Research Article

Critical Behaviour of the Order Parameter From Birefringence and Raman Intensity Data Close to the λ-Transition In NH_4Br

H. Yurtseven

Department of Physics, Middle East Technical University, Ankara, Turkey.

ABSTRACT

The critical behaviour of the order parameter is investigated using the birefringence and Raman intensity data near the λ-phase transition (T_λ=235 K) in NH_4Br. From the analysis of the experimental data using the mean field theory, the critical exponent for the order parameter is determined as $\beta \approx 0.5$. This indicates a second order transition between the phases II (CsCl) and III (tetragonal) in NH_4Br, as expected.Our results show that the mean field model is capable of describing the order-disorder phase transition in the NH_4Br crystal.

1. INTRODUCTION

NH_4Br undergoes various phases with different crystal structures by varying the temperature and pressure. The phase I (α phase) with the NaCl - disordered structure transforms to the phase II with the CsCl – disordered structure at around 411K, as the temperature lowers. This is followed by a phase change from the phase II (β phase) to the antiferro-ordered phase III (γ phase) with the tetragonal structure at about 234K. As the temperature decreases further down to ~78K, phase III is transformed to the phase IV (δ phase) which is ferro-ordered with the CsCl crystal structure. The phase II- phase III transition is an order-disorder (λ type) as studied extensively by using various experimental and theoretical techniques, which we have reviewed in our earlier work[1].

In the disordered β (phase II) with the O_h^1 symmetry (space group *Pm3m*), the NH_4^+ ions are orientated randomly between the two- energetically equivalent positions[2], identified with the up and down orientations of the spin in an Ising model. In the antiferro-ordered γ (phase III) with the $D_{4h}^>$ symmetry (space group *P4/nmm*), the NH_4^+ ions are orientated antiparallel in the a-b plane and they are parallel to the c-axis. When the lower temperatures are reached (T≈78K), all the NH_4^+ ions become parallel to the z-axis in the ferro-ordered γ (phase IV) with the T_d^1 symmetry (space group P43m) in the NH_4^+Br.

Orientations of the NH_4^+ ions coupled with the displacement of the Br^- ion have been studied in an Ising pseudospin-phonon coupled model by Yamada et al[3]. This interaction between one pseudospin and one phonon in NH_4Br has been extended by Matsushita[4] who considered interactions for more than one pseudospin and one phonon. By deriving the temperature dependence of the Raman frequencies and of the damping constant (Raman band width) he explained qualitatively anomalous behavior of the hard modes of ammonium halides (NH_4Br and NH_4Cl) near T_λ (II = III phase transition). The soft mode- hard mode coupling model[5] has been developed on the basis of the Matsushita's theory and applied to the temperature dependence of the some Raman modes of the KDP type crystals[6,7]. We have also applied the soft mode- hard mode coupling model to the ammonium halides (NH_4Cl and NH_4Br) and we calculated the temperature dependence of the Raman bandwidths of the some external and internal modes close to the λ transition (phase II- phase III) in our earlier works[8-10]. Close to the II-III phase transition in NH_4Br, regarding other aspects of our studies we have related the Raman frequency shifts of the

modes to the specific heat Cp[11]. Those correlations have been obtained between the Raman frequency shifts and the thermodynamic quantities (specific heat Cp and the thermal expansivity α_p) close to the I-II transition in NH_4Br[12].

In this study we analyze temperature dependence of the order parameter close to the II-III phase transition in NH_4Br by using the experimental data for the birefringence and neutron diffraction[13] and also for the Raman intensity data[10] for this crystal. Since the birefringence is caused by short-and long- range order and at a phase transition it corresponds to the long range order parameter (the short range order does not contribute because of symmetry reasons)[13], the temperature dependence of the long range order parameters can be analyzed close to the II-III phase transition in NH_4Br. Also, the Raman intensity of the υ (56 cm^{-1}) mode can be associated with the disorder parameter $1-S^2$ in the phase III (γ) of NH_4Br. In this study we correlate between the Raman integrated intensity of this mode and the disorder parameter close to the II-III transition for this crystal by using the mean field theory.

2. ANALYSIS OF THE ORDER PARAMETER

The temperature dependence of the order parameter S was analyzed below the transition temperature (T_λ = 235 K) for the phase II- phase III transition of NH_4Br. For this analysis, the experimental data for the birefringence η and the square of the order parameter S^2, as determined from the neutron diffraction[13], were used according to a power law relation

$$S = A_0^{1/2}\left(\frac{Tc-T}{Tc}\right)^{\beta} \quad (1)$$

where β is the critical exponent and A0 is the amplitude. Since the birefringence η is directly proportional to the order parameter S[13]

$$\eta \propto S^2 \quad (2)$$

the temperature dependence of the birefringence can be expressed as

$$\eta = A_0\left(\frac{Tc-T}{Tc}\right)^{2\beta} \quad (3)$$

or

$$\ln \eta = \ln A_0 + 2\beta \ln\left(\frac{Tc-T}{Tc}\right) \quad (4)$$

From the analysis of the birefringence and the neutron diffraction data[13], the fitted parameters A0 and β were determined from Eq.(4) in the different temperature intervals as given in Table 1. Similarly, the Raman intensity of the lattice mode associated with the disorder parameter $1-S^2$ (S is the order parameter) can be analyzed according to the relation

