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Phase transitions of quartz studied by a.c. calorimetry ☆

Haruhiko Yao [a,*], Ichiro Hatta [b]

[a] *Department of Physics, Tokyo Institute of Technology, Oh-okayama, Meguro, Tokyo 152, Japan*
[b] *Department of Applied Physics, Nagoya University, Nagoya 464-01, Japan*

Abstract

An a.c. calorimetric heat capacity measurement has been performed on high-quality synthetic quartz. It was found that at the incommensurate (IC)–β–phase transition, the heat capacity C_p of as-grown samples show critical behavior, i.e. there is a sharp peak at the IC–β transition. The shapes of the C_p are almost identical in both heating and cooling runs. However, when as-grown samples were annealed in the α-phase just below the α–IC transition, the C_p peak became considerably rounded and, at the same time, the transition temperature slightly increased. The shapes of the C_p peaks on heating and cooling became dissimilar for the annealed samples.

Keywords: A.c. calorimetry; Heat capacity; Incommensurate phase transition; Quartz

1. Introduction

The α–β transition of quartz has been studied by many researchers after its discovery by Le Chatelier in 1889 [1]. In 1983, Gouhara et al. found an intermediate phase between the α- and β-phases by X-ray diffraction topography [2] and a fine-beam X-ray Laue method [3]. Independently, Dolino et al. also reported the intermediate phase by differential scanning calorimetry (DSC) [4] and neutron diffraction [4, 5]. From the X-ray diffraction and neutron diffraction studies, the intermediate phase is characterized as an incommensurate (IC) phase.

The results for the heat capacities of quartz over a wide temperature range up to 1989 are summarized in the paper of Grønvold et al. [6], together with their results obtained by adiabatic shield calorimetry. Near the α–IC and IC–β transitions, Dolino et al. [4]

* Corresponding author.

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performed heat capacity measurement using DSC. From the measurement of various temperature scan rates, it was found that their results on cooling indicate the same behavior near the IC–β transition, however, there is a thermal hysteresis at the α–IC transition. Matsuura et al. [7] and Hatta et al. [8] performed heat capacity measurements in the same temperature range using a.c. calorimetry. From the measurement, the α–IC transition has been found to be first-order and the IC–β transition seems to be second-order. However, detailed behavior at the IC β transition is not yet clear, since it is sensitive to not only the quality of the samples but also their thermal history. In the present study, we undertook the detailed heat capacity measurement of high-quality samples by a.c. calorimetry, and clarify the detailed temperature dependence of the heat capacity at the phase transitions and the effects of thermal history near the phase transitions.

2. Experiment

Samples were prepared from the Y-cut plates of a Y-bar synthetic quartz crystal (Kinseki Ltd., Japan). The Z-growth sector was used as samples, because the Z-growth sector contains less OH impurity than other sectors [9]. The plate, 1 mm thick, was characterized by X-ray diffraction topography (Lang method) prior to the preparation of samples for the heat capacity measurement, and the best part in the plate was chosen where fewer dislocations and striations were included. Topographic observation indicated that few dislocations exist in the samples. The samples were thinned using a lapping mechine and corundum powder. The surface damage was etched off in 50% hydrofluoric acid for 30 min. Typical sample dimensions were 4 mm^2 in area and 50 μm in thickness.

