

Specific Heat of NH_4Cl and $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ Crystals Close to the Ferro-Ordered Phase

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Summary: This study gives calculation of the specific heat C_{vi} of NH_4Cl and $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ under the Ising model for the transition between the disordered (D) and ferro-ordered O(F) phases in these crystalline systems. Our C_{vi} values which we calculated for $x = 0$ and $x = 0.04$, agree both below and above T_c with the observed C_p data from the literature. Our value of $\alpha \cong 0.1$ ($T < T_c$ and $T > T_c$) is in good agreement with the predicted value of $1/8$ (0.125) of a 3D Ising model.

Introduction

Ammonium halides undergo order-disorder phase transitions. As the temperature decreases from the room temperature in the disordered (D) phase, there occur two ordered phases, namely, antiferro-ordered O(AF) and ferro-ordered O(F) phases. In the disordered (D) phase, the NH_4^+ tetrahedra are randomly distributed among the two possible states similar to the up and down orientations of the spins [1]. This phase has the CsCl structure with O_h^1 symmetry for both NH_4Cl and NH_4Br . At about 234 K the disordered (D) phase transforms into the antiferro-ordered O(AF) phase in NH_4Br . For NH_4Cl phase transition occurs at about 242 K from the disordered (D) phase to the ferro-ordered O(F) phase. As the temperature lowers further down to 234 K, the antiferro-ordered O(AF) phase transforms into the ferro-ordered O(F) phase in NH_4Br . In the ferro-ordered O(F) phase which has the CsCl structure of the T_d^1 symmetry, all the NH_4^+ tetrahedra have the parallel arrangement, which corresponds to either up or down orientation of the spins. In the antiferro-ordered O(AF) phase which has a tetragonal structure with the D_{4h} symmetry, the NH_4^+ tetrahedra are oriented antiparallel to each other in the a-b plane and they are parallel along the C-axis [2]. This arrangement of the NH_4^+ tetrahedra in the disordered and ordered phases of the ammonium halides is similar to the up and down orientations of spins in an Ising model. Thus, the order-disorder phase transitions in ammonium halides can be interpreted in terms of the Ising model [3].

Regarding the three phases, namely, the disordered (D), antiferro-ordered O(AF) and the ferro-ordered O(F) phases in the ammonium halides,

various T-P and T-X phase diagrams have been obtained experimentally and theoretically in these crystals. Experimentally, P-T phase diagram of ammonium halides has been obtained by Stevenson [4]. This has been modified by Press *et al.* [5] and a master P-T diagram for ammonium halides has been given by Leung *et al.* [6]. Not only P-T phase diagrams, but also X-T phase diagrams for ammonium halides have been reported in the literature. Experimentally, X-T phase diagrams for $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ system have been obtained by Jahn and Neumann [7], Garland *et al.* [8], Goto *et al.* [9] and Yoshizawa *et al.* [10]. Theoretically, P-T and X-T phase diagrams for ammonium halides have also been obtained. From an Ising pseudospin-phonon coupled model due to Yamada *et al.* [3], they have obtained P-T phase diagram in ammonium halides. Hüller [11] and Vaks and Schneider [12] have also calculated P-T phase diagrams from their models. Using the mean field theory, we have been able to obtain P-T phase diagram for ammonium halides [13]. By means of the mean field theory, we have also obtained T- X_{Br} phase diagram for the $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ system [14].

Various physical properties of ammonium halides close to phase transitions have been studied both experimentally and theoretically. We have reviewed previously some of those studies related to the λ -phase transitions in NH_4Cl [15] and NH_4Br [16]. In particular, the thermal properties of ammonium halides have been investigated using various techniques in the literature. Measurements of the heat capacity near the phase transitions have been performed for NH_4Cl at 1 atm and at high pressures

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[17] and for NH_4Br [18]. Also, a high-resolution acalorimeter has been used to measure C_p for mixed crystals of $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ ($X_{\text{Br}} = 0.04, 0.26$ and 0.51) and NH_4Br crystal [19]. Among those, $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ and NH_4Cl ($X_{\text{Br}} = 0$) exhibit ferro-ordering which is due to direct interactions between the NH_4^+ tetrahedra (spin-spin interactions). The other mixed crystals of $\text{NH}_4\text{Br}_{0.26}\text{Cl}_{0.74}$ and $\text{NH}_4\text{Br}_{0.51}\text{Cl}_{0.49}$ and NH_4Br exhibit antiferro-ordering which is due to indirect interactions between the NH_4 tetrahedra and halide ions (pseudospin-phonon interaction).

