

Thermodynamic Properties and the Ferroelectric Phase Transition of the Trisarcosine Calcium Chloride Complex

TAKASUKE MATSUO,* MARGRET MÅNSSON and STIG SUNNER

Thermochemistry Laboratory, Chemical Center, University of Lund, P.O.B. 740, S-22007 Lund 7, Sweden

The heat capacity of trisarcosine calcium chloride was measured from 13 to 300 K with an adiabatic calorimeter. The standard enthalpy and entropy of the compound were computed. A heat capacity anomaly due to a ferroelectric transition of higher order was found at (130.84 ± 0.10) K with $\Delta_r H = (446 \pm 80)$ J mol⁻¹ and $\Delta_r S = (4.26 \pm 0.80)$ J K⁻¹ mol⁻¹. The entropy value is discussed in terms of an order-disorder model. Critical fluctuation plays a minor role in the transition. Numerical relations among critical exponents are given. The temperature dependence of the anomalous heat capacity is described by thermodynamic theory.

Sarcosine (*N*-methyl glycine) forms a 3:1 complex with calcium chloride, $(\text{CH}_3\text{NH}_2^+\text{CH}_2\text{CO}_2^-)_3\text{CaCl}_2$. The compound undergoes a transition to a ferroelectric state at a temperature reported as 127 K.¹ The transition temperature of the deuterated compound was found to be 149 K.² This isotope effect in the transition temperature indicates that the hydrogen bond is of some importance in the transition mechanism. There is no apparent disorder in the atomic positions as determined by X-ray diffraction at room temperature.³ This suggests the possibility of a displacive mechanism for the transition. On the other hand, the dielectric dispersion¹ at lower temperatures favors an order-disorder mechanism rather than the displacive. However, the experimental value reported for the entropy of transition,¹ 1.6 J K⁻¹ mol⁻¹, is small for an order-disorder transition. There is also an inconsistency in the experimental results as to the temperature interval over which the spontaneous polarization

changes and the temperature interval of the heat capacity anomaly.¹ In addition to the total entropy of transition, the temperature dependence of the anomalous heat capacity near the transition point is interesting in relation to recent developments of the theory of critical phenomena.

From a thermochemical point of view, Gibbs energy data of the present substance will be of significance because the crystal consists of an amino acid and ions which are common in biological systems.

In this paper we report heat capacity data of crystalline trisarcosine calcium chloride from 13 to 300 K and the standard thermodynamic functions derived therefrom, and discuss the anomalous heat capacity in terms of the current theory of ferroelectricity.

EXPERIMENTAL

Preparation and purity determination of the compound. Crystalline trisarcosine calcium chloride was prepared by evaporation of an aqueous solution of sarcosine and calcium chloride in a 3:1 molar ratio. It was recrystallized from water. The crystals were dried, at first in an evacuated desiccator over anhydrous calcium chloride and then by cooling to liquid nitrogen temperature in an evacuated glass vessel to facilitate the escape of occluded water by causing cracking of the crystals around any brine holes. The sample was then heated to 110 °C for 16 h.

The resulting crystals contained 0.03 mass % of occluded water as indicated by a small excess heat capacity at 252 K due to eutectic melting. The mass of water was calculated as the ratio of the excess enthalpy acquired by the calorimetric sample in the 252 K anomaly to the enthalpy of fusion of 1 g

* On leave of absence from the Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.

of pure ice (334 J g^{-1}), which gave 2.6 mg of impurity water in the sample. As an independent test for the water content a sample was pelletized and its mass measured repeatedly from 1.7 min after pelletizing to 20 days. The mass loss that occurred during this period was 0.008%. This method is known as an efficient way of getting occluded liquid out of brine holes.⁴

Analysis for calcium ion by EDTA titration with particular attention given to possible competing complexing capacity of sarcosine, yielded (99.85 ± 0.2) mass % for the purity of the sample.

The quoted uncertainty covers possible interference by the sarcosine.

