Analysis of the specific heat and the free energy of [N(CH₃)₄]₂ZnBr₄ close to the ferro-paraelastic phase transition

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ABSTRACT

A power-law formula deduced from the Ising model was used to analyze the temperature dependence of the specific heat C_p and the Gibbs free energy G of [N(CH$_3$)$_4$]$_2$ZnBr$_4$ compound in the vicinity of the phase transition temperature of $T_C = 287.2$ K. Obtained values of the critical exponents α from the Gibbs free energy were consistent with that predicted from 2-d potts model ($\alpha = 0.3$), while obtained values of α from the specific heat in both ferroelastic and paraelastic phases were consistent with that predicted from the mean field theory ($\alpha = 0$) in the vicinity of the phase transition temperature. This is an indication of that [N(CH$_3$)$_4$]$_2$ZnBr$_4$ compound undergoes a second order type phase transition.

Also, the enthalpy (H) and the entropy (S) of this crystal were calculated in terms of the extracted values of the critical exponent in both ferroelastic and paraelastic phases.

1. Introduction

Tetramethylammonium tetrabromozincate, [N(CH$_3$)$_4$]$_2$ZnBr$_4$, is a member of A$_2$BX$_4$ type dielectrics, where A denotes the tetramethyl ammonium group (N(CH$_3$)$_4$ or shortly TMA), B is the transition metal such as Co, Cu or Zn and X represents the halogen such as Br or Cl. [N(CH$_3$)$_4$]$_2$ZnBr$_4$ (hereafter TMA-ZnBr$_4$) undergoes a second order transition from paraelastic (phase I) to ferroelastic (phase II) at around T$_C = 287.2$ K [1–4]. TMA-ZnBr$_4$ belongs to orthorhombic structure with the space group Pmcn above the transition temperature (paraelastic phase) and its lattice parameters in this structure reported as a = 12.681 Å, b = 9.239 Å and c = 16.025 Å [5]. It is also reported that [6,7] two inequivalent kinds of TMA molecule and one kind of ZnBr$_4$ molecule are all disordered symmetrically with the mirror planes of Pmcn in the paraelastic phase. Below the transition temperature (ferroelastic phase), TMA-ZnBr$_4$ belongs to monoclinic structure with the space group P12$_1$/c1 and the lattice constants in this structure reported to be a = 12.534 Å, b = 9.142 Å, c = 15.722 Å and the monoclinic angle $\beta = 89.69^0$ [8]. Two kinds of chains composed of ZnBr$_4$ and TMA molecules are reported to characterize the structure in the ferroelastic phase [8]. Beyond this, the crystal structure of TMA-CoBr$_4$ and its phase transitions are reported to be similar to those of TMA-ZnBr$_4$ [9,10]. As a ferroelastic material TMA-ZnBr$_4$ has potential applications in industry including optical modulators, optical domain walls memories, and tunable active gratings for lasers, tunable acoustic filters, tunable Bragg gratings and tunable diffraction gratings [11].

Various experimental techniques have been carried out to understand the phase transition mechanism in TMA-ZnBr$_4$. Igartua and co-workers [3] have measured the Raman spectra and the specific heat at various temperatures of this crystal by using the Raman scattering and the adiabatic

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calorimeter techniques. They observed a λ-type anomaly in the vicinity of the transition temperature of $T_C = 287.2$ K, that indicates an order–disorder type transition. Kuok and co-workers [12] showed the softening of the elastic constant C_{55} in both ferroelastic and paraelastic phases by using the Brillouin scattering and the ultrasonic pulse echo overlap techniques. In their x-ray diffraction studies, Hasebe [13] and Shimomuna et al. [14] have observed an anomalous behavior in the monoclinic angle β. The deviation angle $\Delta\beta$ increased rapidly in the paraelectric phase up to the phase transition temperature, as the temperature decreased $\Delta\beta$ decreased almost linearly and below 113 K $\Delta\beta$ changed it sign. Sawada et al. have proposed a simple sublattice model to explain this anomaly [15–17], on the other hand Harada et al. [9] have explained this anomaly by using a coupling term between the order parameter and the shear strains on the basis of the Landau-type free energy. Gesi and co-workers have showed the linear dependence between the hydrostatic pressure and the transition temperature [18–20]. Iwata et al. [21] have observed ferroelastic domains in TMA-ZnBr$_4$ single crystal and also they measured temperature and time dependence of the domain size distribution in this crystal. Optical measurement of TMA-ZnBr$_4$ crystal has been carried out by Etxebarria and co-workers [22]. Recently, Lim [23] has investigated the chemical shifts and the intensities of ^{1}H, ^{13}C and ^{14}N nuclei in TMA-ZnBr$_4$ single crystal by nuclear magnetic resonance (NMR) and magic angle spinning (MAS) NMR spectroscopy.