In this study we calculate the specific heat C_{v1} due to direct interactions for NH_4Cl and the mixed crystal of $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$. For this calculation we use an Ising model superimposed on an Einstein and/or Debye model which we have developed in our earlier study [20]. We have also applied our model to ammonium halides (NH_4Cl and NH_4Br) previously [21]. By considering the fact that our model undergoes weakly first order or nearly second order, here we apply it to NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ crystals. We will then show that the specific heat C_{v1} of both systems can be described adequately close to the transition between the disordered (D) and the ferro-ordered O(F) phases. Below, we give our calculations and results in Section 2. We discuss our results in Section 3. Conclusions are given in Section 4.

Results and Discussion

We present here the critical behaviour of the specific heat C_{v1} according to an Ising model defined as with the Hamiltonian;

$$H_i = -J(V) \sum_{\langle ij \rangle} \sigma_i \sigma_j \quad (1)$$

where σ_i, σ_j represent the nearest spin variables and $J(V)$ is the interaction parameter that depends on the volume of the crystal. The free energy is defined as;

$$F_i(J(V), T) = -kT \ln Z \quad (2)$$

where the partition function is given by

$$Z = \sum_{\{\sigma_i\}} e^{-H_i/kT} \quad (3)$$

By employing the power-law formula for the free energy

$$F_i = A'_0 + A' |\epsilon|^{2-a} \quad (4)$$

we are able to obtain the critical behaviour of the specific heat C_{v1} given by

$$C_{v1} = -\frac{JA_0}{T_c^2} (1-a)(2-a) |\epsilon|^{-a} \quad (5)$$

In Eq. (4) the parameters A'_0 and A' are defined as $A'_0 = JA_0$ and $A' = JA$, $\epsilon = |T - T_c|/T_c$ is the reduced temperature where T_c is the critical temperature. A_0 and A are dimensionless constants. As given in Eq. (5), the specific heat has a power-law, $C_{v1} \propto |\epsilon|^{-a}$ with the critical exponent a . We have developed this model which gives rise to the analytical expressions of the thermodynamic functions such as the specific heat C_{v1} , thermal expansivity α_T and the isothermal compressibility κ_T , and also their critical behaviour close to phase transitions in our earlier study [20]. In particular, the specific heat C_{v1} has also been derived in our earlier study [22].

We calculated here the specific heat C_{v1} using Eq. (5) for NH_4Cl and $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ crystalline systems. In particular, we calculated for $x = 0$ (NH_4Cl) and for $x = 0.04$ ($\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$) in the regions of $T < T_c$ and $T > T_c$ under the Ising model studied here. Our calculations gave us the value of $a \cong 0.1$ for the critical exponent of the specific heat C_{v1} for both $T < T_c$ and $T > T_c$ in NH_4Cl ($T_c = 242.6$ K) and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ ($T_c = 237.25$ K). The exact values of the exponent a , are given in Table-1. We plot our C_{v1} values which we calculated as a function of temperature for NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ in Figs. 1 and 2, respectively. We also plot the observed C_p data due to Lushington and Garland [19] for comparison in Figs. 1 and 2. In Fig. 3, we plot our C_{v1} values against temperatures for both NH_4Cl (Fig. 1) and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ (Fig. 2).

The critical behaviour of the specific heat is the same for NH_4Cl ($T_c = 242.6$ K) and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ ($T_c = 237.25$ K), as shown in Figs. 1 and 2, respectively, except that the transition temperature T_c is shifted by 5.35 K (see Fig. 3). The values of the critical exponent for the specific heat, which we present in Table-1, also indicate that the specific heat behaves the same close to the transition temperature in the region of $T < T_c$ and $T > T_c$ for both NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ crystals.