The heat capacity measurements were performed with a fully automated high-temperature a.c. calorimeter. The design is essentially the same as other light-irradation-type a.c. calorimeters [10]. The temperature of a sample was measured with two thermocouples composed of chromel and alumel wires (50 μm in diameter, Omega Engineering Co., USA) that were glued to the sample with silver paste. The sample suspended with the thermocouple wires was put inside a cavity made of a massive nickel block that serves as a thermal bath. The sample was periodically heated by a chopped light beam from a halogen lamp. The resulting temperature oscillation was detected with one of the thermocouples and fed to a lock-in amplifier (Model 124 A, Princeton Applied Research (PAR)) through a preamplifier (Model 116, PAR, transformer mode). The analog output of the lock-in amplifier was read every 5 s with a digital multimeter (Model TR6856, Takeda-Riken, Japan). The amplitude of the temperature oscillation was about 3 mK. The absolute temperature of the sample was monitored by reading the voltage of the other thermocouple with a digital multimeter (Model 195 A, Keithley Instruments). The accuracy of the absolute temperature values is $\pm$ 0.5% around the transition temperatures according to the specification for the thermocouple wires. The bath temperature was controlled by a temperature controller (Model 5301-E, Artronix, USA) with a short-time stability of 1 mK. The inside of the calorimeter was evacuated with an oil-sealed rotary pump.

The basic equation for determining heat capacity by a.c. calorimetry [11] is given by

$$C_p = P_0/\omega T_{ac} \tag{1}$$

where C_p is the heat capacity of a sample, with addenda such as the paste and thermocouples, P_0 is the heat flux absorbed by the sample, ω is the measuring frequency, and T_{ac} is the temperature amplitude of the sample. The validity of Eq. (1) has been tested by measuring T_{ac} as a function of frequency ω at a fixed temperature, and then the chopping frequency was set to 4 Hz.

3. Results and discussion

The temperature dependence of the heat capacity near the α–IC and IC–β transitions of high-quality as-grown quartz is shown in Fig. 1(a) and (b). Note that the sample was never heated up after its growth. T_c and T_i indicate the α–IC and IC–β transition temperatures, respectively. At the IC–β transition, the heat capacity exhibits a sharp peak with critical behavior. The shapes of the peak on heating and on cooling are almost identical. No thermal hysteresis was observed at T_i. The above facts reconfirm that the IC–β transition is second-order and, furthermore, it was found that the heat capacity exhibits critical behavior. However, the α–IC transition is first-order as previously reported [7,8]. The contribution of latent heat appeared at the mean temperature at the α–IC transition (see crossed points in Fig. 1(a) and (b)). A thermal hysteresis of 0.9 K was also observed in T_c.

Fig. 2(a) and (b) show the results of successive runs for an as-grown sample. The sample was heated up from room temperature (RT) in 7 h, and heating and cooling runs were repeated between 843 and 850 K. Since the scanning rate was set to 0.05 K min^{-1}, each run took $\sim$ 2.3 h. At the beginning, the heat capacity showed a sharp peak near T_i. In the later runs, the C_p peak smeared out and the shapes of the anomaly on heating and cooling became dissimilar as seen in Figs. 2(a) and (b). Simultaneously, T_i increased slightly. After the heat treatment described above, the temperature range of the IC phase expanded from 0.2 K (as-grown) to 0.4 K (heat-treated) on heating, and from 1.1 to 1.3 K on cooling under the condition indicated above. The rounding of the peak appeared particularly on heating from the α-phase.

To clarify what causes the rounding of the C_p peak, we have made the following measurements to examine the effects of heat treatment. Fig. 3 shows the result of the sequential runs described below. At first, an as-grown sample was heated up from RT to 843 K in 8 h and then, the first heating (1H) and cooling (1C) runs were carried out to record the heat capacity for the as-grown sample. Note that the shapes of the C_p peak are almost the same in the heating and cooling runs. After the first runs, the sample was annealed at $T_c - 4$ K for 43 h. Then, the second runs (2H, 2C) and the third heating run (3H) were performed. It is clearly seen in Fig. 3 that the C_p peak is significantly rounded after the annealing at $T_c - 4$ K. Next, the sample was annealed at $T_c + 4$ K for 43 h and then, the third cooling (3C) and the fourth heating (4H) runs were performed. The shapes of the anomaly are almost the same as those of 2H, 2C and 3H after annealing at $T_c - 4$ K.