$$I = I_0 + A(1-S^2) \quad (5)$$

where I_0 denotes the minimum Raman intensity (S=1) since the order parameter varies from 0 to 1. For this analysis, we used the temperature dependence of the order parameter S from the mean field theory [4] according to the relation

$$S = \left[3\left(1-\frac{T}{T}\right)\right]^{1/2} \quad (6)$$

By fitting the calculated S values to the observed Raman intensities of the υ (56 cm^{-1}) mode [10], the parameters I_0 and A were determined, as given in table 2. This analysis was performed for the phase II-phase III transition in NH_4Br. Fig. 1 gives in a log-log plot the order parameter S analyzed using the birefringence and neutron diffraction data[13] as a function of the temperature in the given temperature intervals (Table 1)according to the Eq.(4). In fig. 2 the observed Raman intensity of the υ (56 cm^{-1}) mode [10] is plotted as a function of the disorder parameter ($1-S^2$) according to the Eq.(5) for the phase II-phase III transition in NH_4Br. In fig2 the two straight lines are drawn according to the linear relation (Eq.5) for the two temperature intervals as indicated in Table 2.

3. DISCUSSION

We analyzed here the temperature dependence of the order parameter S using the experimental data for the birefringence η and the neutron diffraction[13] according to the power law formula (Eq.3) for the II-III phase transition in NH_4Br (T_c=235K). When plotted in a log-log scale η against the reduced

temperature $\epsilon = (\frac{Tc-T}{Tc})$, our analysis gave us the value of β= 0, 25 as the critical exponent for the order parameter in the whole temperature interval (99.7< T(K)< 234.2), as given in the Table 1 in the log-log scale within this temperature interval, a linear plot of ln η vs. ln ϵ was not satisfactory since this variation is nonlinear. Instead variation of the order parameter η with the reduced temperature ϵ in a log-log scale was analyzed in the temperature intervals where the linear plots were obtained according to Eq.(4). Values of the critical exponent β and the amplitude A_0 are given in Table1 from our analysis in the temperature intervals indicated. We plot in Fig.1 ln η against ln ϵ as an example in the temperature interval with the exponent value of β=0.20 (Table1). As given in Table 1, the β values change from 0.08 to 0.52 within the temperature intervals, as the transition temperature (T_c=235K) is approached from the low temperatures (from 99.7 to 234.2K) in the antiferro-ordered γ (phase III). This shows that regarding the β values for the order parameter (Table 1), the mean field value (β=0.5) is reached close to the phase II- phase III transition (Tc=235K). Our linear plots of lnη vs. ln ϵ in the temperature intervals indicated (Table 1) are satisfactory. For the whole temperature ranges between 99.7 and 234K the value of β=0.25 which we obtained from our plot of lnη vs. ln ϵ, was also obtained from previous analysis[13]. However, our analysis given in this study shows in some details how to critical exponent β changes systematically in the temperature intervals (Table 1) for the II-III transition of NH_4Br.

We analyzed in this study the Raman integrated intensity (I) of the υ (56 cm^{-1}) mode related to the square of the order parameter (S^2) according to the Eq.(5) for the II-III phase transition in NH_4Br. The Raman intensity does not vary with 1- S^2 linearly.

The temperature dependence of the order parameter S was obtained by analyzing the experimental data for the birefringence and neutron diffraction[13]according to a power law formula with the exponent value of β=0.5 close to the II-III as given above. Also, the temperature dependence of the damping constant calculated from Ising pseudospin- phonon coupled system by using the order parameter given by the mean field theory (Eq.6), predicted adequately the observed behavior of the υ (177 cm^{-1}) Raman bandwidths close to the II-III phase transition in NH_4Br, as reported in our recent study [9]. On the basis, we related the Raman intensity to the disorder parameter 1-S^2 by calculating the temperature dependence of the order parameter S from the mean field theory according to Eq.(6) with the critical exponent β = $\frac{1}{2}$. A linear variation of the Raman intensity I with the disorder parameter 1-S^2 was obtained in the temperature intervals, as given in Table 2. Values of the fitted parameters I_0 and a varied in the temperature intervals studied (Table 2).

In our recent study, we have analyzed the temperature dependence of the Raman integrated intensities of the υ (56 cm^{-1}) according to a power-law formula and obtained the value of β= 0.20 ±0.04 as the critical exponent for the order parameter for the II-III phase transition in NH_4Br[10]. This β value was extracted in a large temperature range and the observed Raman intensities of this mode were scattered close to the II-III phase transition in NH_4Br[10]. Our β value of 0.20 extracted using the Raman intensities of the υ (56 cm^{-1}) [10] corresponds to the same value in the temperature range of 2.3× 10^{-2} < ϵ < 0.29, which we obtained using the birefringence and the neutron diffraction data[13], as given in the Table 1 in this study.