As shown in Figs. 1 and 2, the values which we calculated, are generally in good agreement with

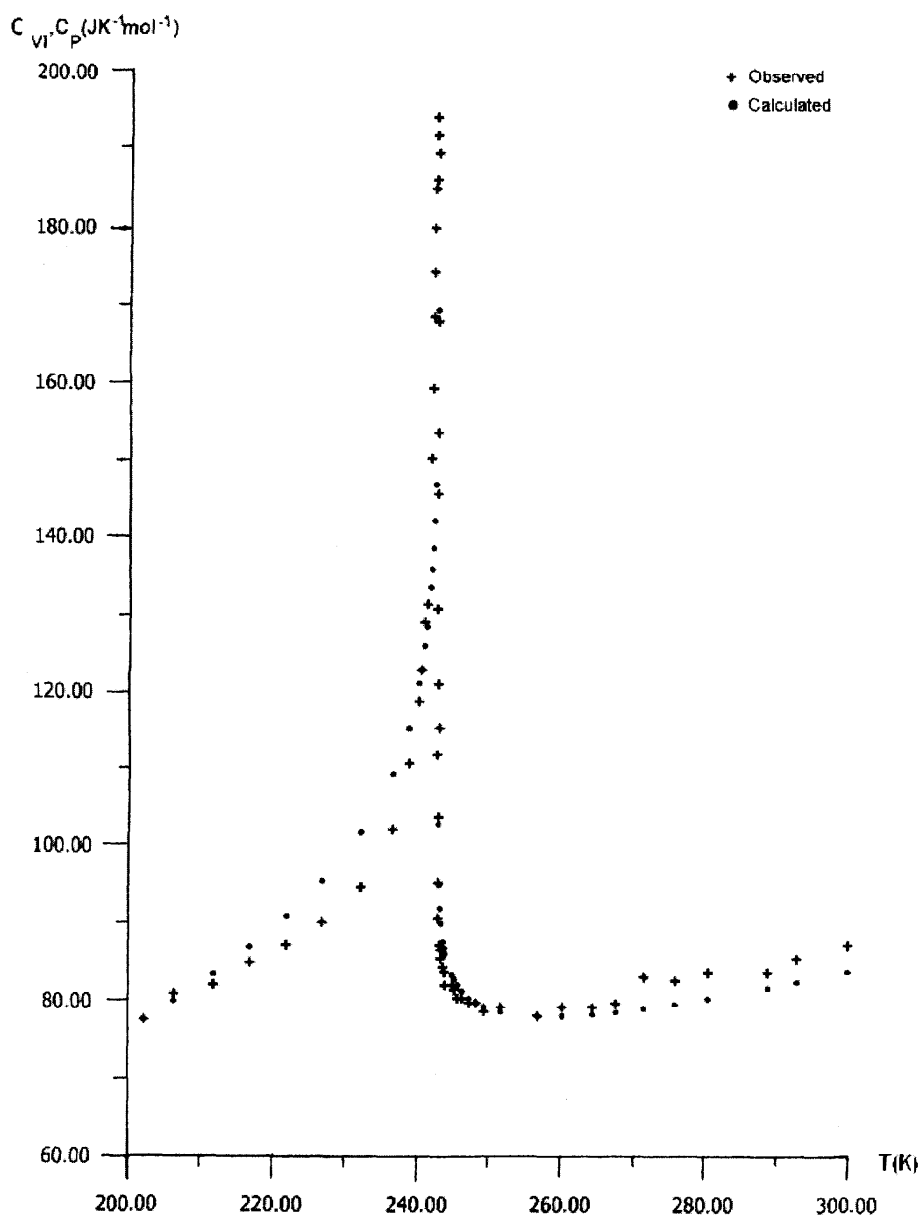


Fig. 1: The specific heat C_{v1} of NH_4Cl which we calculated according to Eq. (5) as a function of temperature ($T_c = 242.6$ K) under the Ising model. The observed C_p data which we plot here is taken from Lushington and Garland [19].

the observed C_p data. In particular, this agreement is good above T_c up to about 260 K for NH_4Cl (Fig. 1). Our calculated values of C_{v1} agree very well with the observed C_p data below T_c down to nearly 220 K for $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ (Fig. 2). For both crystals the C_{v1} or C_p values are associated with ferro-ordering below

T_c . This transition from the disordered (D) phase to the ferro-ordered O(F) phase can be considered as a weakly first order or nearly second order in character. This is due to the fact that there is a large discontinuity accompanied with a small continuity in the specific heat for both NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$,