Temperature scale. The correctness of the temperature scale, as maintained by the platinum thermometer originally calibrated in terms of IPTS-68, was confirmed by measurement of the melting temperature of ice. Approximately 500 mg of distilled and deionized water (conductivity $\approx 10^{-16} \Omega^{-1} \text{ cm}^{-1}$) was transferred to the calorimeter cell by vacuum distillation. Air at atmospheric pressure was introduced into the cell, which was then sealed, set in the cryostat and cooled to 240 K, upon which

Table 1. Heat capacity of $(\text{CH}_3\text{NH}_2^+\text{CH}_2\text{CO}_2^-)_3\text{CaCl}_2$.

T K	C_p $\text{J K}^{-1} \text{ mol}^{-1}$	T K	C_p $\text{J K}^{-1} \text{ mol}^{-1}$	T K	C_p $\text{J K}^{-1} \text{ mol}^{-1}$
12.65	8.11	77.27	189.42	178.86	316.71
14.00	8.60	80.20	195.56	181.25	318.82
15.12	10.28	81.24	197.88	183.63	321.13
16.03	11.42	83.00	201.44	186.00	323.38
16.83	13.51	85.18	205.61	188.35	325.52
17.67	16.00	87.31	210.00	190.69	327.53
18.16	17.29	93.91	222.40	193.03	329.64
19.95	21.96	97.31	228.46	195.35	331.75
21.39	25.95	100.61	234.13	197.65	333.79
22.61	29.58	103.83	239.62	200.42	336.57
24.25	34.54	106.98	244.73	203.38	338.90
25.93	39.81	110.06	249.78	206.32	341.22
26.85	42.76	113.09	254.62	209.24	344.82
27.83	45.98	116.05	259.38	212.15	347.53
29.04	49.92	118.97	264.06	215.61	350.03
30.49	54.73	121.83	268.73	219.63	353.72
32.89	62.85	124.66	273.65	223.62	357.39
34.16	67.23	127.44	279.28	227.59	360.82
35.35	71.26	132.91	272.62	231.53	364.25
36.54	75.31	135.65	274.67	235.45	367.51
38.00	80.23	138.36	277.56	239.33	371.29
40.32	88.00	141.05	280.17	243.40	375.05
43.11	97.06	143.71	282.92	247.65	379.06
45.60	105.09	146.34	285.65	251.85	392.51 ^a
47.87	112.24	148.96	288.11	256.02	387.95 ^a
50.36	119.93	151.55	290.98	260.19	389.80
53.05	127.98	154.12	293.27	264.34	393.55
55.54	135.25	156.67	295.73	268.46	397.42
57.88	141.81	159.20	298.28	272.55	401.08
60.09	147.84	161.71	300.63	276.62	404.78
62.20	153.42	164.21	302.90	280.66	408.52
64.49	159.36	166.69	305.36	284.69	411.88
66.97	165.53	169.15	307.65	288.68	416.21
69.34	171.27	171.60	309.83	292.66	420.26
71.83	177.17	174.03	312.01	296.62	423.78
74.45	183.12	176.45	314.58	299.43	426.52

^a Includes the enthalpy of fusion contribution of the occluded water (0.03 mass per cent).

crystallization took place. The heat capacity was measured as in an ordinary run. The energy input was adjusted so that enough data points were obtained in the melting range. The plot of temperature against $1/f$, where f is the fraction of ice melted, gave the melting temperature of the ice sample as (273.1502 ± 0.0002) K and that of pure ice as (273.1508 ± 0.0002) K. The fraction of liquid-soluble and solid-insoluble impurity in the ice was found to be 5.8×10^{-6} . The extrapolated melting temperature of pure ice was then corrected for the pressure change in the cell due to cooling from room temperature (21.5°C) to 0°C , on the assumption that the melting curve of ice is linear between 273.15 K and 273.16 K. The derived triple point of pure ice was (273.1598 ± 0.0004) K, in agreement with the original calibration and thus IPTS-68.

