International Journal of Thermophysics, Vol. 26, No. 2, March 2005 (© 2005)
DOI: 10.1007/s10765-005-4509-6

Critical Behavior of the Heat Capacity in the Region of the Incommensurate Phase Transition of $SC(NH_2)_2$ Crystals[1]

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The anomalous (nonclassical) behavior of the heat capacity in the region of the second-order phase transition "initial phase–incommensurate phase" was experimentally observed in the $SC(NH_2)_2$ ferroelectric. Such a critical behavior of heat capacity above and below the temperature of incommensurate phase transition is shown to be qualitatively consistent with the fluctuation theory of XY-type systems.

KEY WORDS: critical behavior; ferroelectric; fluctuation; heat capacity; incommensurate phase; phase transition.

1. INTRODUCTION

Heat capacity is one of the most fundamental properties that exhibit temperature anomalies in phase transitions. To explain the anomalies of the heat capacity of ferroelectrics in the region of consecutive transitions, "initial phase–incommensurate phase–polar phase," one usually invokes the Landau theory because of its remarkable simplicity. However, the thermodynamic Landau model qualitatively reproduces the anomalous part of the heat capacity of the incommensurate phase only in the temperature range adjacent to the first-order transition, "incommensurate phase–commensurate ferroelectric phase." Experimental studies of a number of

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[1]Paper presented at the Sixteenth European Conference on Thermophysical Properties, September 1–4, 2002, London, United Kingdom.
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physical properties in the region of the second-order phase transition "initial phase–incommensurate phase" demonstrate dramatic deviations from the classical Landau behavior both above and below the transition. The interpretation usually amounts to comparing the measured critical indices with the corresponding theoretical values adopted in the XY-type model.

The deviations from the behavior predicted by the Landau theory and from the regular behavior may be due not only to fluctuations but also to defects [1]. However, the defect theory has not been adequately developed for the XY systems and incommensurate phases in particular; it does not account for the temperature dependences and critical amplitudes of deviations in both phases, which is necessary for the description of the experiment.

To elucidate the possible nature of deviations from the Landau theory, Levanyuk and Coworkers [2] developed a method for analysis of the experimental data in the region of structural transitions on the basis of fluctuation theory. As a result, it was shown by the example of birefringence and thermal expansion coefficients of a ferroelectric crystal [2, 3] that, in the vicinity $G << |\tau| << G^{1/2}$ of the transition to the incommensurate phase at temperature T_i (G is the Ginzburg number expressed in terms of the coefficients of the thermodynamic potential [4], and $\tau = T/T_i - 1$ is the reduced temperature), the diverging corrections no longer approximate the experiment for $|\tau| \leqslant 10^{-1}$. These corrections become large for the incommensurate transitions in various crystals at reduced temperatures $|\tau|$ on the order of $G \approx 10^{-2}$ (the value of the correction achieves the jump magnitude), which can be taken as the experimental estimate of the Ginzburg number G. If G is not too small, the anomaly becomes broad and the conclusions are only qualitative.

It is worth noting that the weakness of previous experimental studies (their authors admit this fact themselves) is that the critical index α is estimated indirectly (see, e.g., Refs. [2] and [3]) and, in some cases, the accuracy of measurements does not satisfy requirements. In this regard, the elucidation of the role of fluctuation effects in the transition to the incommensurate phases in crystals of different types is of fundamental importance. In this work, with the aim of gaining direct information on the nature of the incommensurate phase, we undertook a careful experimental investigation of the critical behavior of the specific heat in the region of a structural transition to the incommensurate phase in the $SC(NH_2)_2$ ferroelectric with a one-component order parameter.

2. EXPERIMENTAL

$SC(NH_2)_2$ is the well-known molecular crystal, which undergoes an intricate sequence of structural phase transitions, including transitions to the polar and nonpolar phases with incommensurate and long-period structures in the region between the initial nonpolar phase D_{2h}^{16} ($T_i \approx 202$ K) and the ferroelectric phase C_{2v}^{2} ($T_c \approx 169$ K) [1]. Below the temperature $T_i \approx 202$ K, an incommensurate superstructure appears with the modulation wave vector along the b axis. The studies were carried out with $SC(NH_2)_2$ single crystals (unit-cell parameters $a = 7.655$, $b = 8.537$, $c = 5.520$ Å) grown from a solution by the temperature lowering method. The geometric sizes of the samples were $0.50 \times 0.45 \times 0.025$ cm, and their quality was monitored using an optical microscope. The studies were carried out on an automated setup for measuring the specific heat of small samples by ac calorimetry with a relative uncertainty no larger than 0.1% [5]. The average temperature in the calorimeter was measured with a copper–constantan thermocouple with a wire diameter of 100 μm, and the temperature oscillations were measured with a Chromel–constantan thermocouple with a wire diameter of 25 μm. The temperature variation rate did not exceed $0.01\,\mathrm{K \cdot min^{-1}}$; in the vicinity of the transition, it did not exceed 5 mK. The stability of the cryostat temperature was within 5 mK. The measuring process and the processing of experimental data were controlled by the program HEAT-MASTER for automation of thermophysical measurements.