4. CONLUSION

Temperature dependence of the order parameter (S) was analyzed here using the experimental data for the Birefringence, neutron diffraction and the Raman intensity close to the II-III phase transition in NH_4Br. From the analysis of the birefringence and the neutron diffraction data, values of the critical exponent β for the order parameter vary between 0.1 to 0.5 when approaching the transition temperature (T_c=235K) from the

lower phase (phase III) to the higher phase (phase II) temperatures in this crystal. From the analysis of the Raman integrated intensities (I) of the υ (56 cm^{-1}) mode, a linear variation of I with the disorder parameter 1-S^2 was obtained in a certain temperature interval from the mean field theory with the β =1/2 in the antiferro-ordered (phase III) phase of NH_4Br. This indicates that the II-III phase transition is close to a second order and observed critical behavior can be described satisfactorily by the mean field theory.

Table 1: Values of the critical exponent β for the order parameter and amplitude A_0 (Eq.1) in the temperature intervals indicated for the II-III phase transition in NH_4Br

β	A_0	Reduced Temperature $\epsilon = (\frac{Tc - T}{Tc})$
0.08	1.1293	$0.21 < \epsilon < 0.58$
0.20	1.6208	$2.3\times10^{-2} < \epsilon \ll 0.29$
0.52	21.039	$3.6\times10^{-3} < \epsilon \ll 1.8\times10^{-2}$
0.25	1.7961	$3.6\times10^{-3} < \epsilon \ll 0.58$

Table 2: Values of the Raman intensity I_0 and the coefficient A (Eq.5) in the temperature interval indicated for the II- III phase transition in NH_4Br

I_0	A	Temperature Interval
0.061 ± 0.005	0.075 ± 0.013	66.1 < T(K) < 217.6
2.71 ± 0.48	-2.60 ± 0.52	217.6 < T(K) < 231.9

FIGURE 1

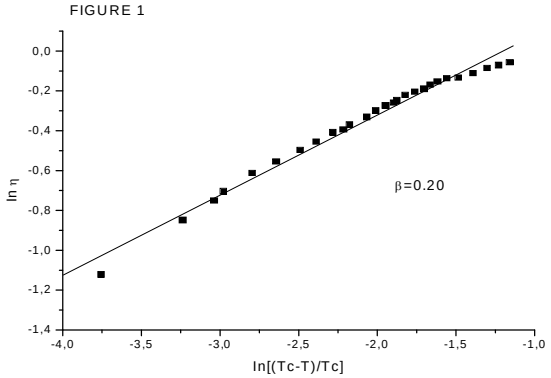

Fig. 1: Birefringence η (Order parameter) and the neutron diffraction[13] as a function of the reduced temperature in a log-log scale according to Eq. (4) for the II-III transition in NH_4Br

FIGURE 2

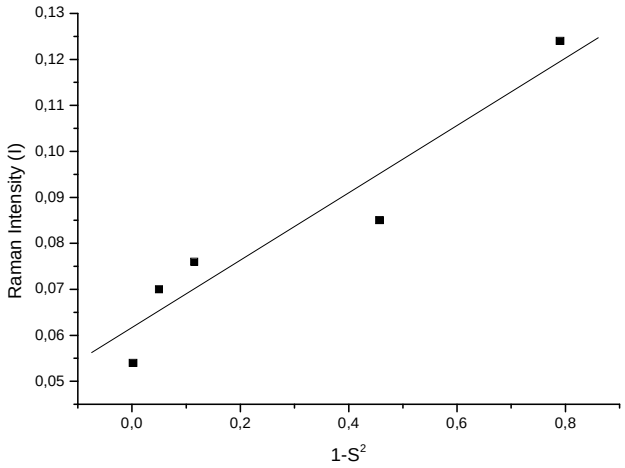

Fig. 2: Raman intensity I as a function of the disorder parameter $1-S^2$ (Eq.5) for the II-III phase transition in NH_4Br

5. REFERENCES

1. Yurtseven H, Güleç M and Sherman WF. Phase Trans. 1996;56:137.
2. Levy HA and Peterson SW. Phys Rev. 1952;86:766.
3. Yamada Y, Mori M and Noda Y. J phys Soc Jpn. 19732:(1972) 1565.
4. Matsushita M. J Chem Phys. 1976;65:23.
5. Holvast J, Stoelinga JHM and Wyder P. Ferroelectrics. 1976;13:543.
6. Lanlicht I and Luknar N. Chem Phys Lett. 1977;47: 237.
7. Lanlicht I. J Chem Phys Solids. 1978;79:901.
8. Yurseven H. Spectrochimica Acta Part A. 2005;62:910.
9. Yurseven H and Karaçalı H. Spectrochimica Acta Part A. 2006;65:421.
10. Yurseven H and Tuzer TU. Spectrochimica Acta Part A. 2008;70:445.
11. Şen S and Yurtseven H. J Mol Struc. 2007;561:834-836.
12. Yurtseven H and Özdemir M. Rad Phys and Chem. 2010;79:692
13. Egert G, Jahn IR and Renz D. Solid State Commun. 1971;9:775.