{1/2}, \tag{6}$$

where R is the gas constant and F is a constant given by $2[\ln(\sqrt{2}+1)]^2\ln(2S+1)/(\pi\ln2)$.

This fact indicates that the critical amplitude A with two-dimensional Ising nature decreases with weaking the anisotropy factor Δ. This means that the behavior should be interpreted in terms of cross-over from a two-dimensional Ising to two-dimensional Heisenberg system. The results obtained from the ac microcalorimetric measurement draw a quantitative expression for the cross-over phenomenon. However, the reason why the exponent for Δ takes 1/2 is left open.

3.4 Heat capacities measured under various conditions

It is of interest to measure heat capacity as a function of not only temperature but also the other parameters, electric field, magnetic field, pressure, etc. An ac microcalorimetry method is useful in such measurements, since it is a kind of steady state method and then, the measurement can be made at a certain fixed temperature.

The heat capacity of a superconductor of thin aluminum films has been measured as a function of magnetic field and the transition from the superconducting to normal state has been observed along the magnetic field axis(ref. 4). It is quite general to measure the heat capacity against temperature at various magnetic fields and pressures to study the nature of phase transitions(ref. 2, 6).

Next I will introduce a case which is specific subject of ac microcalorimetry. In the heat capacity measurement of ferroelectrics, one should pay attention to the conditions of constant electric field E, constant polarization P, and constant electric flux density D. The measurement of C^D and C^E has been carried out(ref. 3), in which the samples of triglycine sulfate and triglycine selenate are thin plates of 2x2x0.1mm and both surfaces perpedicular to the ferroelectric axis are electroded by evaporation of gold. The measurement of C^E can be performed by shortcircuiting the electrodes. When the electrodes of a poled sample are kept open and furthermore, the leak of pyroelectric charge during each cycle of light-irradiation is neglected, C^D can be measured. The latter measurement is possible by making use of an ac microcalorimetric method. The results indicate that C^E shows λ-type anomaly at the transiiton temperature and C^D shows no anomaly. When the dielectric constant is far larger than unity as that in ferroelectrics, C^D is almost equal to C^P. This behavior is consistent with theoretical consideration and therefore, $C^E - C^P$ is a part of the anomalous heat capacity related to the fluctuation of ferroelectric polarization.

3.5 Simultaneous measurements

At a phase transition temperature, various physical properties show anomalies. Relation among them gives a further knowledge for the study of phase transition mechanism.

From this point of view, the simultaneous measurements of the heat capacity and the dielectric constant in an antiferroelectric crystal of $NaNO_2$ have been carried out in the vicinity of the transition temperature. The sample is about 1x1x0.1mm and gold is evaporated on both surfaces as electrodes. Figure 4 is the results of the simultaneous measurements. The heat capacity shows a sharp peak, whish is characteristic of a second order phase transition. The transition temperature T_c is determined by a method of least-squares fitting to equations expressed in terms of critical divergence. On the other hand, the peak of dielectric constant has a broad maximum at a temperature about 0.1K higher than T_c, therefore the maximum of dielectric constant does not indicate the transition temperature in the antiferroelectric crystal of $NaNO_2$. As seen in Fig. 4, the temperature derivative of dielectric constant shows a peak at T_c however.

The above fact is interpreted theoretically : The anomalous heat capacity of an antiferroelectric crystal should be closely similar to the behavior of the temperature derivative of the dielectric constant(ref. 12).
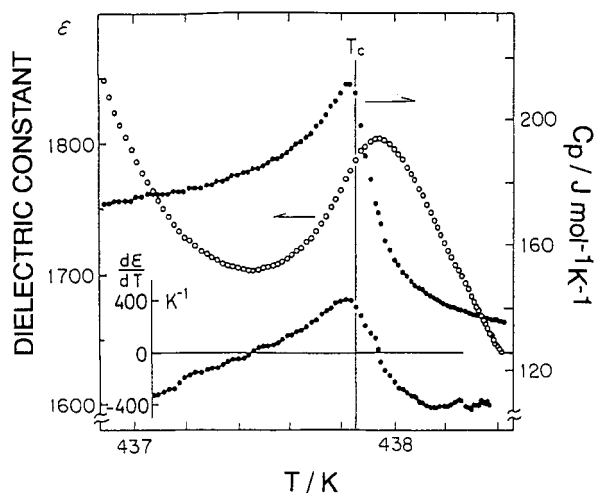

Fig. 4. Temperature dependences of heat capacity, dielectric constant and temperature derivative of dielectric constant near the antiferroelectric phase transition temperature T_c of $NaNO_2$(ref. 7).