Various interpretations have been reported in the literature for the critical behavior of the specific heat in terms of the compressible Ising model. Rice [24], Mathis and Schultz [25] have predicted the specific heat at constant volume (C_v) goes to infinity at the transition temperature for a first order transition. On the contrary, Larkin and Pikin [26] have claimed that the specific heat at constant pressure (C_p) goes to infinity rather than C_v in a compressible Ising lattice which undergoes weakly first order or nearly second order phase transition. Domb [27] considered the finite size of crystal which limits the magnitude of the specific heat. In their studies Baker and Essam [28] also Wagner [29] pointerd out that C_p remains finite as T_C is approached from below. The interaction between spins and phonons (optic and/or acoustic) in a lattice system may play an important role in changing the character of the transition from second order to first order, as reported previously [30]. Such treatments have been taken in to account in a compressible Ising model by Wagner [29] and Ahorny [31]. In his study, Yurtseven [32] developed a compressible Ising model superimposed on a system of lattice vibrations to predict the critical behavior of some thermodynamic functions such as specific heat, isothermal compressibility and thermal expansion close to the T_C for such crystals exhibiting weakly first order or nearly second order phase transitions. The fact that thermodynamic quantities mentioned above are experimentally measurable provides an important opportunity in testing in theory. Yurtseven and co-workers have used this compressible Ising model to investigate the critical behavior of the specific heat near the phase transition temperature for various ferroelectric materials such as NH$_4$Br$_x$Cl$_{1-x}$ [33], LiKSO$_4$ [34] and NH$_4$Cl [35].

In this study, the applicability of the Ising model for the critical behavior of the specific heat close to the phase transition temperature was tested on the dielectric material TMA-ZnBr$_4$. Values of the critical exponent α were extracted from the observed [36] specific heat and the Gibbs energy of TMA-ZnBr$_4$ crystal in terms of the Ising model at various temperature intervals close to the phase transition temperature of $T_C = 287.2$ K. Additionally, the temperature dependence of the enthalpy (H) and the entropy (S) of TMA-ZnBr$_4$ were predicted in the vicinity of the ferro-paraelastic transition temperature.

2. Calculations and results

The free energy G of an Ising sytem is defined as

$$G = -kT\ln Z \qquad (2.1)$$

where Z is the partition function given as

$$Z = \sum_{i,j} e^{-H/kT} \tag{2.2}$$

in Equation (2.2) H is the Ising Hamiltonian given by

$$H = -J \sum_{i,j} \sigma_i \sigma_j \tag{2.3}$$

where σ_i and σ_j are the Ising spin variables and J is the interaction parameter between the nearest-neighbor molecules. In his study, Yurtseven [32] described a power-law formula for the critical behavior of the free energy near the phase transitions given as

$$G = A'_0 + A' |\epsilon|^{2-\alpha} \tag{2.4}$$

in Equation (2.4), $A'_0 = JA_0$ and $A' = JA$ are the parameters in the dimensions of energy with constants A_0 and A, $\varepsilon = |T - T_C|/T_C$ is the reduced temperature and α is the critical exponent. An analytical expression for the critical behavior of the specific heat C has been reported by Yurtseven and Sherman [37] by taking the second derivative of the free energy with respect to the temperature given as

$$C = -\frac{A' T}{T_C^2}(1 - \alpha)(2 - \alpha)|\epsilon|^{-\alpha} \tag{2.5}$$

