

## Specific heat at a first-order phase transition: SbSI

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The temperature dependence of the specific heat of SbSI at zero  $E$  field and atmospheric pressure has been measured accurately from 83 to 330 K using an ac calorimetric method. It is confirmed that the first-order paraelectric-ferroelectric phase transition close to 290 K is in the neighborhood of a tricritical point. The measured curves show excellent agreement with Landau theory except for a small deviation within  $\pm 1$  K around the transition temperature. Close to  $T_c$  we see an additional contribution which on the high-temperature side varies with an exponent with values from 0.8 to 1.5 for different runs.

### I. INTRODUCTION

In cases where dipolar interaction is responsible for a phase transition into a uniaxial ferroelectric low-temperature phase the transition should obey simple Landau theory except<sup>1</sup> in a narrow "critical region" close to the phase transition temperature. This was established<sup>2</sup> for the second-order ferroelectric phase transition of triglycine sulfate (TGS), and also for the first-order transition<sup>3,4</sup> of BaTiO<sub>3</sub>, where in both cases the transition is far from a tricritical point. The temperature dependence of specific heat is quite weak in such cases. Recently, however, it was also shown<sup>5</sup> that the ferroelectric phase transition of NaNO<sub>2</sub> can be put into the Landau picture even if its specific heat has a much stronger temperature dependence. Normally, such strong temperature dependence can be expected in systems which are close to a tricritical point.

In order to study this problem further we have chosen SbSI which is known to have a tricritical point.<sup>6,7</sup> SbSI also has a number of the other interesting properties, including ferroelectricity<sup>8</sup> and photoconductivity.<sup>9</sup> SbSI is semiconducting<sup>9</sup> and pyroelectric,<sup>10</sup> and exhibits large electro-optical<sup>11</sup> and electromechanical<sup>12</sup> effects. The uniaxial paraelectric-ferroelectric phase transition occurring around 290 K has been studied with several techniques<sup>6-8,10-18</sup> showing a displacive<sup>16</sup> first-order<sup>6-8,13</sup> transition. SbSI goes second order when hydrostatic pressure is applied.<sup>6,7</sup> The pressure needed to reach the tricritical point is about the same as for KH<sub>2</sub>PO<sub>4</sub>

(Refs. 19 and 20) but more than an order of magnitude less than that needed for BaTiO<sub>3</sub>.<sup>4</sup> The temperature dependence of both the polarization and the dielectric constant has been suggested to be in accordance with first-order Landau theory,<sup>8,14,15</sup> but no one has been able to fit the measurements to the correct expressions given in Eqs. (2) and (3) below. In this respect we find the analysis done in Refs. 8, 14, and 15 too simple.

In this paper we present specific-heat measurements in a wide temperature range around the phase transition temperature using an automatized system based on an ac calorimetric technique.<sup>21</sup> The measurements are compared with Landau-theory behavior.

### II. THEORY

In Landau theory for first-order transitions the Gibbs energy,  $G$ , has to be expanded to the sixth power of the order parameter, here the polarization  $P$ :

$$G = G_0 + \frac{1}{2}a(T - T_0)P^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \dots \quad (1)$$

The coefficients  $a$  and  $c$  are positive, and  $b$  is negative. Standard calculations based on minimalization of the Gibbs energy give the following results for the square of the spontaneous polarization  $P_s^2$ , the inverse susceptibility  $\chi_T^{-1}$ , and the specific heat  $C_p^E$  for zero field  $E$ :

$$P_s^2 = \begin{cases} -b/2c + (a^{1/2}/c^{1/2})(T_d - T)^{1/2} & \text{for } T < T_1 = T_0 + 3b^2/16ac \\ 0 & \text{for } T > T_1 \end{cases}, \quad (2)$$

$$\chi_T^{-1} = \begin{cases} 4a(T_0 - T) + b^2/c - 2b(a^{1/2}/c^{1/2})(T_d - T)^{1/2} & \text{for } T < T_1 \\ a(T - T_0) & \text{for } T > T_1 \end{cases}, \quad (3)$$

$$C_p^E = C_l + \Delta C = C_l + \begin{cases} T(a^{3/2}/4c^{1/2})(T_d - T)^{-1/2} & \text{for } T < T_1 \\ 0 & \text{for } T > T_1 \end{cases}, \quad (4)$$