3.6 Heat capacity measurements of a small quantity of liquid with a high accuracy

A light-irradiation type ac microcalorimeter has been developed to measure the heat capacity of small solid materials. This is successfully used for the measurement of anomalous heat capacity at phase transitions as mentioned in the former sections. However, when we are going to obtain the total heat capacity of the materials themselves, it is indispensable to estimate the contribution of the addenda, attached thermocouple wires, adhesive, etc., and the magnitude of applied heat energy. On measuring a small quantity of liquid, this problem is solved using a cell composed of a fine tube (ref. 13).

The sample cell of the ac microcalorimeter for liquid is shown in Fig. 5. The cell is made of a very fine stainless steel tube, for instance, $130\mu m$ in inside diameter, $170\mu m$ in outside diameter and 39mm long, which is filled with $0.52\mu l$ of a liquid sample. Polyethylene tubes with low thermal conductivity are connected to the both ends of the tube-like stainless steel cell and through the polyethylene tube the liquid sample is injected into the cell with a microsyringe. Two pairs of thermocouple wires ($12.5\mu m$ in diameter) are welded onto the center of the tube-like stainless steel cell as shown in Fig. 5.

The chopped light is irradiated on one side of the tube-like cell. Since the thermal diffusivity of stainless steel is usually about thirty times greater than that of a liquid sample, the supplied ac heat flux on one side of the tube-like cell propagates immediately to the other side of the tube-like cell and then permeates the inside of the liquid sample. Therefore, the effective thickness of the sample becomes small and finally the internal relaxation time is short. This is favorable in the experimental condition B of Section 2.

To obtain the absolute value of the heat capacity in liquid samples, evaluation of the heat capacity of the empty cell and the amplitude of ac heat flux supplied to the cell is necessary. For the purpose, the amplitudes
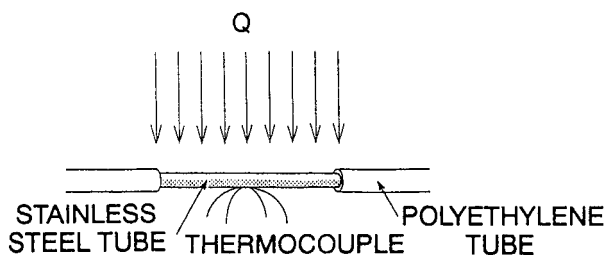

Fig. 5. Schematic view of a tube-like stainless steel cell of an ac microcalorimeter for a small quantity of a liquid sample measured with a high accuracy.

of ac temperature of an empty cell, T_{acc}, a cell filled with a standard liquid with heat capacity c_r per unit volume, T_{acr}, and a cell filled with a liquid sample, T_{acs}, are measured. From them, the heat capacity per unit volume of the liquid sample, c_s, is obtained as

$$c_s = \frac{T_{acs}^{-1} - T_{acc}^{-1}}{T_{acr}^{-1} - T_{acc}^{-1}} c_r \quad . \tag{7}$$

For instance, the heat capacity of pure n-heptane was determined using this method(ref. 13). As a standard sample, water was used. From this measurement, it has been established that the heat capacity of a liquid sample is determined within an accuracy of 1%.

