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First-order phase transitions studied by temperature-modulated calorimetry

Ichiro Hatta*, Sachiyo Nakayama

Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

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Abstract

To study first-order phase transitions, we applied temperature-modulated calorimetry. Especially, in this paper, we carried out the measurements using two kinds of calorimeters, a light-irradiation type AC calorimeter and a temperature-modulated differential scanning calorimeter. The former is useful to obtain the detailed behavior of heat capacity near a first-order phase transition but not the magnitude of latent heat. On the other hand, the latter is useful to obtain the magnitude of latent heat. In a further study on the kinetic mechanism (nucleation, phase boundary motion, etc.) in a hybrid region composed of the mixture of two states associated with low- and high-temperature phase, it is very important to consider the results obtained from the calorimetric measurements which are done under small amplitude of modulated temperature and a wide range of frequency based upon the detailed structure of the hybrid region. © 1998 Elsevier Science B.V.

Keywords: AC calorimetry; Temperature-modulated calorimetry; Temperature-modulated DSC; Phase transition; First-order phase transition; Heat capacity; Latent heat

1. Introduction

AC calorimetry which is a kind of temperature-modulated calorimetry has been applied extensively to heat capacity measurements at phase transitions [1–3]. To study critical phenomena, a conventional AC calorimeter has been widely accepted as a powerful tool since the measurement can be performed with the small amplitude of AC temperature, about 1 mK, and, therefore, heat capacity measurements can be performed very close to the critical temperature with a high accuracy. However, the validity of its application to a first-order phase transition is still not established. Sometimes, the existence of latent heat can be detected but its magnitude cannot be estimated. Sometimes, the apparent heat capacity obtained from an AC calorimeter exhibits peculiar behavior, probably due to the non-linear response of AC temperature.

Recently, another temperature-modulated calorimeter which adds a function to a differential scanning calorimeter has been proposed [4]. The apparatus is supplied commercially so it can be used conveniently by many researchers. Although the amplitude of AC temperature in this apparatus is not so small in comparison with the conventional AC calorimeter, it has a great advantage since the temperature-modulated differential scanning calorimeter makes it possible to obtain the absolute value of heat capacity easily. Furthermore, it should be pointed out that by this method we can perform the measurement of the usual differential scanning calorimeter at the same time.

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*Corresponding author: Tel.: +81 52 7894466; fax: +81 52 7893706; e-mail: hatta@nuap.nagoya-u.ac.jp

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It is of interest to consider how we can use temperature-modulated calorimetry to study a first-order phase transition. In the present paper, first, we will summarize the thermodynamics at a first-order phase transition. Second, some typical experiments at first-order phase transitions are carried out by both conventional AC calorimetry and temperature-modulated differential scanning calorimetry.

2. Thermodynamics at first-order phase transitions

At a first order-phase transition, the curves of the Gibbs function vs. temperature for the two states, 1 and 2, intersect at constant pressure p_0, but there is a discontinuity in their slopes as seen in Fig. 1. The Gibbs function $G_1(p_0, T)$ is lower than $G_2(p_0, T)$ in the lower temperature range than T_0 and vice versa. Since $(\partial G/\partial T)_p = -S$, there is a break in the S vs. T curve, the difference of S, ΔS $(=S_2-S_1)$, between the two phases at T_0 being related to the observed latent heat $L(=H_2-H_1$, where H is enthalpy) by

$$\Delta S = L/T_0 \tag{1}$$

There is also a discontinuous change ΔV in molar volume at T_0, where $(\partial G/\partial T)_T = V$. At a first-order phase transition, from the relation that chemical potentials for the low and high-temperature phases are equal other, Clapeyron–Clausius equation can be derived as [5]

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T_0 \Delta V} \tag{2}$$

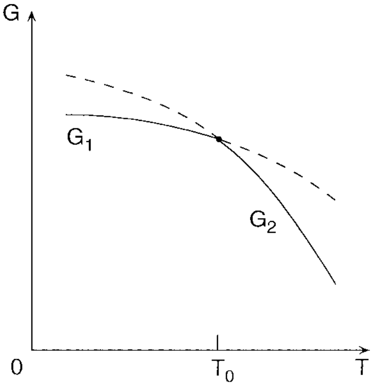

Fig. 1. Gibbs functions at a first-order phase transition. There are states 1 and 2, which are stabilized in low- and high-temperature phases, respectively. The two Gibbs functions intersect at the first-order phase transition temperature, T_0.