where

$$T_d = T_0 + \frac{b^2}{4ac} = T_1 + \frac{b^2}{16ac}. \quad (5)$$

$C_l$  is the usual lattice contribution to the specific heat, while  $\Delta C$  is due to the polarization.  $T_1$  is the phase transition temperature if the sample does not remain in a metastable phase. Because of the energy barrier between the ordered and the disordered state, hysteresis will always be observed, with a maximum possible range of  $T_d - T_0$ .  $T_d$  and  $T_0$  are the metastability limits on cooling and heating, respectively. The actual phase transition temperature we will denote by  $T_c$  which then is different for heating and cooling curves. The above given expressions also apply for a second-order phase transition ( $b > 0$ ) and for tricritical behavior ( $b = 0$ ) where in both cases the phase transition temperature  $T_c = T_0$ . From the expressions given above both  $P_s^2$ ,  $\chi_T^{-1}$ , and  $\Delta C/T$  should deviate from a linear temperature dependence in the low-temperature phase if  $T_d$  is close to  $T_1$ . This will be the case if  $b$  is small. The system is then close to a tricritical point, where  $T_d = T_0$  and the specific heat in the ferroelectric phase goes with an exponent of one-half instead of showing the usual Landau step.

### III. EXPERIMENTAL METHOD

The sample used in our measurements was in the shape of a long thin rectangular prism with dimensions  $7 \times 0.6 \times 0.1$  mm<sup>3</sup>, the polar axis being along the long edge. It was grown by vapor transport reaction from a mixture of Sb, S, and I. To obtain the appropriate thickness of 0.1 mm it was carefully cleaved with a sharp knife. The end surfaces were short-circuited in order to maintain a constant electric field  $E = 0$ .

The measurements were done by an ac calorimetric technique,<sup>21</sup> the sample being heated periodically with white light from a halogen lamp. The light absorbing front surface of the sample was painted black. Two sets of copper-Constantan thermocouples were attached to the rear surface. The sample was placed in a thick-walled copper cavity which could be temperature controlled with an accuracy better than 1 mK by means of an electronic temperature controller (LR-

110, LR-130) with a platinum resistance as sensor. One of the thermocouples was used to detect the temperature difference between the sample and the cavity wall while the other one was used to measure the amplitude of the temperature oscillations of the sample. This latter signal is inversely proportional to the specific heat.

The frequency dependence of the signal was measured accurately between 0.45 and 1.7 Hz showing perfect inverse proportionality as it should.<sup>21</sup> We selected the frequency of 1.0 Hz and a peak-to-peak temperature oscillation of about 15 mK. The absolute calibration of the thermometer was better than 0.1 K. All the measurements were made automatically using a microcomputer to regulate the temperature in steps and to read off the signals. This automation made it possible to go very slowly through the phase transition. Typically a complete one-way temperature sweep would take about 24 h of continuous measurement when a temperature range of 7 K was swept.

### IV. RESULTS

The absolute value of the specific heat was estimated by taking the mean value of the measurement of Mori *et al.*<sup>17</sup> and Pikka *et al.*<sup>18</sup> at 300 K where they agree within 10%. We expect therefore the absolute calibration to be less than 10% in error. We present our measurements in Figs. 1–4. The first sweep was started at 315 K and ended at 243 K after 42 h of continuous measurement. In the region close to  $T_c$  the temperature was regulated in steps of about 25 mK, stabilizing for 5 min at each temperature. This is equivalent to a sweep rate of 0.3 K/h. The same slow temperature variation was used in going up through  $T_c$ . Other details are given in the caption of Fig. 1.

To find the lattice contribution to the specific heat a new sweep was made from 330 to 83 K, see Fig. 3. Using a least-squares program the data were fitted on a computer to the Landau specific heat  $\Delta C$  given in Eq. (4) plus an Einstein lattice contribution:

$$C_l = A + B \left( \frac{\Theta}{T} \right)^2 \frac{e^{\Theta/T}}{(e^{\Theta/T} - 1)^2}, \quad (6)$$

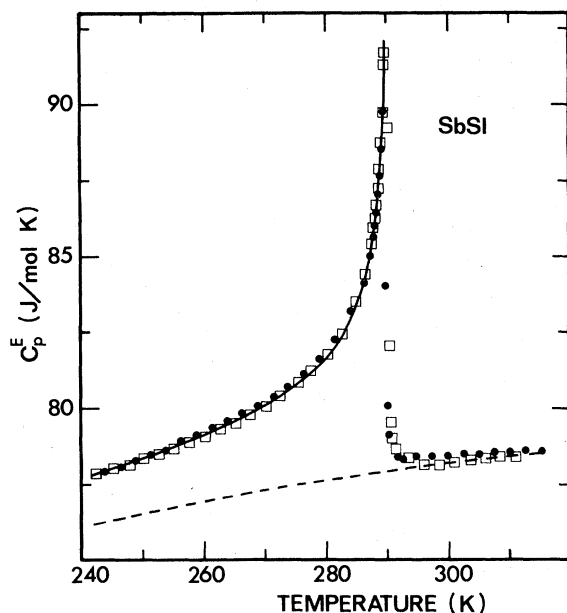


FIG. 1. Specific heat of SbSI measured with decreasing ( $\bullet$ ) and increasing ( $\square$ ) temperature. The fully drawn curve is the total specific heat obtained by fitting Eqs. (4) and (6) to the data. The dashed line is the lattice specific heat, Eq. (6). Only every tenth, or less, of the measured points are shown. In each series the temperature was regulated in steps of about 250 mK between 243 and 286.0 K and between 293.7 and 315 K, stabilizing for four minutes at each point. Between 286.0 and 293.7 K the temperature steps were 25 mK, with a stabilizing period of 5 min. Only the data below 289.7 K measured with increasing temperature ( $\square$ ) were used in the fit shown here.

