A NOTE ON SPECIFIC HEAT BEHAVIOUR OF $NaNO_3$ CRYSTALS NEAR THE SECOND ORDER PHASE TRANSITION POINT

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In the present paper a comparison between the specific heat measurements of $NaNO_3$ single crystals and the Ising model for three dimensional lattices is done. The specific heat of $NaNO_3$ single crystals was found to be $C(T) = -A \ln|1 - T/T_c|$ below the critical point and $C(T) = A'(1 - T_c/T)^{-1/n}$ above the critical point. Theseresults are in good agreement with the Ising model for three dimensional lattices.

INTRODUCTION

Several models explain specific heat behaviour near the second order transition point at present. The most perfect of them is the Ising model for elementary three dimensional lattices [1, 2]. Though the Ising model is used as a model of ferromagnetic-antiferromagnetic transition, after elementary transformations [6] it can be used as order-disorder transition model in alloys, classical lattice gas model etc. Thus we can extend the number of materials the specific heat of which one can compare with the Ising model. According to the Ising model [1, 2] the specific heat for elementary three dimensional lattices below the second order transition point ($T < T_c$, where T_c is the second order transition temperature, in the following critical temperature only) behaves as

$$C(T) = -A \ln|1 - T/T_c|. \tag{1}$$

This is the same behaviour as that according to the two dimnesional Onsager model [3]. In the temperature region above the critical point ($T > T_c$) the specific heat for lattices of the same type behaves as

$$C(T) = A'(1 - T_c/T)^{-1/n}. \tag{2}$$

According to Domb and Sykes [4] we have $0 \leqslant 1/n \leqslant 1/4$ for a face-centerd cubic lattice at a constant magnetic field, according to Sykes and the others [5] we have $1/n = 1/8$ for the same lattice.

The aim here is to compare specific heat measurements of $NaNO_3$ single crystals [7] which have been carried out by the pulse method [13] and the Sokolov and Smidt measurements on polycrystallic $NaNO_3$ [8] with conclusions of the Ising model. $NaNO_3$ crystals represent very interesting material, because their second order phase transition is not satisfactory explained yet. There are two explanations: according to the first the second order phase transition of $NaNO_3$ crystals one can explain as an order-disorder transition type and therefore there exists here a connection with the Ising model [10, 11], according to the second one the transition can be explained by the free rotation of NO_3 groups, in that case we cannot find a connection with the Ising model [10, 11].

EVALUATION

We start from relations (1) and (2). To test the agreement of the relations (1) and (2) with experimental values we must determine the values of the constants A, A', n. According to the method of the least squares [12].

$$A = \frac{\sum_{i=1}^{N} C_i}{\sum_{i=1}^{N} -\ln|1 - T_i/T_c|} \tag{3}$$

where N is the number of the set members, C_i are experimental specific heat values at temperatures T_i. To determine the constants A', n we rewrite the relation (2) in the form

$$\log C = \log A' - \frac{1}{n} \log K$$

from which result the relations

$$\frac{1}{n} = \frac{N \log A' - \sum_{i=1}^{N} \log C_i}{\sum_{i=1}^{N} \log K_i} \tag{4}$$

$$\log A' = \frac{\sum_{i=1}^{N} \log C_i \log K_i \sum_{i=1}^{N} \log K_i - \sum_{i=1}^{N} \log C_i \sum_{i=1}^{N} \log^2 K_i}{\sum_{i=1}^{N} \log K_i \sum_{i=1}^{N} \log K_i - N \sum_{i=1}^{N} \log^2 K_i} \tag{5}$$

The agreement between the set of theoretical values calculated from relations (1) and (2) and the set of experimental values will be tested by the statistical nonparametric Wilcoxon test [9]. Theoretically calculated and experimentally

measured specific heat values below the critical point ($T < 275$ °C) are shown in Table 1. Characteristic quantities of the Wilcoxon test by [9] are for the set [7] the following: $S_+ = 282$, $S_- = 246$, $u = 0.33 < 1.96$; for the set [8] these quantities are: $S_+ = 311$, $S_- = 251$, $u = 0.54 < 1.96$, where 1.96 is

Table 1

Experimental specific heat values from [7] and [8] and theoretical ones calculated for the set [7] from $C_{theor.} = -0.251 \ln|1 - T/T_c|$ and for the set [8] from $C_{theor.} = -221 \ln |1 - T/T_c|$ below the critical point.