Heat capacity measurements. The calorimeter used in the present study has been described⁵ except for the cell. The new cell is of a design similar to the previous one, but has four vertical vanes for thermal equilibration. The main parts of the cell were machined from a solid rod of oxygen-free copper. The internal volume of the cell is 11.3 cm^3 .

An 8.6977 g sample of 2 to 4 mm crystals was introduced into the cell, together with 6.7 kPa of helium gas. The heat capacity of the sample was first measured from 80 to 300 K with temperature increments of 2 to 4 K. An anomaly was found at 130 K corresponding to the ferroelectric transition. Measurements were repeated in the transition region with smaller temperature increments, *ca.* 0.2 K. Below 80 K liquid helium was used as coolant. The

heat capacity of the cell plus helium was measured in a separate experiment.

The contribution from the cell was subtracted from the raw heat capacity data and small corrections for helium gas, gold gasket and water impurity were applied. The net heat capacity thus calculated was converted to molar heat capacity, by the molar mass of trisarcosine calcium chloride taken as 378.27 g.

The deviation of the experimental points from the smoothed curve was typically 0.05% above 50 K and increased gradually to 1% at 20 K. The inaccuracy of the heat capacity values is estimated to be less than 0.15% above 50 K based on measurements on standard reference benzoic acid.⁵

RESULTS AND DISCUSSION

The molar heat capacity of trisarcosine calcium chloride is given in Table 1. The experimental results close to the transition point are given in Table 2. The difference between two consecutive temperatures in the tables is a measure of the temperature increments obtained for the respective energy inputs.

As shown in Fig. 1, the heat capacity is a smoothly increasing function of temperature except at 130 K and 252 K. The latter anomaly was regarded as caused by melting of occluded water as described above.

Table 2. Heat capacity of $(\text{CH}_3\text{NH}_2^+\text{CH}_2\text{CO}_2^-)_3\text{CaCl}_2$ in the transition region.

T K	C_p $\text{J K}^{-1} \text{mol}^{-1}$	T K	C_p $\text{J K}^{-1} \text{mol}^{-1}$	T K	C_p $\text{J K}^{-1} \text{mol}^{-1}$
124.59	273.60	128.23	281.30	131.73	271.99
124.71	273.65	128.45	281.61	131.95	271.99
124.83	273.34	128.67	282.69	132.17	271.86
124.95	274.04	128.89	283.09	132.39	272.30
125.58	275.86	129.11	283.78	132.61	272.21
125.80	275.78	129.33	284.43	132.83	272.69
126.02	276.21	129.54	284.83	133.05	272.65
126.25	276.56	129.76	285.96	133.27	272.69
126.47	277.21	129.98	286.74	133.49	273.08
126.69	277.47	130.19	287.57	133.80	273.39
126.91	278.43	130.41	288.44	134.19	273.68
127.13	278.56	130.62	288.48	134.58	274.21
127.35	279.30	130.84	279.78	134.98	274.34
127.57	279.61	131.06	273.91	135.37	274.77
127.79	280.26	131.29	272.43	135.76	275.04
128.02	280.61	131.51	272.12	136.15	275.38

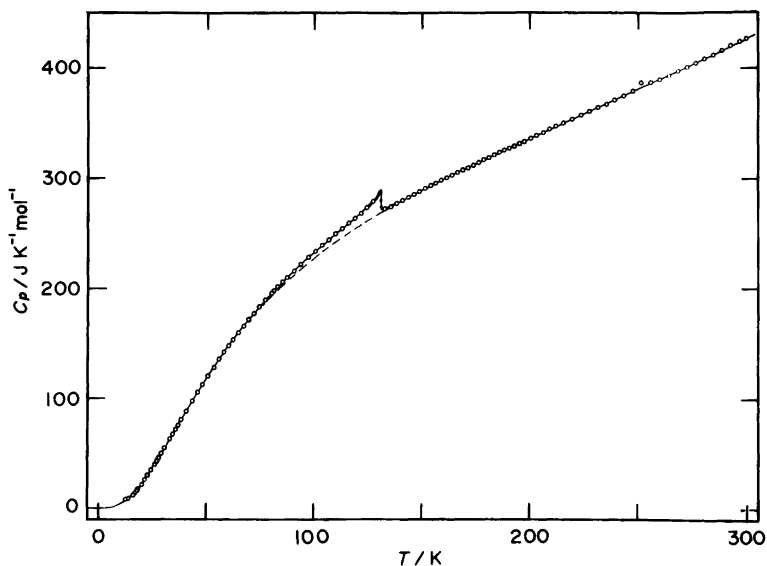


Fig. 1. The molar heat capacity of trisarcosine calcium chloride.

