Evaluation of the Specific Heat Anomaly of $RS_{1-x}-ARS_x$

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Thermal properties of $RS_{1-x}-ARS_x$ studied by an ac calorimetric technique are reported. In order to obtain better values of the transition entropies for the mixed crystals, two problems have remained: evaluation of absolute value of the specific heat and precise determination of background of the very small anomaly. A method to evaluate the absolute value using the ac–calorimeter has been developed and determination of the background has been improved. Finally refinement of the value of the transition entropy are given for these mixed crystals.

I. INTRODUCTION

The mixed crystal system of $RS_{1-x}-ARS_x$, which is composed of Rochelle salt ($NaKC_4H_4O_6 \cdot 4H_2O$, abbreviated to RS) and ammonium Rochelle salt ($NaNH_4C_4H_4O_6 \cdot 4H_2O$, ARS), exhibits an interesting phase diagram. According to dielectric study by Makita and Takagi, [1] this system can be divided into four concentration regions: $0 \leq x \leq 0.025$ (region I), $0.025 \leq x \leq 0.18$ (region II), $0.18 \leq x \leq 0.90$ (region III), $0.90 \leq x \leq 1$ (region IV). The mixed crystals in the region I undergo two successive phase transitions. Only a phase between the two transition temperatures is ferroelectric, where the polar axis is parallel to the a–axis. The upper and lower phases sharing the boundaries with the ferroelectric one are both paraelectric with the same symmetry. No phase transition has been confirmed in the region II, though a broad maximum in the dielectric constant along the a–axis has been observed. In the region III, the mixed crystals have only one transition temperature, below which a ferroelectric phase appears with the spontaneous polarization along the a–axis. The mixed crystals in the region IV undergo a phase transition to a polar phase with decreasing temperature. However the polarization, which is parallel to the b–axis, can be reversed by stress, not by electric field.

In this way, the dielectric behavior of $RS_{1-x}-ARS_x$ has variety according to the variation of x. Many experimental and theoretical investigations on these mixed crystals were made by many workers from various points of view. Nevertheless, the mechanism of their phase transition has not been clear yet. We have been studying the thermal properties of $RS_{1-x}-ARS_x$, as well as the dielectric [2] and the structural [3–5] ones. We have measured the specific heat for several mixed crystals of different concentrations belonging to each region by an ac calori-metric technique. The results of the measurements have been already reported as for the regions IV [6] and III [7].

The specific heat of the mixed crystals in the region IV shows a very large sharp peak at the transition temperature and this behavior is quite similar to that in ARS. Since the peak shows a thermal hysteresis, we have confirmed that the phase transition in the region IV is of the first order as pointed out by Makita and Takagi [1]. At concentrations approaching the boundary between the regions IV and III, the anomaly does not behave like that of ARS.

In the region III, the excess specific heat at the transition temperature is very small. It becomes still smaller as x decreases. The anomaly appears in a broad temperature range compared to that in the region IV. In the previous work, we have calculated the transition entropy in the region III from the excess specific heat in the anomalous temperature region. It was shown that the transition entropy increases with increasing of x. However, we have not calculated that in the region IV. Since the large peak includes a contribution of a latent heat, the amount of the excess specific heat at the peak observed by use of the ac calorimetric technique depends on the heating frequency. [8]

In the measurements using our ac–calorimeter, we can observe the temperature dependence of the relative value of the specific heat with good accuracy. However, evaluation of the absolute value is not so easy. When we calculated the transition entropy in our previous paper, we normalized the magnitude of the specific heat observed for $RS_{1-x}-ARS_x$ to that for RS reported in a literature [9]. In order to get the absolute value at that time, we assumed that the magnitude of the lattice part of the specific heat was independent of x. On the other hand, estimation of the temperature range with the anomaly
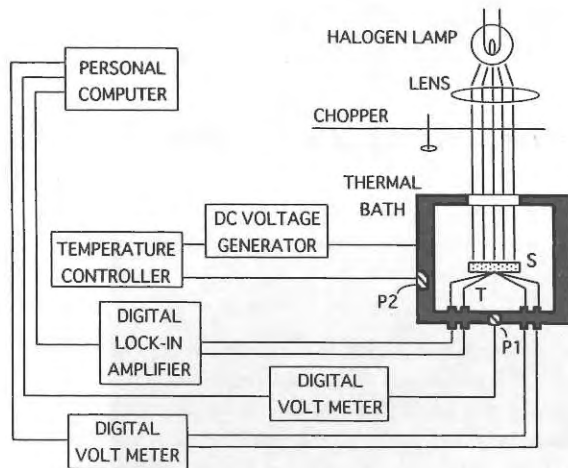