Then, the latent heat and molar volume change at a first-order phase transition is related to the pressure dependence of the transition temperature.

However, some first-order phase transitions take place over a certain temperature range. This might be related to nucleation of the counter state and its growth. A thermodynamic consequence is that additional terms are required in the Gibbs functions for each state in order to represent the contributions from the internal surface energy σ_{12} at the boundaries between the two homogeneous states and from the internal compressive or tensile energy χ_{12} when a domain of the counter state is produced in the matrix [6]. Then the Gibbs function is expressed in terms of the above parameters for the state 1 and 2, respectively, as [6]

$$G_1(p, T, \sigma_{12}, \chi_{12}) \tag{3}$$

and

$$G_2(p, T, \sigma_{12}, \chi_{12}) \tag{4}$$

which are stabilized in the low- and high-temperature phases, respectively. In the first-order phase-transition range, a hybrid region composed of the two states is regarded as containing fraction x of the high temperature phase and fraction 1-x of the low-temperature phase, so that the Gibbs function $\mathrm{G_{hybrid}}$ is given by the composite expression [6]

$$\begin{aligned} G_{\text{hybrid}} &= xG_2(p, T, \sigma_{12}, \chi_{12}) \\ &\quad + (1-x)G_1(p, \sigma_{12}, \chi_{12}) \end{aligned} \tag{5}$$

For a further consideration, it is convenient to distinguish between the transformed and residual parts, then the quantities for the transformed part are denoted by a bracket [] in the following expressions. When x increases, i.e., temperature rises, the Gibbs function G_{hybrid} for a hybrid region is given by [6]

$$\begin{aligned} G_{\text{hybrid}} &= xG_2(p, T, [\sigma_{12}], [\chi_{12}]) \\ &\quad + (1-x)G_1(p, T, \sigma_{12}, \chi_{12}) \end{aligned} \tag{6}$$

On the other hand, when x decreases, i.e., temperature falls, the Gibbs function $\mathrm{G_{hybrid}}$ is given by [6]

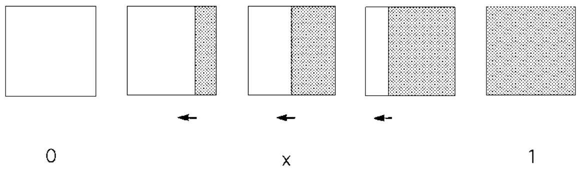

Fig. 2. In a hybrid region composed of the two states in a first-order phase transition range, a phase boundary moves according to temperature rises (x increases) and falls (x decreases). State 2 which is stabilized in high temperature phase is denoted by a shadowed region. When there is no cooling process, the phase boundary moves in the direction indicated by arrows.

$$G_{\mathrm{hybrid}} = xG_2(p, T, \sigma_{12}, \chi_{12}) + (1-x)G_1(p, T, [\sigma_{12}], [\chi_{12}]) \tag{7}$$

First, let us consider the effects of the internal stress energy χ_{12} in a hybrid first-order phase transition region. Mostly, molar volume expands in the high temperature phase. Suppose that there is only a phase boundary in a substance (see Fig. 2). During rising temperature, the compression due to the volume expansion of state 2 suppresses the growth of state 2 which is stabilized in the high temperature phase. This is the case of Eq. (6). On the other hand, during falling temperature, the tensile stress due to the shrinkage of state 1 suppresses the growth of state 1. This is the case of Eq. (7). However, it is quite evident that the heating and cooling processes are not reversible as expected from Eqs. (6) and (7). Therefore, it should be pointed out that the motion of the phase boundaries in principle is non-linear.

However, when the difference of the molar volumes in both states is smaller, the internal stress becomes smaller, and, as a result, the system appears to be close being linear. At the same time, it should be pointed out that the temperature range associated with the first-order transition becomes smaller.

Furthermore, when there are a lot of phase boundaries, heterogeneity in a substance seems to be smeared out, and, therefore, such a mixed system appears to be homogeneous. However, even if such a system might behave as apparently linear, we have to consider the kinetic mechanism in the hybrid region based upon the detailed structure.