3. RESULTS AND DISCUSSION

The results of measuring the specific heat C_p of the $SC(NH_2)_2$ crystal in the temperature range of the second-order structural transition "initial phase–incommensurate phase" at T_i and the first-order transition "incommensurate phase–polar phase" at T_c are presented in Fig. 1. We will focus on the anomaly of C_p in the region of the second-order phase transition "initial phase-incommensurate phase" at $T_i = 201.58$ K. The changes in enthalpy and entropy at the transition point T_i are, respectively, $\Delta H_{trs} = 7.4\,\mathrm{kJ \cdot mol^{-1}}$ and $\Delta S_{trs} = 68\,\mathrm{J{\cdot}mol^{-1} \cdot K^{-1}}$. Heat capacity measurements of $SC(NH_2)_2$ in the temperature range of the incommensurate phase transition from 180 to 220 K are presented in Table I.

According to Refs. [2–4], the experimental temperature dependence of the heat capacity can be represented as the sum of Landau and fluctuation contributions:

$$\begin{aligned} C^{+} &= C_b + \lambda^{+}\tau^{-1/2} \quad \text{at } T > T_i, \\ C^{-} &= C_b + C_L + \lambda^{-}|\tau|^{-1/2} \quad \text{at } T < T_i, \end{aligned} \tag{1}$$

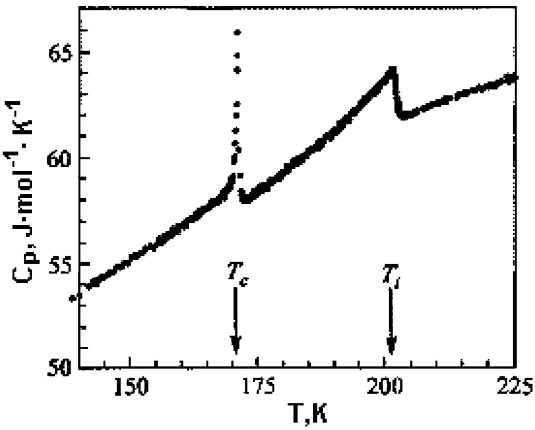

Fig. 1. Temperature dependence of the specific heat C_p of $SC(NH_2)_2$ in the region of phase transitions.

where C_b is the regular part of the heat capacity, C_L is the heat capacity jump at $T = T_i$ (according to Landau), λ^+ and λ^- are constants, and the ratio λ^-/λ^+ is $\sqrt{2}$ for XY-type systems and $2\sqrt{2}$ for Ising systems.

As with the temperature dependences of birefringence and thermal expansion coefficients obtained in Refs. [2] and [3], Eq. (1) with $C_L = \text{const}$ and $\lambda^\pm = \text{const}$ properly approximates experiment only if $C_b \neq \text{const}$ (this imposes a limitation on the domain of applicability of the Landau theory). We will assume that the regular part can be represented as a polynomial suitable for the description of empirical data on the thermal characteristics of solids [6] in a limited temperature range on the order of the Debye temperature:

$$C_b = c_0 + c_1 t + c_2 t^2,$$

where $t = T - T_i$. In this case, Eq. (1) approximates well the experimental dependences in the region from $1 \leqslant t \leqslant 70$ K and $-2K < t \leqslant -20$ K (Fig. 1).

According to Eq. (1), the ratio of critical amplitudes λ^-/λ^+ derived from the measurements of heat capacity ($\lambda^+ = 0.0598 \pm 0.0033$ and $\lambda^- = 0.0862 \pm 0.0038$ for $T > T_i$ and $T < T_i$, respectively) is equal to 1.441, which corresponds to the theoretical estimate $\sqrt{2}$ for XY-type systems ($2\sqrt{2}$ for Ising systems). It follows from the experimental data that the Ginzburg number is $G = 1$ to 2×10^{-2}. Therefore, the corrections are small in the temperature region $|\tau| > G$, while the anomalous scaling behavior can be expected at $|\tau| < |G|$.