Fig. 1. Schematic diagram of our ac–calorimeter. S: Sample, T: Thermocouple, P1: Pt Thermometer for temperature measurement, P2: Pt Thermometer for temperature control.

was quite difficult because of the very small and broad anomaly. Therefore, it seems that there is room for improvement in determination of the background of the anomalous specific heat.

In this work, we have checked on the absolute value of the specific heat for the mixed crystals over the whole system. In order to do this, we have developed a method to estimate the absolute value of the heat capacity using the ac–calorimeter. Moreover, we have improved the way of estimation of the anomalous part of the specific heat using a systematic determination of the background. Then we have calculated the transition entropy again and refined the previous result. The refined transition entropy shows similar x dependence to previous one, though its value is larger than the previous value in the whole of the region III. A difference between the two results arises when present and previous values are compared with the value for RS [9]. The discussion about it will be given.

II. EVALUATION OF ABSOLUTE VALUE OF THE SPECIFIC HEAT

A. Experimental conditions

Our ac–calorimeter is schematically shown in Fig. 1. In our ac calorimetric measurements, a sample is periodically heated by chopped light. In this study, the chopping frequency was 3Hz. The sample configuration was plate type. The typical dimension of the sample was about $2 \times 2 \times 0.1 mm^3$. The light–irradiated face of the specimen was coated with graphite for the sake of efficient absorption of the radiation energy. Two pairs of chromel-constantan thermocouples were attached to the opposite side of the specimen with a small amount of GE7031 varnish. These thermocouples were used to measure the ac– and dc–component of the sample temperature varying periodically as a response to the periodical heating.

B. Process of evaluation

In the ac calorimetric technique, the heat capacity C is given by

$$C = \frac{Q}{\omega \cdot T_{ac}}, \qquad (1)$$

where Q is the amplitude of the ac heat flow supplied to the sample, T_{ac} is the amplitude of the ac temperature and ω is the angular frequency. The heat capacity is obtained from Eq. (1) by measuring T_{ac} under a constant ω. Sensitivity of the measurement by this technique is very high with respect to the temperature dependence of the heat capacity. However we usually obtain only the relative value of the heat capacity because it is quite difficult to determine the value of Q in our ac–calorimeter. In addition, in the case of our measurements, the measured heat capacity includes a contribution of appendages, i.e., varnish, graphite, thermocouples, etc. It can be considered that C in Eq. (1) is approximately given by the sum of the heat capacity of the sample $C^{(s)}$ and that of the appendages $C^{(a)}$. So we rewrite Eq. (1) as

$$C^{(s)} + C^{(a)} = \frac{Q}{\omega \cdot T_{ac}}. \qquad (2)$$

If we know the value of Q and $C^{(a)}$, we can obtain the absolute value of $C^{(s)}$ according to Eq. (2) from usual ac calorimetric measurement. We will show how to evaluate the absolute value of the specific heat of RS_{1-x}–ARS_x using our ac–calorimeter.

We used two kinds of standard sample, copper and nickel, in order to estimate Q and $C^{(a)}$. The light source is a stable halogen lamp. Therefore we believe that Q was constant in all the measurements. It is noted that the amount of the appendages must be constant for all the samples. We have checked that their amount is almost constant by cumulative weighing. A fluctuation of T_{ac} was about $\pm 2mK$ ($\sim 2\%$). These measurements have been made at 280K. Temperature dependence of $C^{(a)}$ was determined by subtracting the values of the heat capacity calculated for copper with the Debye model from the values measured for copper containing the appendages in the temperature range from room temperature to about 10K. Thus the absolute value of $C^{(s)}$ at 280K is obtained, and then the values at the other temperatures can be determined from the temperature dependence of the relative heat capacity of the sample and $C^{(a)}$. Finally we have obtained the absolute specific heat per gram dividing the absolute heat capacity by the sample mass. The error of the obtained values is estimated to be within 30%.