Second, let us briefly consider the effects of the internal surface energy σ_{12}. On cooling a substance lower than the first-order phase-trwansition temperature, the high-temperature phase remains, that is, supercooling takes place. This is due to competition among free energy for formation of nucleus, internal surface energy σ_{12} at the phase boundary and Gibbs energy difference between the two states. Once the balance of these competitive energies is lost, it suddenly undergoes a phase transition. Then, its response is quite non-linear.

3. Experimental results and discussion

The heat capacity measurements at the first-order ferroelectric-to-paraelectric phase transition of a $BaTiO_3$ crystal were carried out using both the temperature-modulated differential scanning calorimeter and a light-irradiation type AC calorimeter. For the former measurement, we used a commercial temperature-modulated differential scanning calorimeter, Type 2920 of TA Instruments. The measurement were performed under the condition that the time-derivative of heating temperature was always positive, that is, we chose that the underlying heating rate was 1.0°C/min and the amplitude of the modulated temperature was 0.1°C for both the periods of 100 and 60 s. It means that the measurement was done only in the process expressed in terms of Eq. (6) Therefore, if the phase boundary moves, it happens in a direction with increasing x (see the direction of arrows in Fig. 2). In this situation we might expect a linear response due to the motion of phase boundary even at a first-order phase transition.

Fig. 3 shows the result of a $BaTiO_3$ crystal for the period of 100 s. The underlying heating is illustrated by a dotted diagonal line, and then the modulated temperature is superimposed on the above line. The modulated heat flow measured exhibits almost a sinusoidal curve except for a sharp drop due to latent heat as seen in the upper side of Fig. 3. Then, this fact indicates that the nucleation process is dominant in the kinetics of the transformation. From the Fourier transform of the curve around the drop, the amplitude of AC temperature becomes apparently big since the first-order phase transition happens near the bottom of the sinusoidal curve in this case. Then, the heat capacity obtained from the modulated heat flow shows a peak as shown in Fig. 4. On the other hand, a similar measurement was done at the period of 60 s. As seen

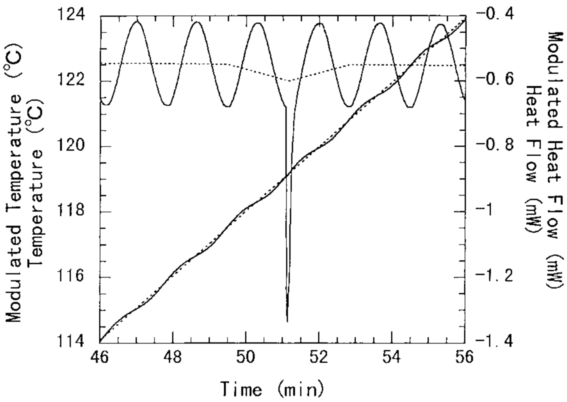

Fig. 3. Result of temperature-modulated differential scanning calorimetry in a $BaTiO_3$ crystal. The underlying scanning temperature is shown by a dotted diagonal line and the modulated temperature shown by a solid line is superimposed on it. The modulated heat flow is shown by a solid curve in the upper side and the total heat flow is obtained as given by a dotted line in it.

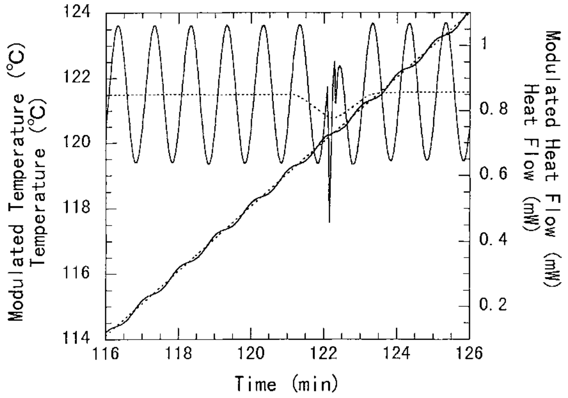

Fig. 5. Another result of temperature-modulated differential scanning calorimetry in a $BaTiO_3$ crystal. The arrangement of each curve is the same as in Fig. 3.