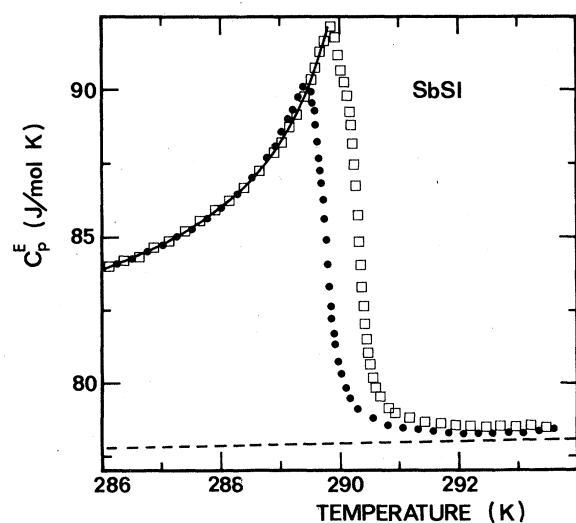


FIG. 2. Expanded plot of specific-heat data taken in a narrow region near the maximum of Fig. 1. All symbols have the same meaning as in Fig. 1. Except close to  $T_c$  only every tenth measured point is shown.

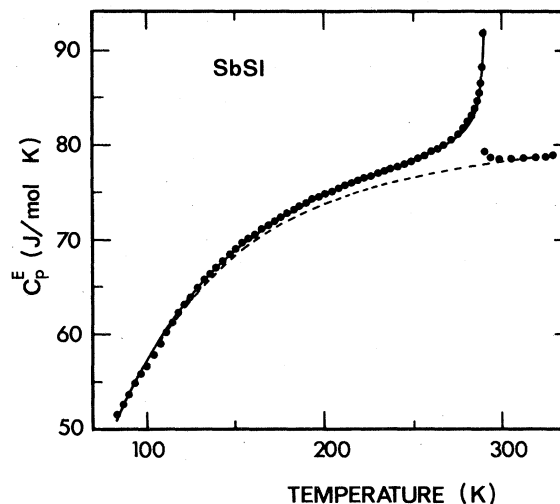


FIG. 3. Specific heat of SbSI measured to determine the lattice specific heat. Symbols are explained in the caption of Fig. 1. Only every third measured point is shown. From 330 to 275 K the temperature was regulated in steps of about 250 mK stabilizing for 5 min at each point. From 275 to 83 K steps of about 1.25 K were taken, stabilizing for 3 min at each point. Only the data below 248 K were used in fitting Eqs. (4) and (6) to the data.

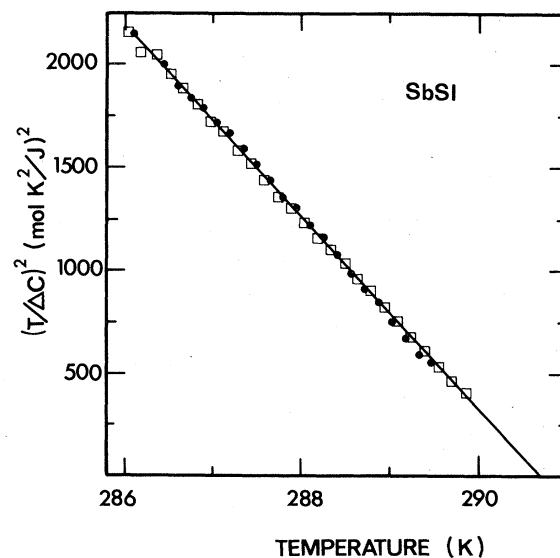


FIG. 4.  $(T/\Delta C)^2$  as calculated from the data in Fig. 2.  $\Delta C$  is the Landau contribution to the specific heat and is obtained by subtracting the fitted lattice specific heat, Eq. (6), from the measured values. The straight line is the prediction, Eq. (4). Only every sixth measured point is shown.