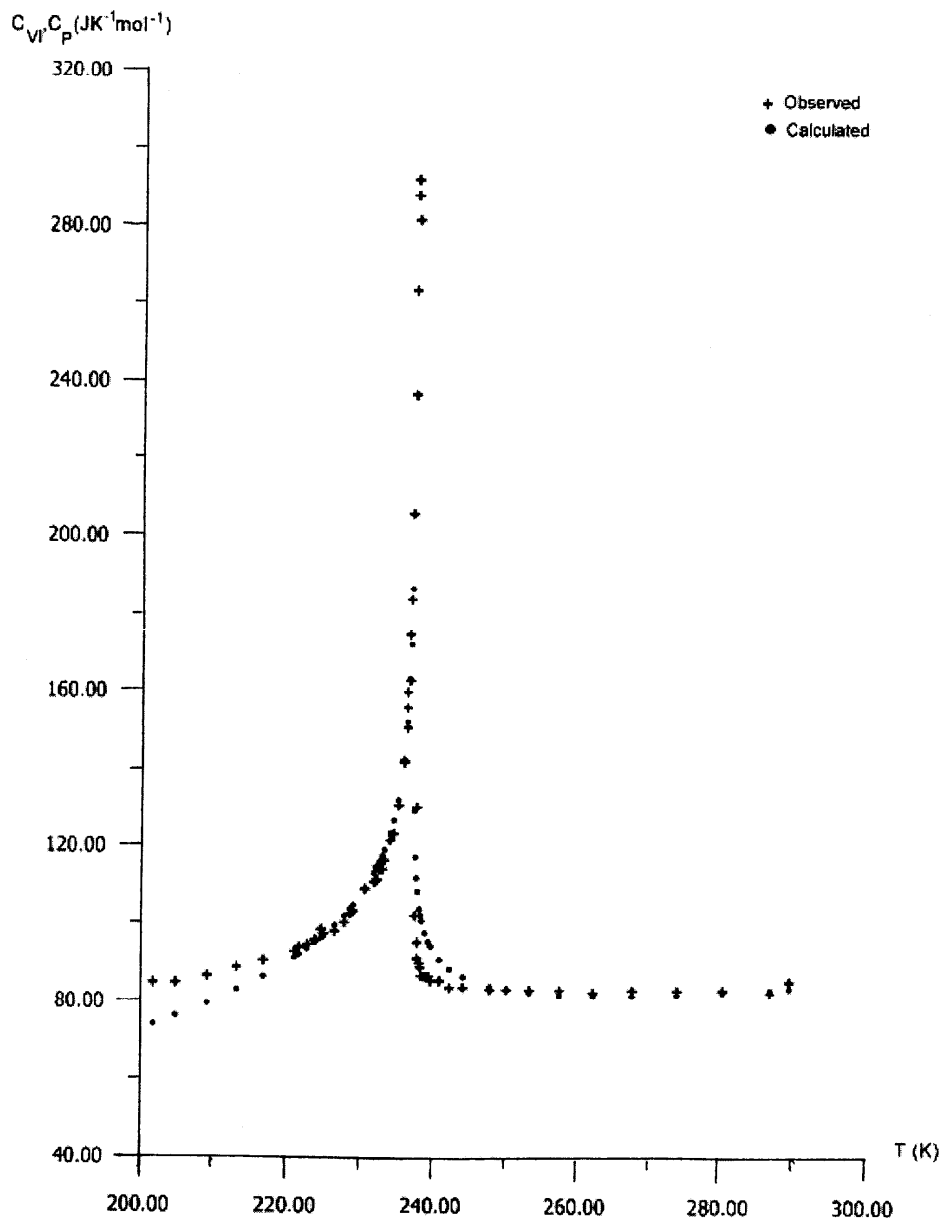


Fig. 2: The specific heat C_{VI} of and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ which we calculated according to Eq. (5) as a function of temperature ($T_c = 237.25$ K) under the Ising model. The observed C_p data which we plot here is taken from Lushington and Garland [19].

as shown in Figs. 1 and 2, respectively. In particular, the specific heat C_{VI} which has this large discontinuity at the transition temperature, decreases continuously just below T in the ferro-ordered phase O(F) for both crystals. Also, our exponent value of $a \cong 0.1$ is very close to the predicted value of a 3D

Ising model. So, our exact values of $a \cong 0.1$ (NH_4Cl) and $a = 0.15$ ($\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$) for $T < T_c$ (Table-1) are very close to the value of $0.066 (= 1/16)$ predicted by a 3D Ising model. For $T > T_c$ our values of $a = 0.06$ (NH_4Cl) and $a = 0.10$ ($\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$) are also very close to the value of $0.125 (= 1/8)$ due to a 3D