	Set [7]			Set [8]	
T [°C]	$C_{exp.}$ [cal/g deg]	$C_{theor.}$ [cal/g deg]	T [°C]	$C_{exp.}$ [cal/g deg]	$C_{theor.}$ [cal/g deg]
197.9	0.3686	0.3191	196.91	0.3768	0.2792
214.9	.3803	.3818	201.03	.3824	.2912
216.9	.4069	.3902	202.98	.3867	.2971
225.9	.4637	.4325	205.69	.3887	.3056
228.4	.4426	.4454	207.71	.3912	.3122
237.7	.5263	.5015	209.67	.3959	.3187
237.9	.5515	.5028	213.33	.4004	.3315
244.9	.5663	.5551	215.31	.4039	.3388
245.1	.5506	.5570	217.26	.4077	.3461
250.9	.6394	.6110	221.25	.4159	.3620
251.2	.6006	.6139	223.22	.4192	.3705
251.7	.5216	.6195	225.24	.4254	.3791
254.7	.6394	.6541	227.25	.4320	.3882
255.4	.6194	.6629	230.45	.4370	.4036
259.9	.7470	.7284	232.41	.4434	.4136
260.5	.6955	.7386	234.42	.4481	.4243
260.6	.7470	.7403	238.30	.4619	.4466
261.2	.7470	.7509	240.29	.4679	.4590
261.4	.6723	.7546	242.30	.4744	.4722
261.9	.6955	.7642	244.26	.4839	.4859
262.9	.8404	.7832	247.89	.4993	.5138
267.9	.9168	.9179	250.07	.5098	.5324
268.4	.9604	.9361	253.11	.5299	.5612
269.2	1.1205	.9685	255.00	.5437	.5812
271.9	.9604	1.1256	255.20	.5490	.5835
272.1	1.0085	1.1424	257.22	.5597	.6074
272.9	1.1864	1.2234	260.65	.5917	.6549
273.1	1.2606	1.2486	262.60	.6154	.6873
274.4	1.8336	1.5371	264.57	.6401	.7256
274.7	1.3446	1.7099	266.51	.6729	.7713
274.9	2.2410	1.9834	269.52	.7441	.8683
			271.48	.8150	.9665
			273.78	.9698	1.2034

the critical value for the significance level $\alpha = .05$. Theoretically calculated and experimentally measured specific heat values above the critical point ($T > T_c = 275$ °C) are shown in Table 2. Characteristic quantities of the

Table 2

Experimental specific heat values from [7] and [8] and theoretical ones calculated for the set [7] from $C_{theor.} = 0.0856\ (1 - T_c/T)^{-1/2.9}$ and for the set [8] from $C_{theor.} = 0.241\ (1 - T_c/T)^{-1/6}$ above the critical point.

	Set [7]			Set [8]	
T [°C]	$C_{exp.}$ [cal/g deg]	$C_{theor.}$ [cal/g deg]	T [°C]	$C_{exp.}$ [cal/g deg]	$C_{theor.}$ [cal/g deg]
275.2	1.8336	1.0329	275.66	0.8389	0.6548
275.3	.6302	.8996	276.52	.4829	.5708
275.7	.5451	.6720	279.50	.4236	.4785
275.9	.5172	.6159	281.23	.4148	.4535
276.2	.6112	.5582	283.25	.4053	.4338
276.4	.5172	.5295	286.64	.3968	.4103
276.6	.4690	.5058	288.63	.3945	.4002
277.2	.4116	.4513	290.56	.3925	.3919
277.4	.4356	.4402	293.43	.3883	.3817
281.3	.4201	.3172	295.22	.3887	.3763
			299.34	.3853	.3658
			301.40	.3852	.3613
			304.12	.3857	.3561
	$A' = 0.0856$, $n \doteq 2.9$			$A' = 0.241$, $n \doteq 6$	

Wilcoxon test by [9] are for the set [7] as follows: $S_+ = 22 > S_{cr.} = 8$, $S_- = 33$, and for the set [8] $S_+ = 48$, $S_- = 43 > S_{cr.} = 17$. Conclusions of these tests are the same: there is no significant statistical difference between the sets which have been tested. To compare sets [7] and [8] above the critical

Table 3

Experimental specific heat values from [8] and theoretical ones calculated from $C_{theor.} = 0.125\ (1 - T_c/T)^{-1/3.37}$ above the critical point.

