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TRUE BEHAVIOR OF HEAT CAPACITY IN α, INCOMMENSURATE AND β PHASES OF QUARTZ

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ABSTRACT

Detailed behavior of the heat capacity of quartz at α-to-incommensurate transition (T_C) and incommensurate-to-β transition (T_Q) is revealed by ac calorimetry. The heat capacity anomaly at T_C is a typical one at a first-order transition and its width is a few hundred mK at most in contrast with a rather wide anomaly observed by differential scanning calorimetry. In cooling, a clear hump which indicates a second-order transition takes place at T_Q, in heating however the hump smears out due to some transient phenomena accompanied by the first-order transition which lies just below T_Q.

INTRODUCTION

Recently it has been established that there exists an incommensurate phase between α and β phases of quartz which lies in a narrow temperature range of 1.25 ± 0.05 K in cooling (ref.1 and see references in it). To get a further knowledge of the phase transitions, it is of interest to study thermodynamic properties. Prior to the establishment of the incommensurate phase, Bachheimer (ref.2) suggested a second-order transition at about 1.3 K above the well-known first-order transition (T_C, hereafter) in cooling based upon the measurements of thermal expansion and elastic compliance. Later, Dolino et al. (ref.3) also reported an anomaly of heat capacity at the incommensurate-to-β phase transition (T_Q, hereafter) from an experiment by differential scanning calorimetry (DSC).

In a consideration for the thermodynamic properties the detailed result of heat capacity is indispensable. A DSC experiment makes possible to obtain heat capacity under not a steady state but a temperature scanning condition and then, does not give precise behavior of heat capacity especially around a transition temperature. We propose that in such a case ac calorimetry works as one of powerful tools in the observation of the detailed temperature dependence of heat capacity. In the present paper, the results obtained from ac calorimetry will be shown and compared with that obtained from DSC.

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EXPERIMENT AND RESULTS

The ac calorimetry technique has widely been applied to heat capacity measurements in solids, liquid crystals and liquids. The amplitude of ac temperature of a sample, T_{ac}, is inversely proportional to the heat capacity as given by $C = Q/\omega T_{ac}$, where Q is the amplitude of ac input heat energy and ω is angular measuring frequency. In the case when using light irradiation as the input heat energy, a small sample with for instance 10 mg in weight is required in the ac measurement and furthermore, the contribution of a sample cell, heater, etc. to the heat capacity of the sample can be reduced in contrast with a direct heating ac method. The general principle of ac calorimetry and details of the present method have already been mentioned elsewhere (ref.4) and hence, we do not discuss them further.

The sample was prepared from synthetic quartz. The size was about 0.05 mm in thickness and about 2×2 mm^2 in area, say about 5 mg. Both the sample temperature and the ac temperature were measured by chromel-alumel thermocouples with diameter of 50 µm. The thermocouple used was the standard type of Omega Engineering Co. The limit of error of the thermocouple is ± 0.75 % of the °C temperature being measured. The node of the thermocouple wires was glued to the sample surface with silver paste. The ac frequency was set by chopping light

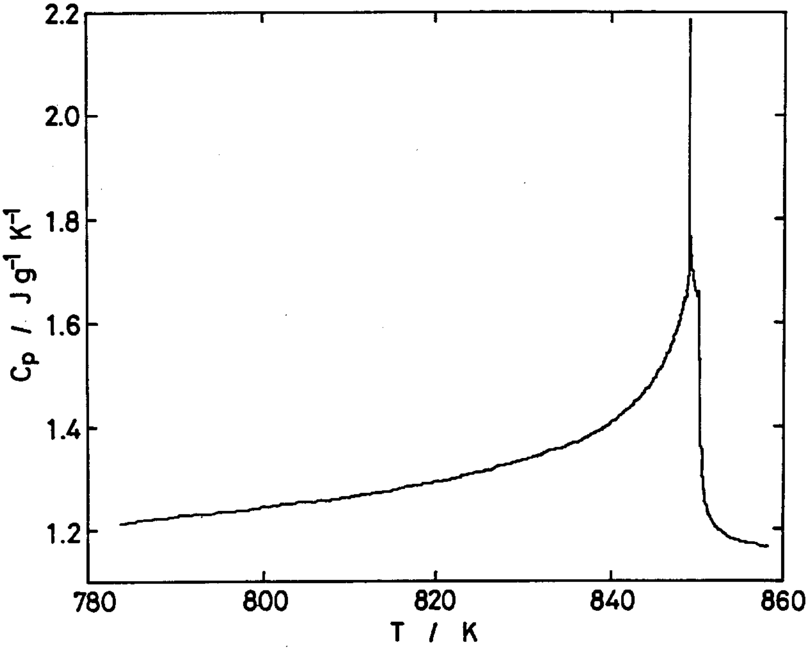

Fig. 1. ac heat capacity of quartz observed in cooling in a wide temperature range. Z-sector crystal was used as a sample.