The thermodynamic functions. The experimental heat capacities were smoothed by fitting to polynomials in three temperature ranges, 13–45 K, 45–125 K and 135–300 K, and then integrated analytically. The lowest region was extrapolated to 0 K by the Debye T^3 law. In the transition region, 125–135 K, the heat capacity was integrated graphically. The smoothed molar heat capacity, the

tempered enthalpy and the entropy are given in Table 3 for selected temperatures.

The transition temperature and the order of the transition. The maximum of the heat capacity occurred at (130.62 ± 0.10) K and the steepest decrease at (130.84 ± 0.10) K, where the uncertainties are defined by the temperature increments of the measurements. The latter temperature is appropriate for the

Table 3. Thermodynamic functions of $(\text{CH}_3\text{NH}_2^+\text{CH}_2\text{CO}_2^-)_3\text{CaCl}_2$.

I ^a	II	III	IV	I	II	III	IV
10	2.96	0.74	0.99	100	233.1	112.96	186.44
15	9.97	2.50	3.33	120	265.7	135.73	231.9
20	22.16	5.76	7.71	140	279.2	165.66	274.3
25	36.86	10.49	14.22	160	299.0	181.10	312.9
30	53.10	16.22	22.35	180	317.7	195.25	349.2
35	70.13	22.70	31.81	200	336.0	208.4	383.6
40	86.84	29.68	42.27	220	354.1	220.8	416.5
45	103.23	36.94	53.45	240	372.0	232.7	448.1
50	118.86	44.36	65.14	260	389.7	244.1	478.5
60	147.58	59.22	89.41	280	407.9	255.1	508.1
70	172.87	73.69	114.10	300	427.1	265.9	536.9
80	195.22	87.51	138.67	273.15	401.6	251.4	498.0
90	215.1	100.60	162.83	298.15	425.3	265.0	534.2

^a Column I. T/K . Column II. $C_p(T)/\text{J K}^{-1} \text{mol}^{-1}$. Column III. $(H^\circ(T) - H^\circ(0))T^{-1}/\text{J K}^{-1} \text{mol}^{-1}$. Column IV. $(S^\circ(T) - S^\circ(0))/\text{J K}^{-1} \text{mol}^{-1}$.

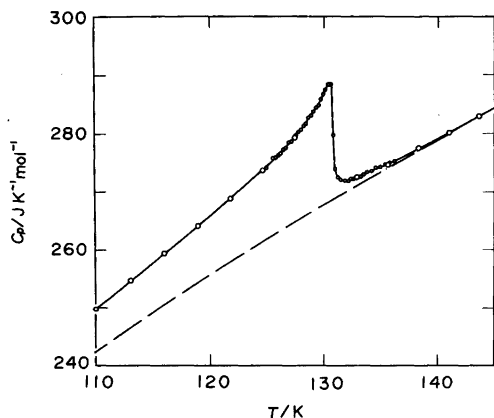


Fig. 2. The molar heat capacity of trisarcosine calcium chloride in the transition region.

transition temperature because the transition is essentially of the second order as will be discussed below.

Whether the small difference between this temperature and that determined from the spontaneous polarization,⁶ (131.15 ± 0.1) K, is a real difference cannot be decided, since the temperature scale used was not specified in Ref. 6. The generally accepted transition temperature, 127 K,^{1,2,7,8} is lower than the value reported here. Again, detailed comparison is not possible because clear definition of the temperature scale used in previous work^{1,7} is lacking.