2.1. Analysis of the specific heat and the Gibbs free energy

The observed [36] data of the Gibbs free energy of TMA-ZnBr$_4$ were analyzed according to Equation (2.4) close to the phase transition temperature of $T_C = 287.2$ K, and the fitting parameters A'_0, A' and also the critical exponent α were extracted in the temperature intervals indicated, as given in Table 1. Figure 1 shows the Gibbs free energy G as a function of the reduced temperature ε according to Equation (2.4) for the temperature interval of $282.9 < T(K) < 286.9$. Also, the heat capacity data (C_p) of this crystal [36] were analyzed according to Equation (2.5) and the fitting parameter A' and the critical exponent α were deduced (Table 2) in both ferroelastic ($T < T_C$) and paraelastic ($T > T_C$) phases of TMA-ZnBr$_4$. Figure 2 shows C_p against the reduced temperature ε according to Equation (2.5) in the temperature intervals of $284.2 < T(K) < 286.9$ (ferroelastic phase) and $287.4 < T(K) < 287.9$ (paraelastic phase), respectively. It is obvious from Figure 2 that Equation (2.5) describe the experimental data better in the ferroelastic phase ($T < T_C$) than the paraelastic ($T > T_C$) phase for the temperature intervals indicated. The extracted values of the critical exponent α from the Gibbs free energy (Equation (2.4)) and also from the heat capacity (Equation (2.5)) were given in Figure 3 as a function of the change in temperature (ΔT) according to the temperature intervals indicated in Tables 1 and 2. Furthermore, the fitting parameter A' calculated from the Gibbs free energy (Equation (2.4)) and also from the specific [36] (Equation (2.5)) was given in Figure 4 in the

Table 1. Values of the A'_0, A' and critical exponent α according to Equation (2.4) in the ferroelastic phase ($T < T_C$) of TMA-ZnBr$_4$ ($T_C = 287.2$ K) for the temperature intervals indicated.

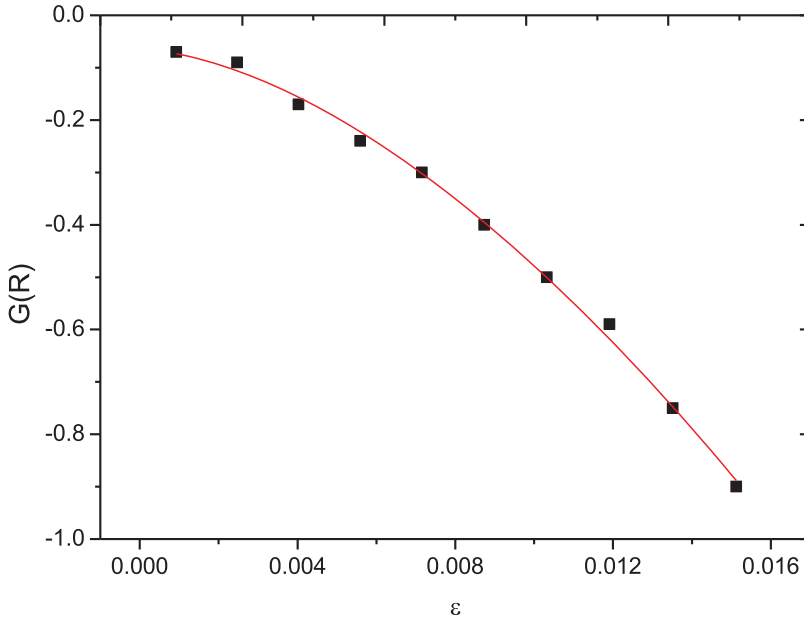| $-A'_0$ (J)	$-A'$ (J)	α	Temperature interval (K)	ΔT (K)
0.56 ± 0.05	8444 ± 289	0.31 ± 0.01	$277.2 < T < 286.9$	9.7
0.55 ± 0.06	8373 ± 436	0.31 ± 0.02	$278.6 < T < 286.9$	8.3
0.57 ± 0.07	8756 ± 742	0.30 ± 0.02	$280.1 < T < 286.9$	6.9
0.58 ± 0.08	9090 ± 1446	0.29 ± 0.04	$281.5 < T < 286.9$	5.5
0.55 ± 0.10	7376 ± 2542	0.33 ± 0.08	$282.9 < T < 286.9$	4.1
0.44 ± 0.11	3497 ± 1945	0.50 ± 0.12	$284.2 < T < 286.9$	2.7
0.49 ± 0.17	17803 ± 53894	0.20 ± 0.60	$285.6 < T < 286.9$	1.3