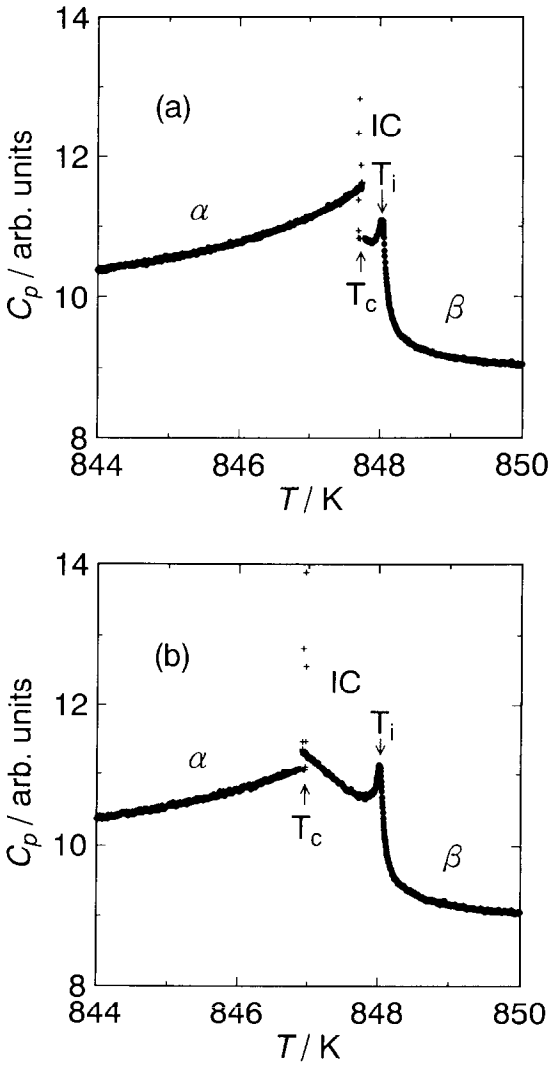

Fig. 1. Heat capacity of an as-grown quartz sample in the α-, incommensurate (IC) and β-phases. (a) Heating. (b) Cooling. Both heating and cooling rates were 0.05 K min^{-1}. At the α–IC transition, + indicates the apparent heat capacity at the mean temperature. Note that the curve obtained by connecting the crosses is not straight due to the existence of latent heat. Comparing the results on heating and cooling, we can see a large thermal hysteresis at the α–IC transition, and coincidence near the IC–β transition and above this temperature.

Fig. 4 shows the result of the other sequential runs described below. In the measurement, an as-grown sample was heated up from RT to 843 K in 7 h and then, the first heating run (1H) was performed to record the heat capacity for the as-grown sample. After the run, the sample was annealed at $T_c + 4$ K for 43 h. After the annealing, the first cooling run (1C) and the second runs (2H, 2C) were performed. As seen in Fig. 4, the