As illustrated in Fig. 2, the heat capacity decreases quasi-discontinuously at the transition temperature. The entropy is continuous at the transition point. Thus the phase transition is of higher, probably second, order in agreement with the earlier conclusion.^{1,7}

The entropy of transition. The normal, *i.e.* non-transitional, heat capacity to be subtracted from the experimental heat capacity for evaluation of the anomalous contribution is assumed to be a continuous function of the temperature. It was approximated by a fourth degree polynomial,

$$C_p(\text{normal}) = \sum_{i=1}^5 A_i X^{i-1} \quad (1)$$

where X is a reduced temperature, defined by

$$X = (T/\text{K} - 130)/110 \quad (2)$$

The coefficients A_i ($i=1, \dots, 5$) were determined by an orthogonal-polynomial least squares method using the experimental data outside the transition region. All of the experimental points between 32 and 60 K and between 146 and 228 K were used in the calculation. The choice of the transition region, 60 to 146 K, was based on the observation that the spontaneous polarization saturates at 60 K¹ and that the positive curvature of the heat capacity *versus* temperature curve above the transition becomes negligibly small at about 146 K. The best-fitting parameters are $A_1=267.74$, $A_2=127.40$, $A_3=-58.57$, $A_4=53.00$ and $A_5=-17.21$, all in $\text{J K}^{-1} \text{mol}^{-1}$. The broken lines in Figs. 1 and 2 represent the normal heat capacity computed by eqn. (1). The anomalous heat capacity $\Delta C(T) = C_p(\text{experimental}) - C_p(\text{normal})$ was integrated graphically to give the enthalpy of the transition $\Delta_{\text{tr}}H = \int \Delta C(T) dT = 446 \text{ J mol}^{-1}$ and the corresponding entropy $\Delta_{\text{tr}}S = \int \Delta C(T) T^{-1} dT = 4.26 \text{ J K}^{-1} \text{mol}^{-1}$. The inaccuracy in these values is dominated by the inaccuracy in the determination of the normal heat capacity. A reasonable variation of the range utilized in calculating the normal heat capacity changes the transition enthalpy and entropy by $\pm 80 \text{ J mol}^{-1}$ and $\pm 0.8 \text{ J K}^{-1} \text{mol}^{-1}$, respectively.

The entropy of transition is slightly smaller but comparable with $R \ln 2 = 5.76 \text{ J K}^{-1} \text{mol}^{-1}$, which suggests that there is two-fold disorder in the atomic arrangement of the high-temperature structure.

One of the three sarcosine zwitterions in the crystal, designated (1) in Ref. 3, lies in the mirror plane perpendicular to the b -axis which coincides with the ferroelectric axis. The other two occupy general positions. An entropy of transition of $R \ln 2$ is explained, as is the uniaxial ferroelectricity along the b -axis, if one assumes that the mirror plane is a pseudo-symmetry element caused by a two-fold orientational disorder of sarcosine (1) and that the disorder disappears in the low temperature phase. It is important to note that the disorder must be subtle since it was not detected by X-ray diffraction.³ The Curie-Weiss constant, which is a measure of the magnitude of the elementary dipole associated with the disordering unit, is small, consistent with the above model. Many of the lines in the Raman and infrared spectra sharpen and split at low temperature,⁹ particularly those due to the vibration of the $=\text{NH}_2^+$ and $-\text{CO}_2^-$ groups. Change in the vibrational states may modify the order-disorder nature of the transition as in the case of a similar

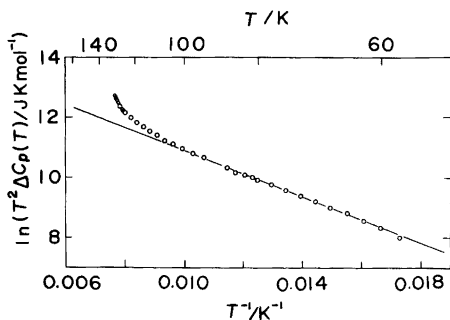


Fig. 3. The linear relation between the reciprocal temperature and the logarithm of the anomalous heat capacity of trisarcosine calcium chloride multiplied by the squared temperature.