Figure 1. Gibbs free energy [36], *G*, as a function of reduced temperature ε according to Equation (2.4) in the ferroelastic phase (T < T_C) of TMA-ZnBr$_4$ for the temperature interval of 282.9 < T(K) < 286.9 (T_C = 287.2 K). The solid line is guide to the eye.

ferroelastic phase of TMA-ZnBr$_4$. For the appropriate unit of A' (Joule), the following quantities were used for TMA-ZnBr$_4$: mass (m) = 32. 4308 g [36], atomic weight (M_A) = 533.2854 g/mol and the gas constant (R) = 8.3145 J/mol. K

2.2. Calculation of the enthalpy and the entropy

The enthalpy (H), as a function of temperature, can be calculated for the ferroelastic-paraelastic phase transition in TMA-ZnBr$_4$ by using the simple definition of the specific heat $C_P = \partial H/\partial T$. Inserting Equation (2.5) in that definition and integrating both sides leads

$$H = -\frac{A' \, T}{T_C^2}(1-\alpha)(2-\alpha)\int_T^{T_C}\left|\frac{T-T_C}{T_C}\right|^{-\alpha}\mathrm{d}T + H_0 \qquad (2.6)$$

Table 2. Values of the *A'* and critical exponent α according to Equation (2.5) in both ferroelastic (T < T_C) and paraelastic (T > T_C) phases of TMA-ZnBr$_4$ (T_C = 287.2 K) for the temperature intervals indicated.

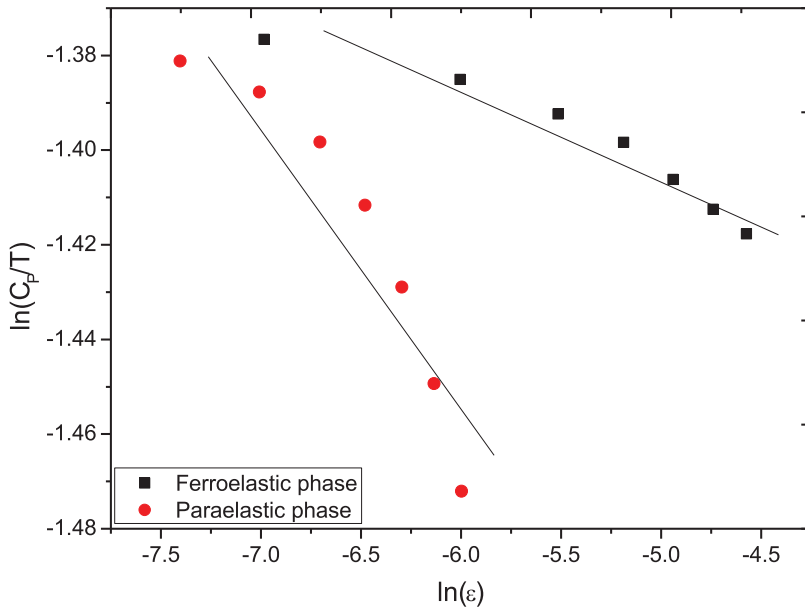| Phase	−*A'* (J)	α	Temperature interval (K)	ΔT (K)
Ferroelastic (T < T_C)	8987 ± 81	0.031 ± 0.002	277.2 < T < 286.9	9.7
	9057 ± 82	0.029 ± 0.002	278.6 < T < 286.9	8.3
	9132 ± 100	0.027 ± 0.002	280.1 < T < 286.9	6.9
	9147 ± 101	0.024 ± 0.002	281.5 < T < 286.9	5.5
	9357 ± 112	0.021 ± 0.002	282.9 < T < 286.9	4.1
	9533 ± 105	0.017 ± 0.002	284.2 < T < 286.9	2.7
	9959 ± 90	0.012 ± 0.002	285.6 < T < 286.9	1.3
Paraelastic (T > T_C)	6092 ± 305	0.094 ± 0.008	287.4 < T < 302.3	14.9
	5674 ± 306	0.109 ± 0.009	287.4 < T < 293.1	5.7
	5567 ± 445	0.115 ± 0.012	287.4 < T < 288.5	1.1
	6212 ± 551	0.094 ± 0.013	287.4 < T < 288.2	0.8
	7303 ± 548	0.062 ± 0.011	287.4 < T < 287.9	0.5
	8603 ± 387	0.032 ± 0.006	287.4 < T < 287.6	0.3