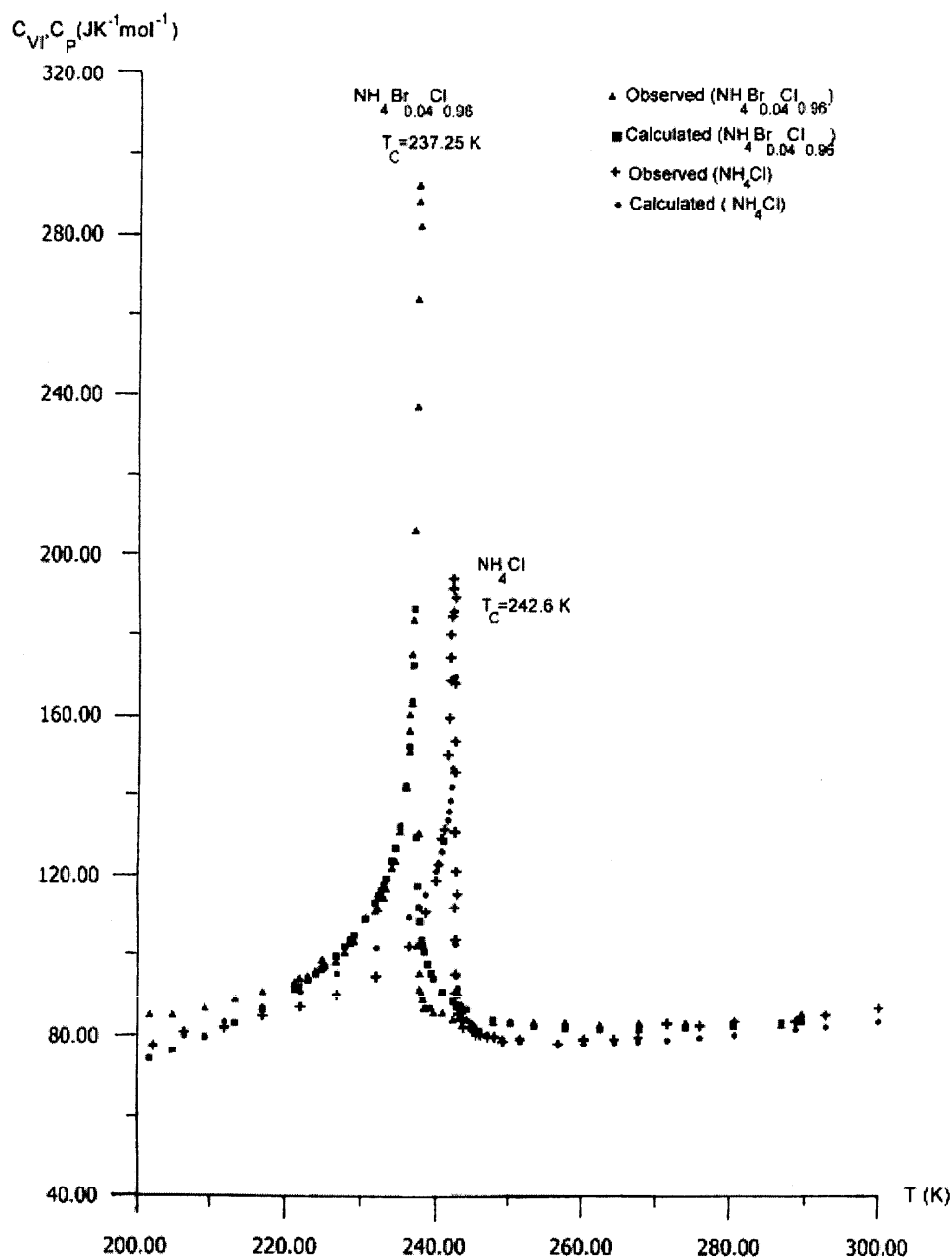


Fig. 3: The specific heat C_{VI} of $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ crystals which we calculated according to Eq. (5) as a function of temperature under the Ising model for $x = 0$ (NH_4Cl , $T_c = 242.6$ K, see Fig. 1) and $x = 0.04$ ($\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$, $T_c = 237.25$ K, see Fig. 2). The observed C_p data which we plot here is taken from Lushington and Garland [19].

Ising model. Our values of the critical exponent for the specific heat C_{vi} can also be compared with those predicted from an Ising lattice with the coupling between spins and phonons. Such a model has been

introduced by Yamada *et al.* [3] for ammonium halides. According to the renormalization analysis of this model, there occur four fixed points, namely, a Gaussian fixed point, an Ising ($n = 1$) fixed point, a

Table-1: Our values of the critical exponent a of the specific heat and the JA values (Eq.5) for NH_4Cl and $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ ($X_{\text{Br}} = 0.04$) crystals close to the transition between the disordered (D) and ferro-ordered O(F) phases. X_{Br} denotes the concentration of bromide.