transition in triglycine sulfate.^{10,11}

If one accepts an order-disorder nature of the transition, the energy required for producing disorder in the crystal can be evaluated from the low temperature region of the anomalous heat capacity.¹² The slope of the plot of $\ln(T^2\Delta C(T))$ against T^{-1} , Fig. 3, gives the energy (3.2 ± 0.3) kJ mol⁻¹ for the excitation of one mol of sarcosine to the deviant state in the almost ordered crystal. The same energy should characterize the initial decrease of the spontaneous polarization.¹ However, quantitative comparison between the calorimetric and polarization measurements is not possible because of lack of numerical data for the latter.

The critical properties. Three critical exponents¹³ are known for the sarcosine compound, the order parameter exponent $\beta = 0.49 \pm 0.01$, the susceptibility exponent $\gamma = \gamma' = 1.00 \pm 0.02$ and the isotherm exponent $\delta = 3.1 \pm 0.1$.⁶ As shown in Fig. 4, the logarithmic plot of the excess heat capacity is curved and approaches a horizontal line as the temperature tends to $T_c = 130.84$ K from below. The heat capacity exponent α' is estimated from

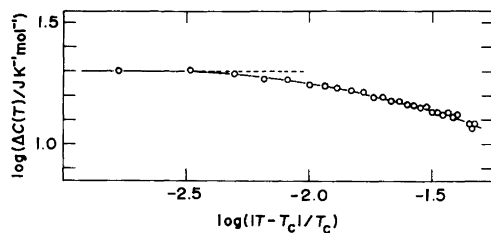


Fig. 4. The logarithmic plot of the anomalous heat capacity of trisarcosine calcium chloride.

the plot as $\alpha' = 0.00 \pm 0.05$. The following relations hold among the exponent values.

$$\begin{aligned}\alpha' + 2\beta + \gamma' &= 1.98 \pm 0.06 \\ \alpha' + \beta(\delta + 1) &= 2.01 \pm 0.07 \\ \gamma'(\delta + 1) - (2 - \alpha')(\delta - 1) &= -0.1 \pm 0.2\end{aligned}$$

Thus, the Rushbrooke inequality¹³ and the Griffiths inequalities¹³ are satisfied as equalities. These exponent values are the same as the mean field values¹³ and show that long range interaction is responsible for the transition.

The non-zero heat capacity anomaly above the transition point is not explained by the mean field behaviour. It may be accounted for as the logarithmic correction to the mean field calculation¹⁴ or as an anomaly of vibrational origin.¹¹ However, the excess entropy acquired above T_c is 0.08 J K⁻¹ mol⁻¹, which is less than 2% of the total transition entropy. This shows that fluctuational effects are relatively unimportant in this phase transition.

Thermodynamic description of the phase transition.

The mean field behavior of the phase transition is described quantitatively by thermodynamics.¹⁵ The Gibbs energy density $\bar{G}(T, P)$ of the crystal is expanded in powers of the polarization P .

$$\bar{G}(T, P) = \bar{G}_0(T) + (1/2)A(T)P^2 + (1/4)\xi P^4 + (1/6)\zeta P^6 \quad (3)$$

Here $\bar{G}_0(T)$ is the Gibbs energy density of the unpolarized crystal at temperature T and ξ and ζ

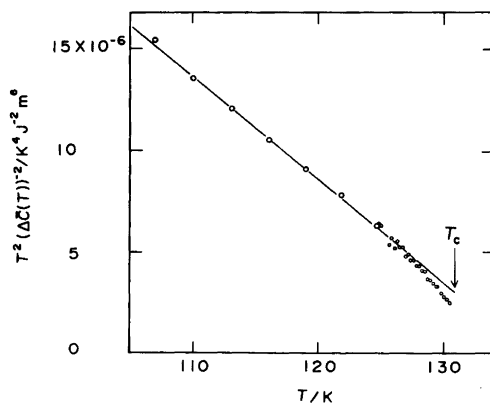


Fig. 5. The linear relation between the temperature and the squared ratio of the temperature to the anomalous heat capacity density of trisarcosine calcium chloride. The arrow indicates the transition temperature.