Figure 2. Specific heat [36], C_P, as a function of reduced temperature ε in a ln-ln scale according to Equation (2.5) for the temperature intervals of 284.2 < T(K) < 286.9 (ferroelastic phase) and 287.4 < T(K) < 287.9 (paraelectric phase) in TMA-ZnBr$_4$. The solid lines are guide to the eye.
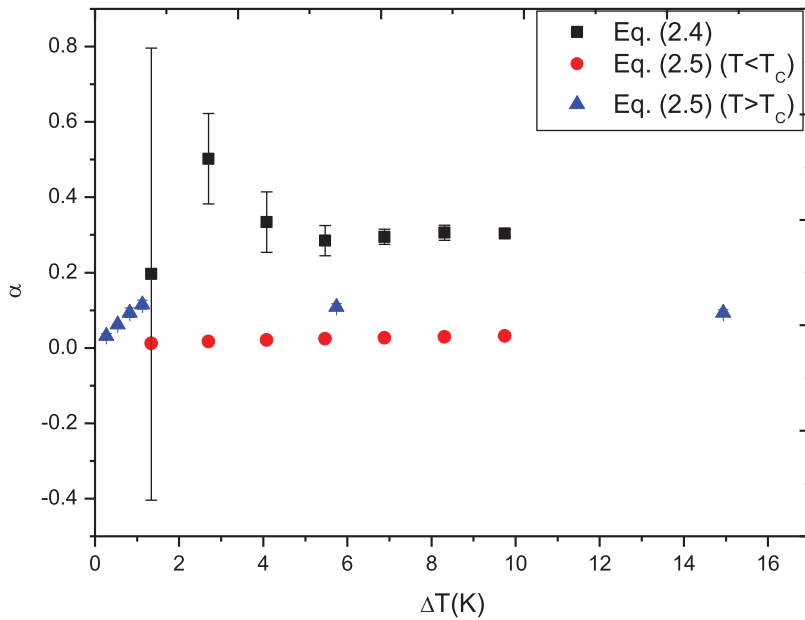

Figure 3. Values of the critical exponent α as a function of temperature ΔT (Tables 1 and 2) calculated from the Gibbs free energy [36] in the ferroelastic phase (T < T$_C$) and from the specific heat data [36] in both ferroelastic (T < T$_C$) and paraelastic (T > T$_C$) phases of TMA-ZnBr$_4$ according to Equations (2.4) and (2.5), respectively.
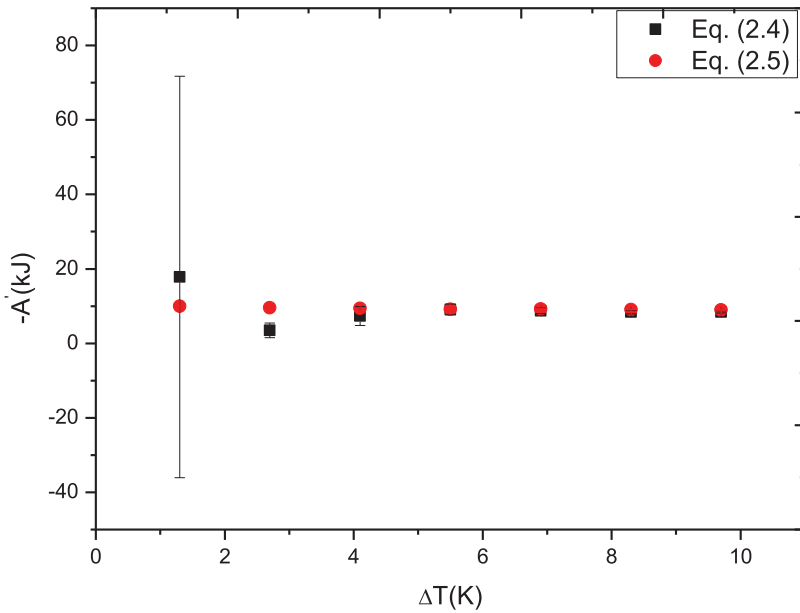
Figure 4. The fitting parameter A' deduced, independently, according to Equations (2.4) and (2.5) in the ferroelastic ($T < T_C$) phase of TMA-ZnBr$_4$ ($T_C = 287.2$ K).