TABLE I. The parameters for the lattice specific heat  $C_l$  and the Landau specific heat  $\Delta C$  as obtained from least-squares fitting to the data. Note that in determining the first five parameters listed we have taken  $q = \frac{1}{2}$ . Note also that the 10% uncertainty in absolute calibration is not taken into account in the stated uncertainties for  $A$ ,  $B$ , and  $a^{3/2}/4c^{1/2}$

$A$	(J/molK)	32.9 $\pm$ 0.4
$B$	(J/molK)	49.4 $\pm$ 0.7
$\Theta$	(K)	304.6 $\pm$ 2.0
$10^3 a^{3/2}/4c^{1/2}$	(J/molK <sup>3/2</sup> )	46.8 $\pm$ 0.4
$T_d$	(K)	290.64 $\pm$ 0.04
$\bar{q}$		0.49 $\pm$ 0.4

where  $A$ ,  $B$ , and  $\Theta$  are parameters to be determined. The expression for  $C_l$  should be looked upon as an empirical representation of the lattice specific heat. It has just enough parameters to make possible a good fit to the measured curve. These parameters will be determined by the curve shape far below  $T_c$  while the parameters in the expression of  $\Delta C$  will be determined by the curve shape close to  $T_c$ .

The fitted curve obtained from data taken with increasing temperature is shown as a continuous line in Figs. 1–3, with the lattice background  $C_l$  as a dashed line. In this fit the data below 289.7 K in Figs. 1 and 2, and below 248 K in Fig. 3 were used. As we see the calculated lattice specific-heat curve meets the measured level above  $T_c$  very nicely when extrapolated from the ferroelectric phase. Since no points above  $T_c$  are used in the fit we think that this is a very strong test of our data analysis. It shows that Eq. (6) which fits the specific-heat curve well below  $T_c$  also gives a correct subtraction of the lattice specific heat near  $T_c$ . Another similarly good fit was made to the data taken with decreasing temperature. The two resulting parameter sets differ more than the statistical uncertainties which were 1% or better. This shows that some systematic error is present. We ascribe this to a slight drift in the light intensity. In Table I we give the mean value of the parameters from the two fits displaying also the systematic error. We have also calculated  $\Delta C = C_p^E - C_l$  and plotted  $(T/\Delta C)^2$  as a function of temperature, as shown in Fig. 4. It falls on a straight line as it should according to Eq. (4). As a further check the data were fitted once more to  $C_p^E = C_l + \Delta C$ , with  $\Delta C = DT(T_d - T)^{-q}$ ,  $q$  also being taken as a free parameter. This gave  $q = 0.45 \pm 0.015$  and  $0.53 \pm 0.015$ , respectively, for decreasing and increasing temperatures, with a mean value  $\bar{q} = 0.49 \pm 0.04$ . The systematic error is of the origin mentioned above. We find the results

to be in very satisfactory agreement with Landau theory for a first-order phase transition in the neighborhood of a tricritical point. We note in particular that this agreement extends over the entire temperature region where the polarization contributes to the specific heat for  $T < T_c$ .

As can be seen from Fig. 1 and Table I  $T_d$  is very close to  $T_1$ . Taking the mean value of the temperatures at the maxima in the figure as  $T_1$  gives  $T_d - T_1 = b^2/16ac = 1.0$  K. Because of this both  $P_s^2$  and  $\chi_T^{-1}$  given in Eqs. (2) and (3) will show large curvature for all temperatures below  $T_1$ . Therefore, in an analysis based on Landau theory one should not try to fit measured curves for these quantities to a linear temperature dependence as was done in Refs. 8, 14, and 15.

Above the transition temperature  $T_c$  the specific-heat curves have a short tail. The same kind of deviation from Landau theory has been seen in measurements of polarization<sup>15</sup> and dielectric constant.<sup>14</sup> The specific-heat tail fits well to a power law  $(T - T_c)^{-\alpha}$ . The exponent is the same for heating and cooling curves but depends on the history of the sample. For two different runs the exponent  $\alpha$  is  $0.8 \pm 0.1$  when measuring after cooling from 315 to 294 K during 4.5 h and  $\alpha = 1.5 \pm 0.1$  when measuring after cooling through the same temperature range during 45 min. The data in an interval of about 2 K above the inflection point were used for fitting. We think that these contributions to the specific heat are caused by impurities. Such an effect has been seen in TGS (Ref. 22) and BaTiO<sub>3</sub> (Ref. 3) and has been treated theoretically by Levanyuk *et al.*<sup>23</sup> On the cooling curve of Fig. 2 we also see a small extra contribution below  $T_c$ , probably of similar origin.

Since SbSI is photoconducting one might worry about the possibility that the absorbed light could influence the specific-heat curve. However, the applied light intensity was rather weak, and most of it was absorbed in the painted surface. As a check, measurements were made with five times higher light intensity. The same specific-heat curves were obtained. Also, cutting the leads which short-circuited the end surfaces of the sample had no effect, indicating that the chosen period of light intensity variations of 1 s is higher than the Maxwell relaxation time  $\tau = \rho\epsilon$ . Several runs have given the same  $T_c$  within 0.1 K showing negligible aging effects within the time interval of one complete run.

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