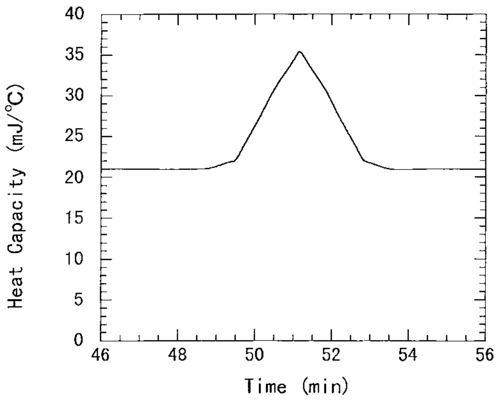

Fig. 4. Calculated heat capacity of a $BaTiO_3$ crystal obtained from the result of Fig. 3.

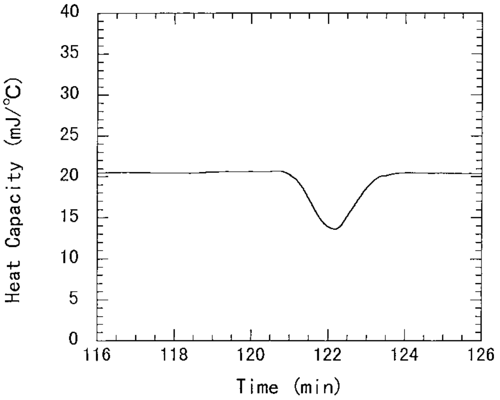

Fig. 6. Calculated heat capacity of a $BaTiO_3$ crystal obtained from the result of Fig. 5.

in Fig. 5, the modulated heat flow is almost sinusoidal except for the two successive sharp drops which indicate that the first-order phase transition takes place with two nuclei. Contrary to the above result for 100 s the amplitude of AC temperature becomes apparently small since the first-order phase transition happens near the top to the sinusoidal curve. This behavior appears accidentally and is not due to the short period. Then, the apparent heat capacity shows a dip as shown in Fig. 6. This is unusual behavior but an expected result as discussed above. As a result, in the heat capacity measurement for such a sharp first-order phase transition the amplitude in AC temperature should be small.

A light-irradiation type AC calorimeter is a more proper method to attain the small amplitude of modulated temperature. Using the AC calorimeter the heat capacity of a $BaTiO_3$ crystal has been measured [7]. The measurement was done under a quasi-isothermal condition, and the amplitude of AC temperature was a few mK. In this method, the AC temperature was detected by a lock-in amplifier with the frequency of 16.7 Hz, and then the deformation of the AC temperature was not observed directly. The result is shown in Fig. 7. A jump at the first-order phase transition takes place, and, furthermore, a sharp peak

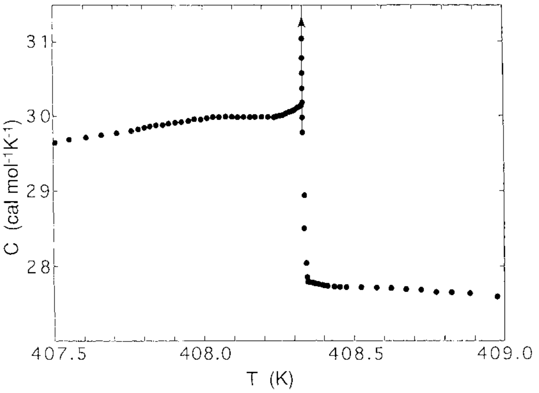

Fig. 7. Heat capacity of a $BaTiO_3$ crystal obtained from a light-irradiation type AC calorimeter [7]. For the energy units in the ordinate, 1 cal is equivalent to 4.1855 J.

corresponding to latent heat appears. Thus, we can obtain the detailed behavior of the heat capacity except for the magnitude of latent heat. Therefore, it is concluded that it is better to use small amplitude of AC or modulated temperature in order to obtain the detailed behavior of heat capacity at such sharp first-order phase transition.