where H_0 is the enthalpy value at $T = T_C$. From Equation (2.6), the temperature dependence of H in both phases of TMA-ZnBr$_4$ can be calculated as

$$H = -A' \left[(1-\alpha) \left| \frac{T - T_C}{T_C} \right|^{2-\alpha} + (2-\alpha) \left| \frac{T - T_C}{T_C} \right|^{1-\alpha} \right] + H_0 \qquad (2.7)$$

The extracted values of α and A' (Table 2) were used to calculate the temperature dependence of the enthalpy change $\Delta H = H - H_0$ in both ferroelestic and paraelastic phases of TMA-ZnBr$_4$ according to Equation (2.7) as given in Figure 5.

Likewise, the temperature dependence of the entropy S can also be calculated for the ferroelastic-paraelastic phase transition in TMA-ZnBr$_4$ by defining $C_P = T(\partial S / \partial T_P)$. Integration of this definition leads to

$$S = \frac{C_P}{T} \ \mathrm{d}T + S_0 \qquad (2.8)$$

where S_0 is the entropy at $T = T_C$. Inserting Equation (2.5) in Equation (2.8) one gets,

$$S = -A' \ \frac{(2-\alpha)}{T_C} \left| \frac{T - T_C}{T_C} \right|^{1-\alpha} + S_0 \qquad (2.9)$$

as it performed for the calculation of the enthalpy change ΔH, the temperature dependence of the entropy change $\Delta S = S - S_0$ was calculated according to Equation (2.9) by using the extracted values of α and A' (Table 2) in both phases of TMA-ZnBr$_4$ crystal. Figure 6 gives the entropy difference ΔS as a function of temperature in the ferroelastic and paraelestic phases of this crystal.

3. Discussion

The fitting parameters A_0', A' and critical exponent α were calculated from the reported [36] data of the Gibbs free energy for TMA-ZnBr$_4$ according to Equation (2.4) at various temperature intervals
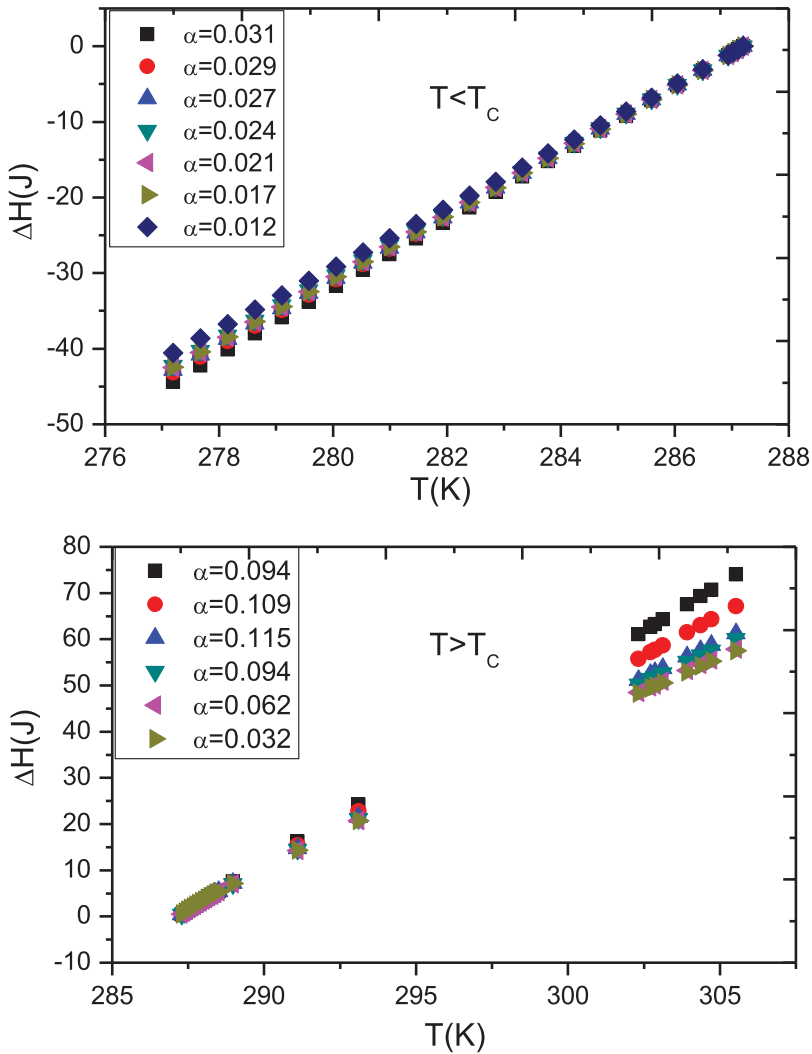
Figure 5. The enthalpy difference ΔH as a function of temperature according to Equation (2.7) in both ferroelastic ($T < T_C$) and paraelastic ($T > T_C$) phases of TMA-ZnBr$_4$ ($T_C = 287.2$ K).