X_{Br}	T_c (K)	$T < T_c$		$T > T_c$	
		a	$-JA$ (J/mol.)	a	$-JA$ (J/mol.)
0	242.6	0.10	11022.27	0.06	8267.03
0.04	237.25	0.15	9884.12	0.10	8185.38

cubic ($n = 3$) fixed point and a tetracritical ($n = 4$) fixed point, as also pointed out in an earlier study [19]. Here n represents the spin dimensionality. If the transition is of a second order in general, the transition from the disordered (D) phase to the ferro-ordered O(F) phase in NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ can be classified as an Ising-like with the exponent value of $a \cong 0.12$, as also reported in the work of Lushington and Garland [19]. Thus, our exponent value of $a \cong 0.1$ is exactly the same as that predicted by an Ising ($n = 1$) fixed point. This is also appropriate with our model which we have developed as an Ising model superimposed on an Einstein and/or Debye model [20], which undergoes a weakly first order or nearly second order. Since our model assumes the volume dependence of the exchange integral which defines the interactions between the nearest-neighbour spins, or between the NH_4^+ tetrahedra in the case of ammonium halides, an Ising lattice with the coupling between spins and phonons according to Yamada *et al.* [3], should predict the same value of the critical exponent for the specific heat as that predicted by our model. In fact, in addition to bilinear coupling between spins and the transverse phonons for wave vectors $k \neq 0$, there can be quadratic coupling between spins and the longitudinal phonons, which give rise to the first order phase transition in a compressible lattice, as reported by Lushington and Garland [19]. In that case, the value of the critical exponent for the specific heat becomes $\alpha' = 0.5$ ($T < T_c$), which corresponds to the tricritical value in an Ising model. In fact, this is the same value obtained experimentally by Lushington and Garland [19] when they analysed their observed C_p data for the ferro-ordered phase O(F) in NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$. This value of $\alpha' = 0.5$ however, does not define a weakly first order phase transition in NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ according to our predictions. Instead, this value corresponds to the tricritical phase transition in NH_4Cl at 1500 bar and in ND_4Cl at 1 bar, which has

also been obtained experimentally by Lushington and Garland [19]. Hence, our exponent value of $a \cong 0.1$ which we have obtained in this study, describes satisfactorily a weakly first order or nearly second order phase transition in NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ crystals.

Experimental

The heat capacity of NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ single crystals was measured using a high-resolution ac-calorimeter over the range of 200-300 K by Lushington and Garland [19]. The measurements of the heat capacity were performed in the stability of cryostat temperature (± 0.5 mK over periods of nearly 1 h), as stated previously [19]. Random errors in the measurements caused standard deviations in C_p of 0.8 J/K.mol for the $x = 0.04$ sample and systematic errors in C_p occurred due to nonuniform heat fluxes across the heater [19]. Some details related to the experimental measurements are also available [19].

In this study we performed the analysis of the experimental C_p data for NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ obtained by Lushington and Garland [19] according to a power-law formula.

Conclusions

In conclusion, the specific heat has been calculated here for the NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ ($X_{\text{Br}} = 0.04$) crystals under an Ising model which undergoes a weakly first order or nearly second order phase transition. We analysed the observed C_p data from the literature for NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ according to the C_{V1} expression predicted by the Ising model which we have developed. Our analysis gave us the value of $a \cong 0.1$ both above and below T_c , which describes the critical behaviour of the specific heat in NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ crystalline systems. Our value is very close to the expected values of $0.125(1/8)$ for $T > T_c$ and $0.066 (= 1/16)$ for $T < T_c$ according to a 3D Ising model. But our value of $a \cong 0.1$ does not agree with the quasicritical or quasitricritical value of $\alpha' = 0.5$ ($T < T_c$) which has been obtained from an analysis of the observed C_p data for those crystals studied. Compared with the observed C_p data, our C_{V1} values which we calculated are particularly in good agreement above T_c and below T_c for NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$, respectively. We conclude here that the Ising model

undergoing a weakly first order or nearly second order, describes adequately the observed behaviour of NH_4Cl and $\text{NH}_4\text{Br}_{0.04}\text{Cl}_{0.96}$ crystals for their transition from the disordered (D) phase to the ferro-ordered O(F) phase.

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