Table I. Heat Capacity C_p of $SC(NH_2)_2$

T (K)	$C_p(J \cdot mol^{-1} \cdot K^{-1})$	T (K)	$C_p(J \cdot mol^{-1} \cdot K^{-1})$	T (K)	$C_p(J \cdot mol^{-1} \cdot K^{-1})$
180.973	59.407	193.747	62.063	202.339	62.554
181.316	59.452	193.962	62.143	202.475	62.410
181.553	59.499	194.115	62.134	202.535	62.318
181.733	59.528	194.634	62.215	202.613	62.321
181.878	59.549	194.951	62.294	202.617	62.223
181.988	59.556	195.186	62.545	202.702	62.200
182.133	59.595	195.536	62.469	202.786	62.096
182.205	59.647	195.935	62.726	202.907	62.049
182.275	59.777	196.601	62.743	202.956	62.016
182.314	59.790	196.845	62.800	203.054	61.926
182.621	59.857	196.985	62.911	203.265	61.889
183.038	59.792	197.369	63.058	203.705	61.876
183.327	59.899	197.683	63.061	203.869	61.935
183.472	59.941	198.101	63.163	204.077	61.939
183.834	59.944	198.274	63.139	204.314	61.905
184.195	60.033	198.516	63.168	204.754	61.984
184.412	60.040	198.590	63.318	204.990	61.923
185.114	60.253	198.676	63.344	205.429	62.015
185.423	60.235	199.073	63.405	205.793	62.069
185.652	60.322	199.327	63.507	206.272	62.166
185.999	60.374	199.818	63.572	207.404	62.272
186.396	60.382	200.007	63.684	207.636	62.235
186.714	60.451	200.145	63.634	208.102	62.328
186.946	60.582	200.521	63.780	208.469	62.351
187.319	60.706	200.765	63.947	208.764	62.413
188.042	60.692	201.109	63.971	209.479	62.446
188.290	60.842	201.225	64.084	210.148	62.525
188.660	60.969	201.418	63.948	210.868	62.564
189.373	60.856	201.487	64.065	211.255	62.636
189.626	61.090	201.521	64.095	211.783	62.711
189.841	61.115	201.581	64.153	212.277	62.720
190.009	61.235	201.581	64.152	212.487	62.726
190.810	61.234	201.606	64.068	213.800	62.800
191.054	61.250	201.634	64.021	214.116	62.834
191.258	61.582	201.699	63.952	214.360	62.923
191.411	61.421	201.782	63.843	215.200	62.949
191.658	61.584	201.853	63.731	215.990	63.018
192.086	61.587	201.898	63.723	217.034	63.112
192.370	61.715	201.967	63.469	217.525	63.113
192.583	61.836	202.090	63.293	218.290	63.223
192.877	61.769	202.138	63.058	219.667	63.265
193.0376	61.755	202.180	62.979	220.455	63.379
193.469	61.992	202.266	62.729		

The dependence of $\log \Delta C_p$ on $\log \tau$ above and below the transition point T_i, where ΔC_p is the singular part of the specific heat, is shown for the $SC(NH_2)_2$ crystal in Fig. 2. Experiment shows that the specific heat of $SC(NH_2)_2$ exhibits anomalous (nonclassical) behavior above T_i; in the temperature range $0.02\,K < (T - T_i) < 0.36\,K$ $(1.0 \times 10^{-4} < |\tau| < 0.18 \times 10^{-2})$ and below T_i, in the range $0.05\,K < |T_i - T| < 1.82\,K$ $(2.5 \times 10^{-4} < |\tau| < 0.9 \times 10^{-2})$, with the critical indices being, respectively, $\alpha = -0.04 \pm 0.01$ and $\alpha' = -0.04 \pm 0.01$ in qualitative agreement with the fluctuation theory ($\Delta C_p \sim |\tau|^{-\alpha}$, the Landau value is $\alpha = 0$).The temperature $T_i = 201.581\,K$ (where C_p is a maximum) was calculated to within an uncertainty of $\pm 0.005\,K$ for both cold and heat modes. It follows from the experimental data that, when T_i changes by 0.01 K, the value of α changes by $\sim 2\%$.

Note that the value obtained for α correlates with the results of studies where the critical index α was estimated indirectly for the improper ferroelectric Rb_2ZnBr_4 by the birefringence ($\alpha = -0.05 \pm 0.02$) [2] and thermal expansion ($0 < |\alpha| < 0.07$) [3] methods.

Recall that the known calculated value for the XY model lies in the range $-0.04 \leqslant \alpha < 0$ [7]. Nevertheless, our conclusions about the critical index are only qualitative because the "infinitely sharp" scaling peak is not observed experimentally.

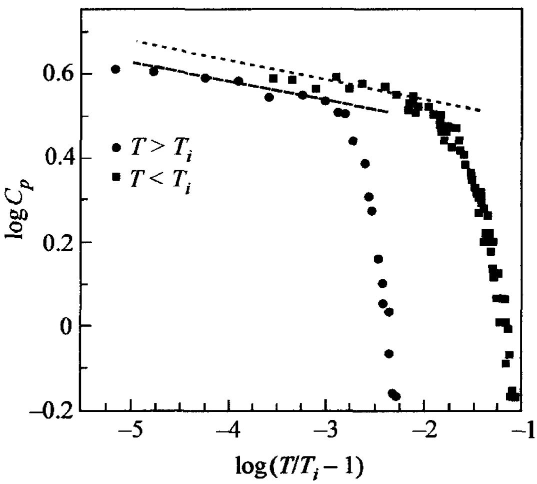

Fig. 2. Log–log plot of the anomalous part of the specific heat of $SC(NH_2)_2$ against the reduced temperature $\tau = T/T_i - 1$; $T_i = 201.58\,K$.

4. CONCLUSION

In summary, the results of our study on the specific heat of $SC(NH_2)_2$ and the corresponding theoretical analysis, according to Ref. [2], provide evidence that there is a critical region in the vicinity of the incommensurate phase transition T_i, where the anomalous behavior agrees qualitatively with the theory while making allowance for the critical fluctuations of the order parameter.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation for Basic Research (Project Nos. 00-07-90241, 00-15-96662, 02-07-06048).

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