close to the ferroelestic-paraelastic phase transition temperature of 287.2 K, as given in Table 1. The obtained values of α for the change in temperature (ΔT) of 9.7, 8.3, 6.9, 5.4 and 4.1 K (Table 1) were almost 0.3 that are consistent with that predicted from the 2-d potts model. Unexpectedly, for the temperature change of 2.7 K a value of 0.5 was found for the critical exponent α. A value of 0.2 was found for the 1.3 K change in temperature between the temperature interval of $285.6 < T(K) < 286.9$. Values of the critical exponent α extracted from the Gibbs free energy tends to decrease, except the value of 0.5 extracted for $\Delta T = 2.7$ K, as ΔT decreses (see Figure 3). Also note that, the error part of α between $285.6 > T(K) < 286.9$ was found to be 0.6 which was much higher than those error parts of the remaining ones changing from 0.01 to 0.12, as given in Table 1.

The specific heat data [36] of TMA-ZnBr$_4$ were also analyzed according to Equation (2.5) in both ferroelastic ($T < T_C$) and paraelastic ($T > T_C$) phases for various temperatures intervals indicated in Table 2. The extracted values of the critical exponent α in the ferroelastic phase changing between 0.03 and 0.01 (Table 2) are consistent with that predicted from the mean field theory (α=0), while α values deduced in the paraelastic phase for the temperature change (ΔT) of 14.9, 5.7, 1.1 and 0.8 K
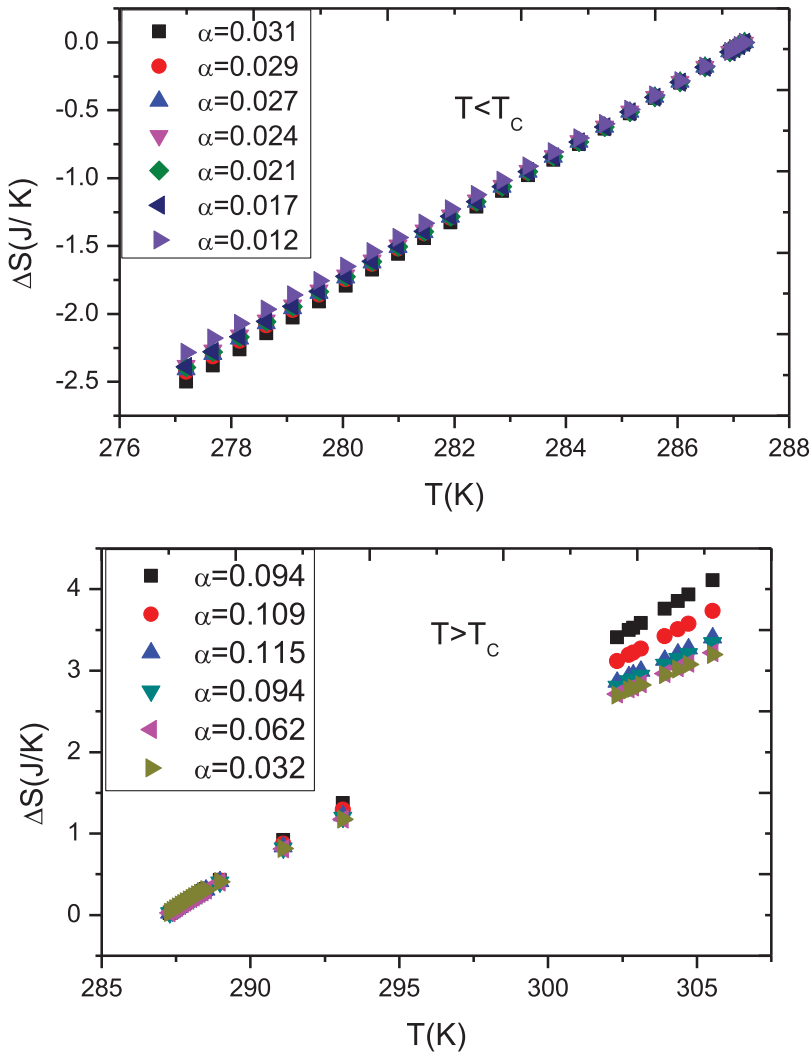
Figure 6. The entropy difference ΔS as a function of temperature according to Equation (2.9) in both ferroelastic ($T < T_C$) and para-elastic ($T > T_C$) phases of TMA-ZnBr$_4$ ($T_C = 287.2$ K).