C. Results

In Fig. 2, we show the absolute values of the specific heat at 280K for RS_{1-x}–ARS_x of some concentrations
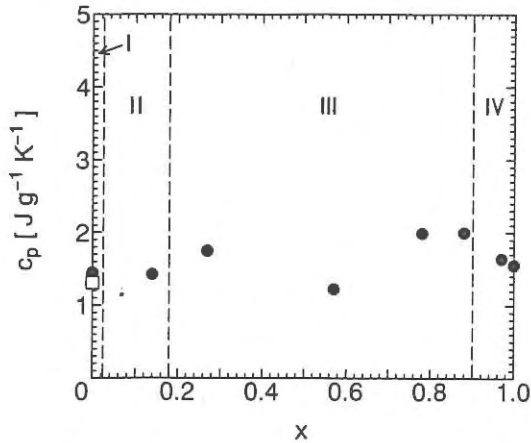
Fig. 2. Absolute value of the specific heat of RS$_{1-x}$–ARS$_x$ at 280K. Close circles show our results and a open square is the value for RS obtained by Tatsumi *et al.* [9] Roman numerals indicate the regions.
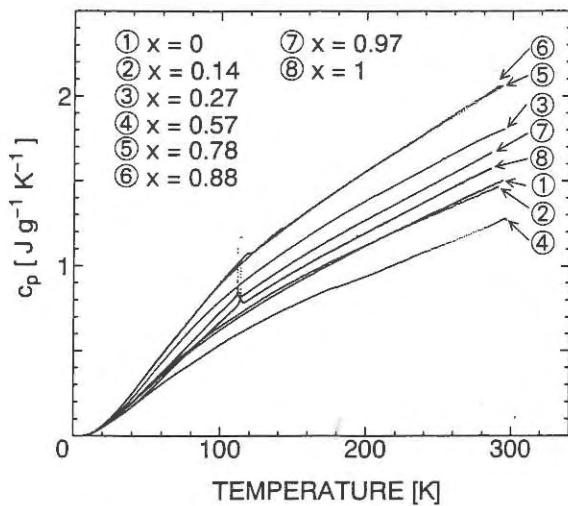

Fig. 3. Temperature dependence of the absolute specific heat of some mixed crystals.

Fig. 4. Δc_p vs. $T - T_c$, where Δc_p is the excess specific heat, T is the temperature and T_c is the temperature at which Δc_p indicates its maxmum. $T_c \simeq$ 200K ($x = 0.27$), 175K ($x = 0.57$), 139K ($x = 0.78$) and 118K ($x = 0.88$).

together with that for RS measured by Tatsumi *et al.* [9] using an adiabatic calorimeter. Figure 2 shows that our value for RS agrees with that from Tatsumi *et al.* It indicates that such evaluation of the absolute value of the specific heat gives adequate results. Consequently the absolute specific heat of RS$_{1-x}$–ARS$_x$ can be thought to be nearly independent of x. The temperature dependence is shown in Fig. 3.