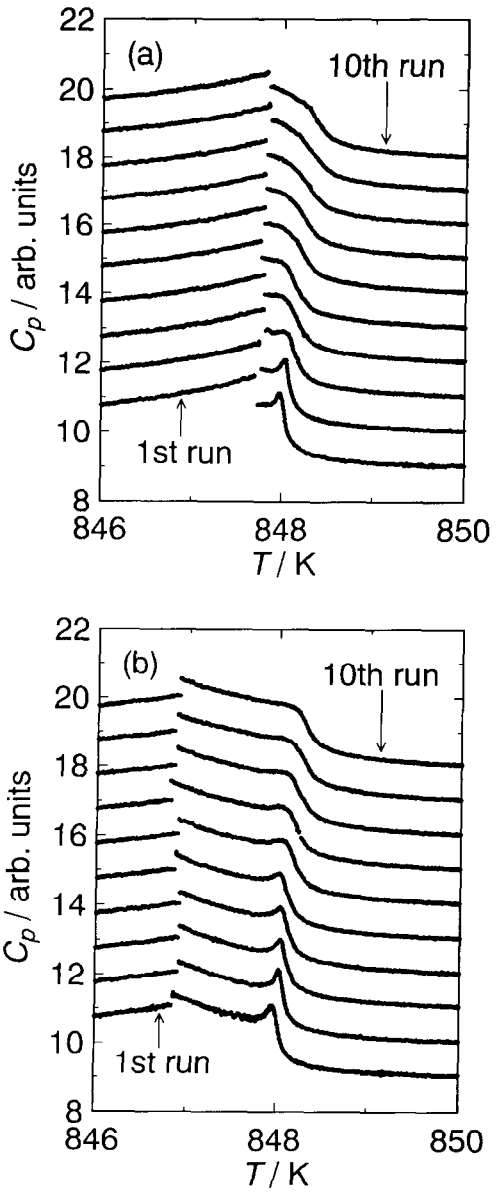

Fig. 2. Heat capacity variation obtained from the successive runs. (a) Results in heating runs. (b) Results in cooling runs. For the thermal treatment see text. The C_p data are drawn from the 1st run to the 2nd run by shifting consecutively for convenience. The IC–β transition temperature increased slightly and the shape became broad with each run.

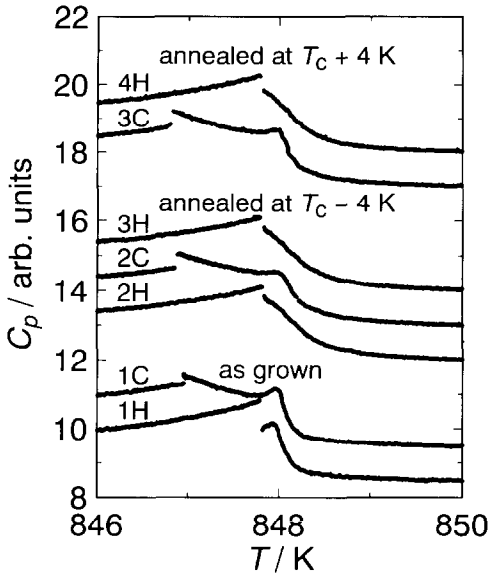

Fig. 3. Effects of annealing in the α-phase on the temperature dependence of the heat capacity, together with the results for the β-phase. The results for the 1st heating (1H) and cooling (1C) runs are for an as-grown sample. The results for the 2nd runs (2H, 2C) and the 3rd heating run (3H) are for the sample annealed at $T_c - 4$ K. Results for the 3rd cooling (3C) and 4th heating (4H) runs are for the sample annealed at $T_c + 4$ K. The data are moved in a vertical direction as described in the caption of Fig. 2.

anomaly of 1C is almost the same as that of 1H. Thus, the first effects of annealing at $T_c + 4$ K are small, in contrast to that at $T_c - 4$ K. Next, the sample was annealed at $T_c - 4$ K for 43 h and then, the third runs (3H, 3C) were performed. Similar to 2H and 2C in Fig. 3, the anomaly significantly rounded after annealing at $T_c - 4$ K.

The present results are consistent with the former a.c. calorimetric results [7, 8]. The critical behavior near the IC–β transition was not evident in the previous results. Furthermore, the shapes of the anomaly on heating and on cooling are rather different in the previous results. This might be due to the careless heat treatment in the previous measurement.

In general, an IC-phase is characterized by the modulation wave-vector q and amplitude η. When the system is brought to a non-equilibrium state, for instance by an abrupt change of temperature, both q and η vary, yielding new equilibrium values. However, it is generally expected that the relaxation of q proceeds more slowly than that of η close to T_c. In this case, the heat capacity can be divided into q-dependent and q-independent parts with respect to the relaxation time. This type of C_p relaxation has been found in the IC-phase of $NaNO_2$ close to the IC–commensurate phase transition [12]. In the present study, the sample temperature oscillated at a frequency of 4 Hz. Therefore, it is likely that the wave-vector q cannot follow the temperature oscillation near T_c and that the present C_p data close to T_c represent the q-independent part of the C_p in the IC-phase.