were found to be 0.09, 0.10, 0.12 and 0.09, respectively (Table 2). These values of α are very close to that predicted from the 3-d Ising model ($\alpha = 0.125$). Furthermore, for ΔT of 0.5 and 0.3 K in the paraelastic phase of TMA-ZnBr$_4$ the values of the critical exponent α were found to be 0.06 and 0.03, respectively, which are very close to the value of $\alpha = 0$ predicted from the mean field theory. The critical exponent α calculated for both phases in TMA-ZnBr$_4$ tend to decrease, as also found in the analysis of the Gibbs free energy, as temperature get closer to the transition temperature of $T_C = 287.2$ K (Figure 3). Those calculated values of the critical exponent α in both ferroeleastic ($\alpha = 0.01$) and paraelastic phases ($\alpha = 0.03$) of TMA-ZnBr$_4$ for the temperature change of 1.3 and 0.3 K, respectively can also be compared with that reported value of $\alpha = 0.01$ in both phases of TMA-CuBr$_4$ [38]. Those extracted values of the fitting parameter $A^,$ according to Equations (2.4) and (2.5), independently, for the same temperature intervals (Tables 1 and 2) in the ferroelastic phase of TMA-ZnBr$_4$ were very close to each other, as given in Figure 4. This is an evidence for the applicability of the compressible Ising model to describe the ferroelastic-paraelastic phase transition in TMA-ZnBr$_4$.

The enthalpy H and the entropy S of TMA-ZnBr$_4$ were also calculated in this study in terms of the Equations (2.7) and (2.9), respectively. For these calculations of H and S, the extracted values of the critical exponent α and the coefficient $A^{,}$ from the specific heat data (Table 2) in both phases of this compound were used. As expected, the enthalpy H and the entropy S of increase as the temperature increases in both phases of TMA-ZnBr$_4$, as given in Figures 5 and 6, respectively.

4. Conclusions

The critical behavior of the specific heat and also the Gibbs free energy in TMA-ZnBr$_4$ crystal are analyzed by using the compressible Ising model in the vicinity of the phase transition temperature of 287.2 K. The values of 0.01 and 0.03 for the critical exponent were found as the phase transition temperature was approached for the change in temperature of 1.3 and 0.3 K in ferroelastic and para-elastic phases, respectively. Both values are very close to that predicted from the mean-field theory. This is an indication of that the compressible Ising model is adequate to describe the second order ferroelastic-paraelastic phase transition of TMA-ZnBr$_4$. This model can also be applied to the other member of A$_2$BX$_4$ type dielectrics.

Also, the temperature dependence of the enthalpy and the entropy which we predicted in this study can be compared with the calorimetric measurement when they are available in the literature.

Disclosure statement

No potential conflict of interest was reported by the author.

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