Using this method, the heat capacity of a phospholipid, dipalmitoylphosphatidylcholine, has been measured at a frequency of 0.6 Hz. The sample is the phospholipid vesicles suspended in water. The total quantity of the suspension is about 0.5μl and the concentration of the phospholipid is 10 wt%. Then, the weight of the phospholipid used is about 50 μg. The results near the main transition temperature are shown in Fig. 6. These obtained in heating drawn by thin solid curve and in cooling drawn by thick solid curve
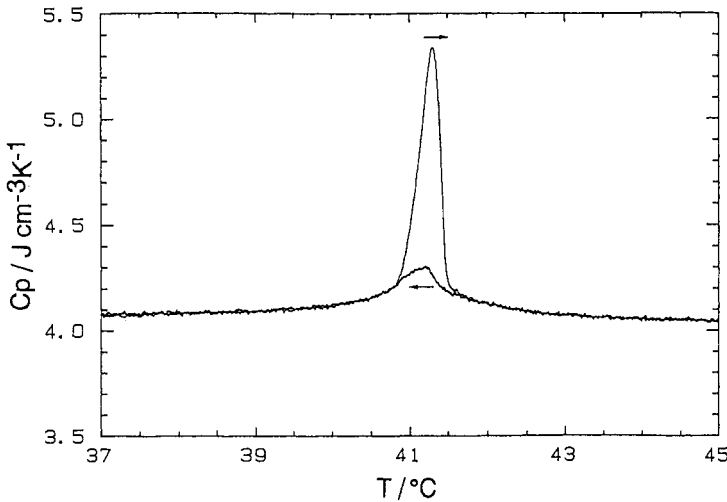

Fig. 6. Temperature dependence of heat capacity of dipalmitoylphosphatidyl-choline vesicles suspended in water.

coincide with each other fairly well except for at the main transition.

At the main transition, in which the low temperature phase is called Pβ' phase and the high temperature phase called Lα phase, the heat capacity exhibits a sharp maximum in heating and on the other hand, a small anomaly in cooling, but the maximum temperatures remain at almost the same. However, the latter behavior is not understood in terms of nature of usual first order phase transition. This has been explained as follows(ref. 14). In heating the phospholipid undergoes normal Pβ'-to-Lα phase transition but in cooling metastable Pβ' phase takes place. Therefore, the transition enthalpy is smaller in cooling than in heating.

It is worth while pointing out that the anomalous heat capacity observed by ac microcalorimetry is smaller than by differential scanning calorimetry. This might be partly due to the first order nature of the phase transition, since the contribution of latent heat is not always detectable in ac microcalorimetry. Furthermore, the frequency dependence of the heat capacity should be considered in this phase transition, i.e., at a low frequency the frequency dispersion of the heat capacity might take place.

3.7 Heat capacity spectroscopy

Recently a new technique that allows us to measure the frequency dependence of heat capacity over a wide frequency range(ref. 9). This technique has been applied to measurement of dynamic heat capacity of glycerol near the glass transition(ref. 9).

Figure 7 shows schematically the measuring method. A thin metal film for Joule-heating resistor yielding ac heat flux is evaporated on a substrate denoted by B in Fig. 7. This is attached tightly to a sample A whose frequency dependence of heat capacity is measured. When ac heat flux Q with an angular frequency ω
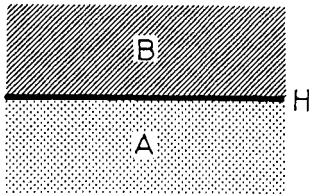

Fig. 7. Schematic view of a heat capacity spectrometer. A is a sample, B is a substrate for a heater and H is a heater of a thin metal film.

is applied, the ac temperature at the heater is given by

$$T_{ac} = \frac{Q}{\sqrt{\omega c \kappa} + \sqrt{\omega c_s \kappa_s}} \exp(i\pi/4), \tag{8}$$

where c and c_s are heat capacities per unit volume of the sample and the substrate, respectively, and κ and κ_s are thermal conductivities of the sample and the substrate, respectively. Usually the material for a substrate is chosen one with frequency-independent $c_s\kappa_s$. From the amplitude and the phase of the ac temperature, we obtain real and imaginary parts of $c\kappa$(thermal effusivity) at each frequency using eqn 8. At the glass transition of glycerol, the measurement has been carried out in the frequency range, 0.2<f<6000Hz. The frequency dispersion of real and imaginary parts of $c\kappa$ was observed in this frequency range. Since the change of $c\kappa$ against temperature is thought to be dominated by the behavior of c, the results on $c\kappa$ offer knowledge for dynamic heat capacity. In the above measurement the upper frequency is restricted by the thickness of the thin metal film because at a high frequency the thickness of the film is no longer negligible.

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