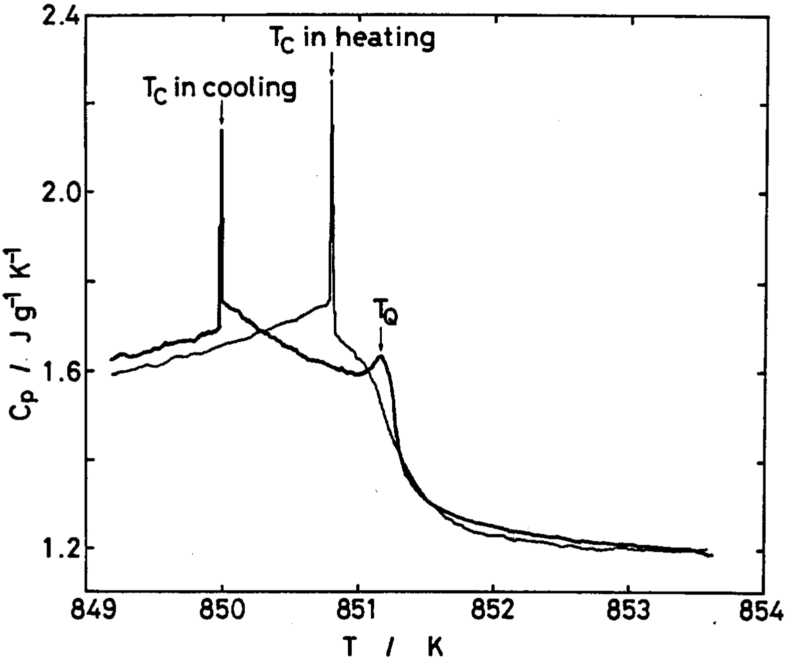

Fig. 2. ac heat capacity of quartz near T_C and T_Q. The thick and thin curves indicate the data with cooling rate of 0.014 K min^{-1} and with heating rate of 0.069 K min^{-1}, respectively. Z-sector crystal was used as a sample.

beam with 4 Hz usually. At room temperature where density of quartz: 2.64 g cm^{-3}; heat capacity: 0.799 J $g^{-1}K^{-1}$; thermal conductivity: 0.068 W $cm^{-1}K^{-1}$, the thermal diffusion length, $\sqrt{(2D/\omega)}$, was estimated to be about 0.5 mm where D is thermal diffusivity of quartz. Then, the thermal diffusion length was one figure bigger than the thickness of the samples, i.e., the experimental condition for ac heat capacity measurement was satisfied sufficiently in the present case. It is worth while pointing out that the ac temperature within a small part under the surface of the samples enclosed by a radius less than the thermal diffusion length is detected by the thermocouple locating at the center. The present ac calorimetry method has an advantage that the experiment can be carried out for a small portion with good quality. Our results were partly published elsewhere (ref.1). In this paper, we consider a different viewpoint that the results are compared with those obtained by the other experimental methods.

Figure 1 shows the heat capacity of quartz measured in cooling by ac calorimetry in a wide temperature range. The absolute values of heat capacity were estimated by comparing the result of Moser by an adiabatic method (ref.5). The detailed treatment was discussed in ref.1. Although the data of ref.5 were taken every a rather wide temperature-interval and are lacking near the transition

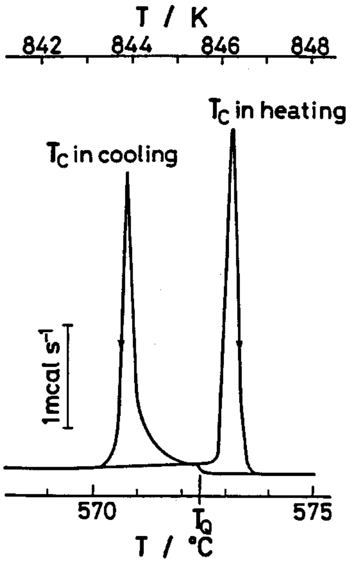

Fig. 3. DSC signal of quartz single crystal with 38 mg in cooling and heating rates of 0.62 K min^{-1} reproduced from ref.3.