	Set [8]	
T [°C]	$C_{exp.}$ [cal/g deg]	$C_{theor.}$ [cal/g deg]
275.66	0.8389	0.7480
276.52	.4829	.5846
279.50	.4236	.4250
281.23	.4148	.3865
	$A' = 0.125$ $n = 3.37$	

point by means of the constants A', n, the constants A', n have been calculated in the temperature region 275—281.3 °C for the set [8] (Table 3). A small difference between values of the constant n($n \doteq 2.9$, $n \doteq 3.3$) is in the limits

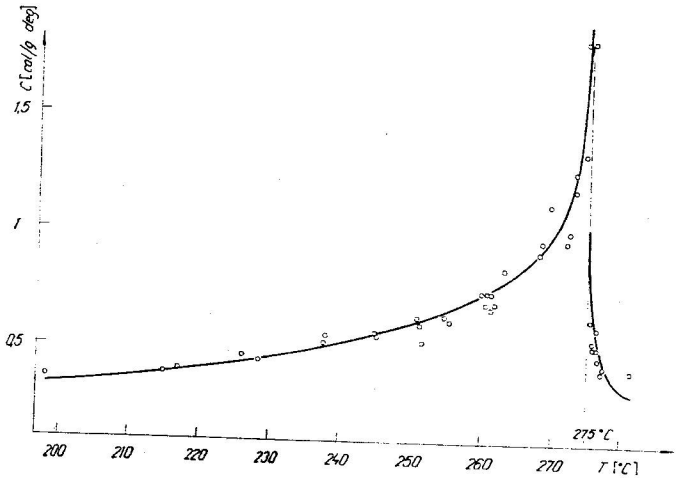

Fig. 1. Temperature dependence of the specific heat values near the critical point by [7]; full line — theoretical, dots — experimental.

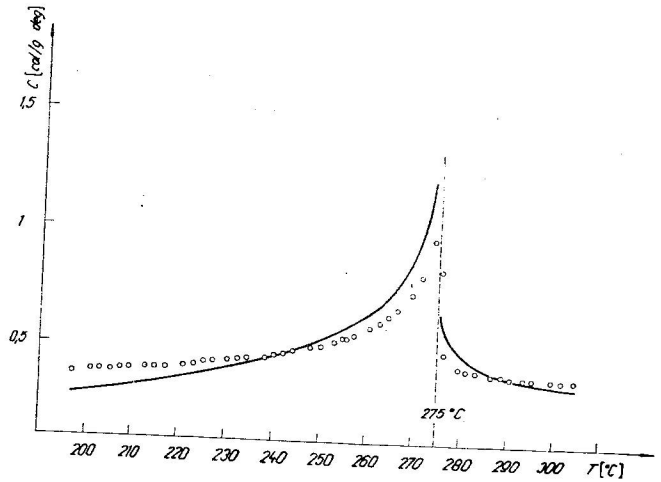

Fig. 2. Temperature dependence of the specific heat values near the critical point by [8]; full line — theoretical, dots — experimental.

of the pulse method error. For more accurate comparison it would be useful to have more values from the set [8] in the temprature region 275—281.3 °C and to use the same material for both sets [7, 8], that is the $NaNO_3$ single crystal. With respect to the determination of n in [1, 2, 4, 5] we can say that $n \doteq 3$ in the temperature region 275—281.3 °C.

The specific heat values from Tables 1 and 2 are plotted in Figs. 1 and 2

CONCLUSION

Based on results of tests we can state that the specific heat of $NaNO_3$ crystals behaves as function (1) in the temperature region $195 < T < 275$ °C and as function (2) above the critical point, where $n \doteq 3$ for $275 < T < 281.3$ °C and $n \doteq 6$ for $275 < T < 305$ °C. Based on the analysis of our material we have determined that the specific heat behaviour of $NaNO_3$ crystals near the critical point is in good agreement with the Ising model for single three dimensional lattices. Considering the connection between the Ising model and the order-disorder model, our conclusion seems to support the hypothesis that the phase transition of $NaNO_3$ crystals is of the order-disorder transition type. For a final conclusion as regards the validity of the first or the second hypothesis it would be necessary to analyse deeper both hypotheses and to carry out supplementary measurements.*)

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