III. ESTIMATION OF THE ANOMALOUS PART OF THE SPECIFIC HEAT

In order to calculate the transition entropy, we have to estimate the anomalous part of the specific heat as exactly as possible. We previously determined a background of the anomaly from the data in the temperature regions far above and below the transition temperature
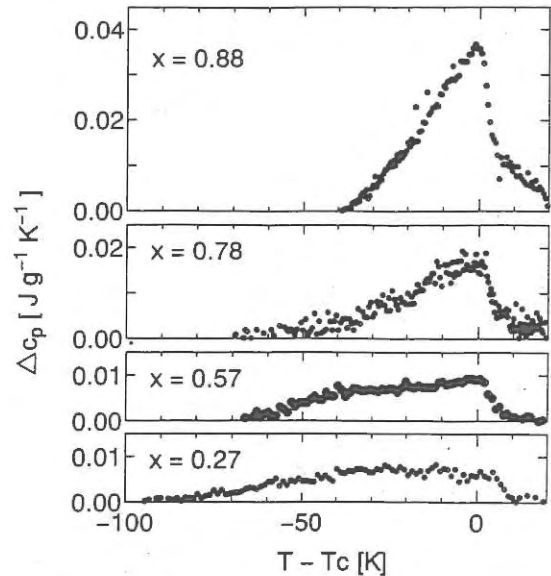
by a least–squares fit. However it seems that anomalous region extends much far lower temperature, though the excess specific heat is very small in the region III. On the other hand, the lower temperature limit of the data was about 80K. This temperature might not be low enough because of a possible distribution of the anomaly below 80K. Moreover, the background determined by such a way depends on the choice of the temperature region for the fit. Therefore we have introduced more systematic way to determine the background using the data between room temperature and about 10K.

It is considered that the temperature dependence of the lattice part of the specific heat scarcely depends on x. [7] Therefore, if the specific heat c_p is normalized to the same value at a temperature for RS$_{1-x}$–ARS$_x$ of all x, their $c_p - T$ curves coincide except for the anomalous part, where T is the temperature. Since the temperature region with the specific heat anomaly is different among the mixed crystals for different x, we can obtain the lattice part of the specific heat in the anomalous temperature region for one x from the $c_p - T$ curves for the other x. We have determined the background of the anomalous specific heat making use of the lattice part of the specific heat obtained in this way. Then we can evaluate the specific heat anomaly. In Fig. 4, we show the excess specific heat Δc_p against $T - T_c$ for some concentrations in the region III, where T_c is the temperature at which Δc_p indicates its maximum. The values of T_c are about 200K for $x = 0.27$, 175K for $x = 0.57$, 139K for $x = 0.78$ and 118K for $x = 0.88$, respectively. It can be seen that, as x decreases, the maximum of Δc_p also decreases and there is a wide stretch of Δc_p toward lower temperature.
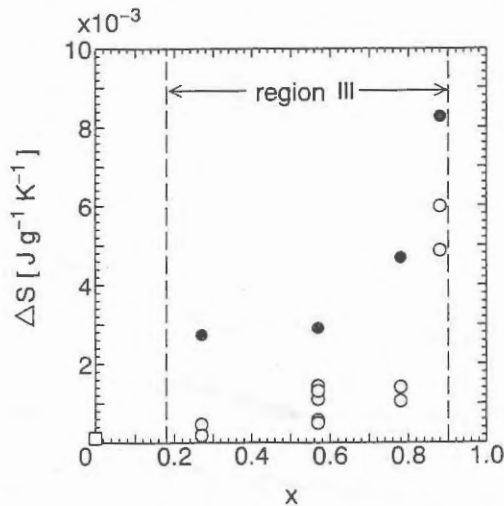
Fig. 5. x dependence of transition entropy ΔS. Close and open circles are our values in the present and the previous work, respectively. A open square shows the result for RS obtained by Tatsumi *et al.* [9]; according to them ΔS is almost the same around both the upper and lower transition temperature.

IV. RESULTS AND DISCUSSION

We have calculated the transition entropy in the region III from the excess specific heat estimated by using of the method just described above. We believe that the previous result is refined. Present and previous results are shown in Fig. 5 together with that for RS obtained by Tatsumi *et al.* [9] Although the present values are larger than the previous values in the whole of the region III, a tendency to increase with x is the same in both results. A difference between the two results is seen around small x. In the previous result, the transition entropy approaches the value for RS as x decreases. However, in the present one, there seems to be a gap of the transition entropy between the crystals in the region I and those for smaller x in the region III.

In a study of the dielectric relaxation of $RS_{1-x}-ARS_x$, an interesting result has been reported. [2] The elementary process of dipolar relaxation in the region III is explained by using the double-minimum potential model. However, this model is not valid for $x = 0$ (region I). It could be considered that the difference of the elementary process between in the two regions is reflected to the gap of the transition entropy described above. Consequently, from the gap of the transition entropy, it is suggested that there are some difference in the mechanism of the phase transition between the regions I and III.

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