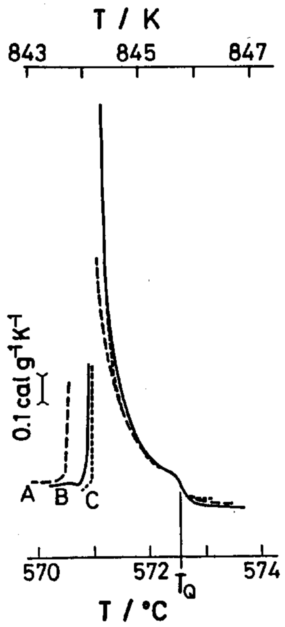

Fig. 4. Temperature dependence of the DSC heat capacity measured in cooling for the same sample as in Fig.3 (ref.3). The cooling rate was 1.25 K min^{-1} for run A, 0.62 K min^{-1} for run B and 0.31 K min^{-1} for run C.

temperatures, the result is consistent with our result. Figure 2 exhibits the ac heat capacity near T_C and T_Q, where the cooling and heating rates were 0.014 K min^{-1} and 0.069 K min^{-1}, respectively. Distinct temperature hysteresis takes place at the first-order transition of T_C. The width of the peaks at T_C is less than a few hundred mK. Below T_C and above T_Q but not very close to T_Q the both curves almost coincide with each other, where small difference might be due to slight drift during the measurement. In cooling, a clear hump appears at T_Q. When warming up just above T_C during cooling, we can also observe the hump at T_Q in this heating run. It is expected that the hump becomes sharper when a more qualified sample is used. On the other hand, the hump observed at T_Q disappears in a usual heating run as seen in Fig.2. This might be caused by some transient phenomena in consequence of the existence of T_C lying just below T_Q.

DISCUSSION

The heat capacity of quartz measured by DSC was reproduced in Figs.3 and 4 from Figs.1 and 2 of ref.3, respectively. By comparing the present Figs.2 and 3, first there can be seen a discrepancy of the order of transition temperatures,

T_C in heating and T_Q; second in cooling there appears a clear hump at T_Q in the ac heat capacity but not in the DSC heat capacity; third the width of the DSC heat capacity at T_C is far bigger than that of the ac heat capacity and the peak height at T_C in DSC is larger than that in ac calorimetry; fourth the absolute values of T_C in both cooling and heating and T_Q are different between the two results.

The first should be related to a fast temperature-scanning rate in DSC, because the magnitude of the temperature hysteresis of T_C is 0.8 K in ac calorimetry and has a further big value of 2.4 K in DSC.

The second depends on the quality of the samples and also the fast temperature-scanning rate in DSC. When we used a little worse sample, e.g., a +X-sector sample which contains internal strains in comparison with a Z-sector one, only similar step-like behavior to the DSC result was observed at T_Q.

The third indicates that in DSC a latent heat anomaly at T_C usually becomes wider as temperature-scanning rate increases. It has been well-established that DSC peaks at first-order transitions should not be described in terms of peak height, peak width, shape index and baseline displacement, that is, the peaks are changed as a result of retardation of heat transfer in a DSC apparatus (see e.g., refs.6 and 7). The width observed in ac calorimetry seems to be close to true one. On the other hand, the ac heat capacity does not exhibit the exact height at a first-order transition in principle (ref.4) and takes a small value. At a first-order transition, the transition enthalpy can be estimated from the DSC heat capacity.

The fourth is partly due to the difference of the samples and partly due to the accuracy of temperature measurement. As far as we are interested in the temperature dependence near the transition temperatures, this is not a serious problem in the present case.

The DSC experiment was carried out in various temperature-scanning rates by Dolino et al.(ref.3) in cooling runs (see Fig.4). They have said that the heat capacity curve is independent of the cooling rate from 0.31 to 1.25 K min^{-1} at least down to 1.25 K lower than T_Q. It is however rather difficult to predict from the above experiment what happens in a much slower temperature-scanning. Actually the present ac heat capacity provides the data with a slow cooling rate of 0.014 K min^{-1} (see Fig.1) and does not exhibit such a steep increase toward T_C as in Fig.4. Even for the present case it is preferable to measure under a much slower temperature-scanning, since the ac heat capacity shows behavior associated with transient phenomena near T_C and T_Q.

Recently it was pointed out that the divergences of the DSC heat capacity, the thermal expansion and the elastic compliance could be related by Pippard-Garland relations in the three phases of quartz (ref.8). This fact requires that the heat capacity increases steeply near T_C as in Fig.4. On the other hand, the

DSC result is inconsistent with the behavior of the ac heat capacity. It is puzzling that if the true behavior of the heat capacity is taken into account Pippard-Garland relations hold no longer.

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