However, it should be pointed out that the temperature-modulated differential scanning calorimeter is still useful for the study of a first-order phase transition, because except for the transition range, the heat capacity is determined easily and the latent heat is obtained by standard differential scanning calorimetry (DSC) which can be done simultaneously. For a $BaTiO_3$ crystal, with the AC temperature amplitude of 1.0°C, we obtained a typical result as shown in Fig. 8, which includes the heat capacity of a sample pan. Usually, when we use a relatively large amplitude of AC temperature, we get similar behavior at first-order phase transitions. In fact, for a $NaNO_2$ crystal, the similar behavior has been observed as seen in Fig. 9, i.e., we can determine the heat capacity denoted by ACC [8], except for the first-order transition range which begins from the temperature illustrated by a vertical dotted line and spreads over the range indicated by a dotted background line. At the second-order phase transition of about 165°C the shape of the heat capacities denoted by DSC and ACC coincides with each other as expected.

It is worth noting that the heat capacity at the beginning of the first-order phase transition exhibits

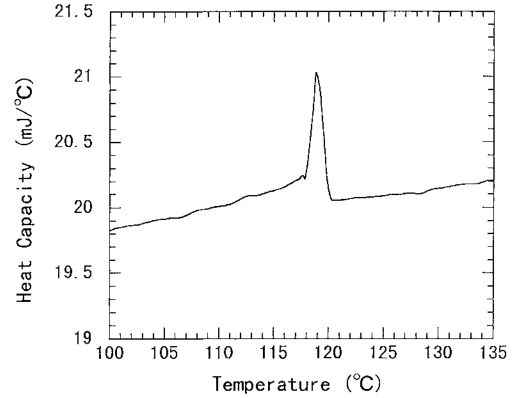

Fig. 8. Heat capacity of a $BaTiO_3$ crystal obtained from a temperature-modulated differential scanning calorimeter, where the measurement was performed under the large amplitude of modulated temperature, 1.0°C.

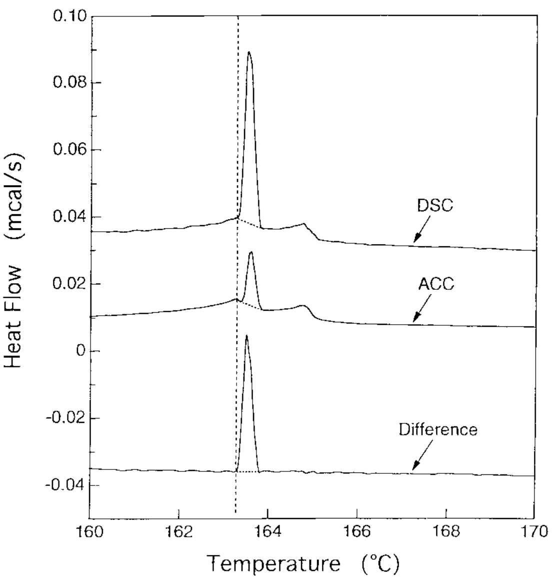

Fig. 9. Comparison among the heat capacity denoted by ACC, the total heat flow denoted by DSC, and their difference in a $NaNO_2$ crystal, obtained from a temperature-modulated differential scanning calorimetric measurement [8]. The latent heat at the first-order phase transition temperature, 163.50°C can be obtained from the part of the area above the dotted background line in the curve denoted by DSC. At the second-order phase transition temperature, 165.0°C, the curves denoted by DSC and ACC coincide with each other as expected. For the energy units in the ordinate, 1 cal is equivalent to 4.1855 J.

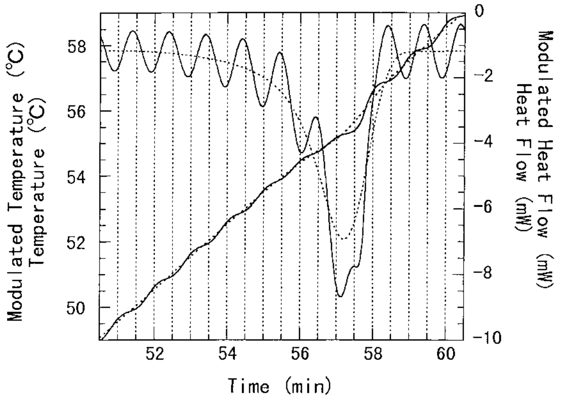

Fig. 10. Result of temperature-modulated differential scanning calorimetry in a liquid crystal, octyloxycyanobiphenyl, at the first-order phase transition of crystalline to smectic A phase. The arrangement of each curve is the same as in Fig. 3. The vertical dotted lines are shown for convenience to see the relation among the phases.

common behavior as seen in Fig. 8 and in ACC of Fig. 9. It might be due to the fact that, when the first-order phase transition begins, the sinusoidal temperature is deformed, and, as a result, heat capacity deviates downward and/or shows a small peak as seen in the above figures.