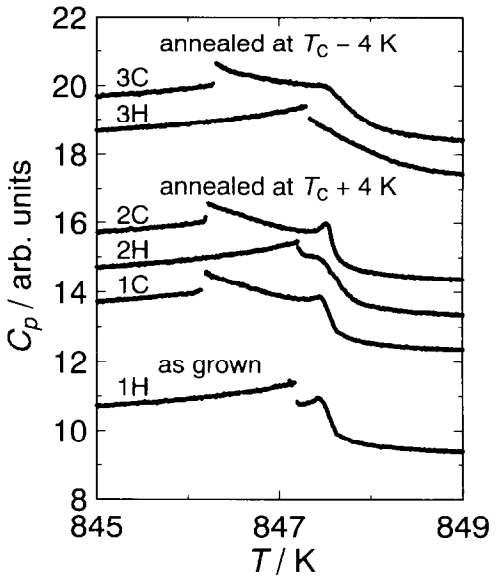

Fig. 4. Effects of annealing in the β-phase on the temperature dependence of the heat capacity, together with the results for the α-phase. The results for the 1st heating run (1H) are for an as-grown sample. The results for the 1st cooling run (1C) and the 2nd runs (2H, 2C) are for the sample annealed at $T_c + 4$ K. The results for the 3rd runs (3H, 3C) are for the sample annealed at $T_c - 4$ K.

It has been pointed out recently that a single-q IC ($1q$) phase at zero stress exists in a narrow temperature range of 0.05–0.1 K, between the usual triple-q IC ($3q$) phase and the β-phase [13]. However, as far as observed by the present a.c. calorimetry, we could not obtain an anomaly related to the $1q$–$3q$ transition. It is not evident that this is due to either the quality of the samples or the intrinsically small anomaly.

Theoretically, it has been predicted by fluctuations that the IC–β transition is of first-order [14]. However, there is no evidence that the IC–β transition is of first-order for high-quality as-grown quartz samples in the experiments, while the heat capacity exhibited critical behavior near the IC–β transition. The preliminary results of the analysis with the renormalization-group expression show that the anomaly can be explained by the three-dimensional XY model. A detailed analysis of the critical behavior is now in progress.

It is seen from Figs. 3 and 4 that the effects of heat treatment were significant when an as-grown sample was annealed at $T_c - 4$ K. The difference in the activation energies at $T_c - 4$ K and $T_c + 4$ K is negligibly small. Notwithstanding, the rounding of the C_p peak at T_i was promoted at the lower temperature, $T_c - 4$ K. Thus, the effects of heat treatment are associated with the phase at which the sample was annealed. We also performed successive runs between the IC- and β-phases, but the C_p peak was not rounded over 48 h (data not shown). Hence, the rounding does not occur by annealing in the IC- and β-phases. Therefore, it is concluded that the rounding of the C_p peak is promoted when a sample is annealed in the α-phase. Although full recovery was not

seen in our experiment, small recovery was sometimes observed after a sample was annealed in the β-phase, as seen in 2C in Fig. 4 and 3C in Fig. 3.

The origin of the rounding is unclear at present. It is known that milky precipitates are formed by heat treatment due to the decomposition of OH impurity [15]. However, the Z growth sector of normal quality is not deteriorated by heat treatment, in contrast to the $-$X growth sector [16]. Since it has been reported that the formation of the precipitates has no relationship to the α–β transition temperature [15], it is inconsistent with the present results. These facts suggest that the rounding is not caused by OH impurity. Since it has been shown that the IC-phase of quartz is very sensitive to the presence of small impurity concentrations [17], it is possible that the rounding is caused by other impurities. At any rate, the strong correlation with annealing in the α-phase will be a key to understanding the rounding observed in this study.

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