are the temperature-independent parameters to be determined experimentally. $A(T)$ is related to the Curie-Weiss constant C by the relation $A(T) = (T - T_c)/C$ where T_c is the Curie temperature. Minimization of the Gibbs energy density with respect to P gives the equilibrium spontaneous polarization P_s from which the heat capacity density $\Delta\bar{C}(T)$ is obtained as follows.

$$\Delta\bar{C}(T) = (T/2C^2)(\xi^2 - 4\zeta(T - T_c)/C)^{-1/2} \quad (4)$$

Thus, a straight line should be obtained if $(T/\Delta\bar{C}(T))^2$ is plotted against T . The slope of the plot is equal to $-16C^3\zeta$ from which ζ is calculated, provided the Curie-Weiss constant is known independently. ξ is also determined from the same plot: $\xi = (T/\Delta\bar{C}(T_c))/(2C^2)$. As shown in Fig. 5, the plot of $(T/\Delta\bar{C}(T))^2$ against T is a straight line between 107 and 127 K. (The crystal density used in the calculations was 1.530 g cm^{-3} .) Two sets of data are available on the dielectric susceptibility and spontaneous polarization.^{1,6} If $C/\epsilon_0 = 59 \text{ K}$ is used,¹ $C = 5.22 \times 10^{-10} \text{ K F m}^{-1}$, $\xi = 0.321 \times 10^{16} \text{ J m}^5 \text{ C}^{-4}$ and $\zeta = 0.223 \times 10^{21} \text{ J m}^9 \text{ C}^{-6}$ are obtained. This set of the parameters gives the calculated spontaneous polarization $P_s = 1.6 \text{ mC m}^{-2}$ at $T = T_c - 5 \text{ K}$ in agreement with the experimental value 1.5 mC m^{-2} from Ref. 1. Similar calculation using $C/\epsilon_0 = 17.1 \text{ K}$ ⁶ leads to $C = 1.51 \times 10^{-10} \text{ K F m}^{-1}$, $\xi = 3.82 \times 10^{16} \text{ J m}^5 \text{ C}^{-4}$, $\zeta = 9.15 \times 10^{21} \text{ J m}^9 \text{ C}^{-6}$ and $P_s(T = T_c - 5 \text{ K}) = 0.9 \text{ mC m}^{-2}$ in reasonable agreement with the experimental value given in Ref. 6. In the calculation of these quantities the deviation from linearity of the plot in Fig. 5 at $T = 127 - 131 \text{ K}$ was neglected because the critical fluctuation, as evidenced by the anomalous heat capacity above T_c , should be operative below T_c as well and should be left out of the thermodynamic description.

The calculation presented here shows that the anomalous heat capacity of trisarcosine calcium chloride is described with reasonable precision by the Landau theory but the values of the parameters involved depend critically on the dielectric data. Accurate experimental values of the Curie constant and spontaneous polarization of the untwinned crystal are needed before conclusive values of the parameters can be given.

CONCLUSION

The order-disorder mechanism of the transition arrived at here is in agreement with conclusions

from earlier studies using different experimental methods.^{1,7,9} The heat capacity data presented in this report show that the transitional behavior is dominantly classical and that the critical fluctuation plays a minor role contrary to the conclusion from ESR experiments⁷ but in agreement with nuclear relaxation measurements.²

The atomic disorder assumed in the high temperature phase is yet to be proved by structural studies.

Acknowledgements. The authors are grateful to Drs. Bengt Falk and George Coffy for their kind instruction on the operation of the apparatus and to Mr. Jan-Erik Falk for his skillful construction of the calorimeter cell. They are indebted to Mrs. Stina Bergström for making the chemical analysis. One of the authors (T.M.) thanks the Sven and Dagmar Salén Foundation and the Naito Foundation for financial support.

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Received April 18, 1979.