A further study was carried out at the first-order phase transition of a liquid crystal, octyloxycyanobiphenyl. The modulated heat flow is shown in Fig. 10, which is the same plot as Figs. 3 and 5 for a $BaTiO_3$ crystal. As can be seen in Fig. 10, the modulated temperature of the sample side is slightly deformed and at the same time the phase of the modulated heat deviates from the regular periodicity due to non-linear effects at the first-order phase transition. From the analysis of these data, we finally got the plot of Fig. 11. A shallow dip appearing at temperature above the peak of the heat capacity is unusual behavior. This might be caused by the above non-linear effects. It is possible to reduce the effects by using a much smaller amplitude of AC temperature. In fact in the light-irradiation type AC calorimetric measurement where the amplitude of AC temperature was a few mK, we have obtained normal behavior in the heat capacity which is flat above the transition temperature as seen in Fig. 12 [9]. Then, it is important that the amplitude of AC temperature be as small as possible in the study of first-order phase transitions to obtain the detailed behavior of heat capacity.

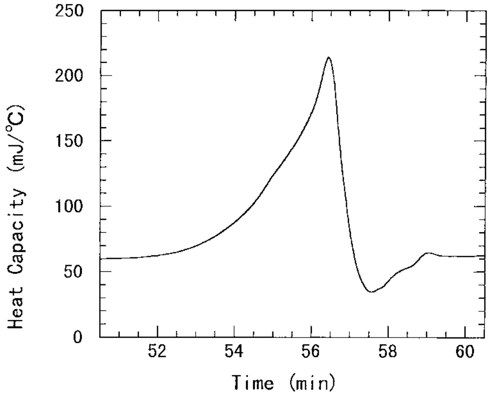

Fig. 11. Calculated heat capacity of a liquid crystal of octyloxy-cyanobiphenyl from the result in Fig. 10.

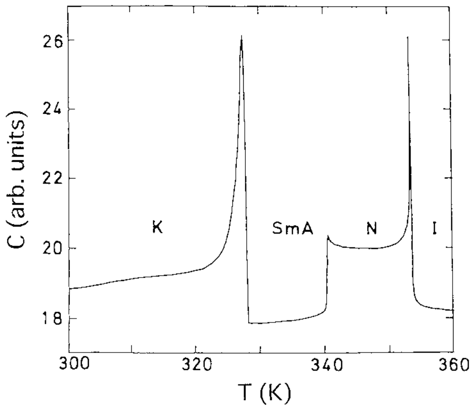

Fig. 12. Heat capacity of a liquid crystal of octyloxycyanobiphenyl obtained from a light-irradiation type AC calorimeter [9]. Above the first-order phase transition from crystalline (K) to smectic A (SmA) phase, the heat capacity is flat.

4. Conclusions

For the heat capacity measurements at first-order phase transitions we can use both a temperature-modulated differential scanning calorimeter and an AC calorimeter.

1. A heat capacity measurement at a first-order phase transition should be performed with the amplitude

of AC or modulated temperature as small as possible. From the measurement made under such a condition, we can obtain the detailed behavior of the heat capacity except for the magnitude of latent heat.

2. Using a temperature-modulated differential scanning calorimeter, we can clearly distinguish the part of latent heat from the part of linear heat capacity and then estimate the magnitude of the latent heat with high accuracy.
3. When we are interested in the kinetics of phase boundary, the temperature-modulated calorimetric measurement should be carried out under the condition that the time-derivative of the modulated heating is positive, i.e., there is no cooling process during the measurement. For a further consideration on the results of the calorimetric measurements, it is highly desirable to discuss based upon a structural evidence of a hybrid region.

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