

## ELECTRICAL AND THERMAL PROPERTIES OF $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ SINGLE CRYSTAL

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(Received 2 May 1988)

### ABSTRACT

The effect of partial replacement of  $\text{Cl}^-$  ions by  $\text{Br}^-$  ions in the mixed system of ammonium chloride and ammonium bromide during a set of thermal heating cycles is studied. The study includes electrical measurements (d.c. resistivity, dielectric constant and the spontaneous thermal current), differential thermal analysis and dilatometric thermal analysis in the temperature range from  $-60$  to  $30^\circ\text{C}$ . The results show a large change in those measured parameters which are sensitive to the thermal agitation process and to the presence of the bromine ions in the mixed crystal system close to the morphotropic boundary,  $x = 0.5$ . At this boundary, the temperature region of the ordered phase is extended by about  $28^\circ\text{C}$  and the transformation enthalpy was reduced to  $41.3 \text{ cal mol}^{-1}$ . According to the different experimental data of the system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ , a phase diagram predicted that the order-disorder phase transition point changed widely according to the value of  $x$ , and reached  $-2^\circ\text{C}$  when the mixed crystal system contained 50%  $\text{Br}^-$  ions.

### INTRODUCTION

Ammonium chloride possesses three different phases: I, II and III. The transformation from the ordered phase III to the disordered phase II takes place at  $-30^\circ\text{C}$ . The two phases are isostructural with  $\text{CsCl}$  and their space groups are  $P43m$  and  $Pm3m$  for phase III and phase II respectively, but whereas phase III is piezoelectric, phase II is not so that phase II has a centre of symmetry which is lacking in phase III. The disordered phase I is f.c.c. and the space group is  $Fm3m$ . The change from the disordered phase II to the disordered phase I occurs at about  $185^\circ\text{C}$  [1]. The energy of a particular ammonium ion with respect to the neighbouring cations depends on the degree of orientational order, so that the potential energy of the ion as it rotates must also be a function of the degree of order [2–4]. The relation between the temperature and the degree of order in phase III of  $\text{NH}_4\text{Cl}$  has been studied by neutron diffraction experiments on a single crystal [5,6]. In particular, careful studies [7–11] of properties which can be measured isothermally have shown that while the transition begins gradu-

ally, it is undoubtedly completed isothermally at normal pressures, so that it is partly gradual and partly first order.

$\text{NH}_4\text{Br}$  has been found to exist in four phases: I, II, III and IV. Transformation from phase I to phase II occurs at  $138^\circ\text{C}$ : transformation from phase II to phase III occurs at  $-38^\circ\text{C}$  during cooling; with further cooling, phase III transforms to phase IV at  $-196^\circ\text{C}$ .

The mixed crystal system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  has been studied in order to examine the effect of partial replacement of bromine ion by chlorine ion on the order-disorder phase transition process. An interpretation will be introduced based on a series of electrical and thermal measurements.

## EXPERIMENTAL

Mixed crystals of  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  were prepared by slowly cooling a large volume of saturated aqueous solutions containing ammonium chloride, ammonium bromide and urea in known proportions. These solutions were kept in a desiccator at constant temperature for a few days. The resulting crystals were free from visible defects and had well developed (100) faces. The samples are coated with silver paste on two opposite faces, and inserted into a special cell [12] in which the accuracy of the temperature being measured is about  $\pm 1^\circ$  in the temperature range  $-60$ – $30^\circ\text{C}$ .

The dielectric constant was obtained from measurements of the sample capacity using an HLC bridge [13,14] at 1 kHz. The d.c. resistivity,  $\rho_{\text{d.c.}}$ , was measured using a conventional circuit. Experimental runs were repeated several times for each sample. Data obtained for different samples were found to be concordant and reproducible. Differential thermal analysis (DTA) [15] was carried out using a DTA system type Heraeus TA 500, provided with a thermoanalyser fitted with a temperature programmer, a differential amplifier and an automatic voltage stabilizer. The heating rate could be set in eleven steps ranging from  $0.1$  to  $200^\circ\text{C min}^{-1}$  in the range  $-180$ – $1000^\circ\text{C}$ . The samples were placed in a glass tube together with a NiCr–Ni thermocouple which was placed in contact with the sample.

The dilatometric measurements were carried out on a dilatometer system type Heraeus, described in detail in a previous work [14].

## RESULTS

### *Electrical measurements*

Figure 1 shows the temperature dependence of the dielectric constant and the d.c. resistivity of mixed crystal samples of ammonium chloride and ammonium bromide at different values of  $x$ . It is clear here that the absolute

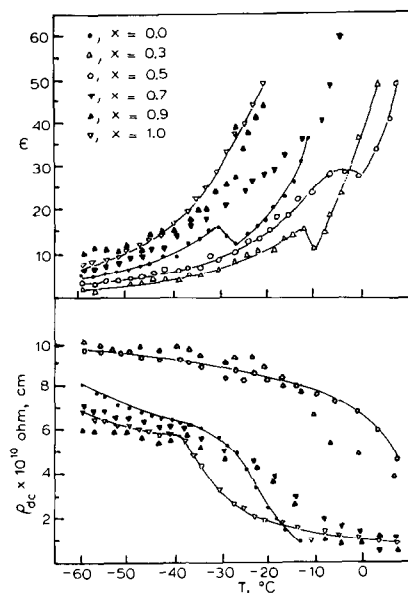


Fig. 1. Temperature dependence of the dielectric constant and d.c. resistivity of the mixed crystal system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  for various values of  $x$ .

values of  $\epsilon$  and  $\rho_{d.c.}$  change according to the value of  $x$ . The bending point of each curve of  $\epsilon$  and  $\rho_{d.c.}$  (the phase transition point) is clearly observed, whatever the value of  $x$ . But as the concentration of  $\text{Br}^-$  ions increases, the transition point gradually increases within the concentration range  $0.5 \geq x > 0$ . The transition temperature being  $-2^\circ\text{C}$  at  $x = 0.5$  and  $-30^\circ\text{C}$  at  $x = 0$ . However, when  $x = 1$ , it was  $-38^\circ\text{C}$ , which is the well-known phase transition point between the disordered phase II and the ordered phase I of pure  $\text{NH}_4\text{Br}$ . In spite of the fact that the general behaviour of  $\epsilon$  and  $\rho_{d.c.}$  of the mixed crystals is no different from that of pure  $\text{NH}_4\text{Cl}$ , the absolute values of  $\epsilon$  and  $\rho_{d.c.}$  adjacent to the transition point are much changed in the presence of  $\text{Br}^-$  ions. This is clearly seen in Fig. 2 which illustrates that  $\epsilon$  and  $\rho_{d.c.}$  are very sensitive to any partial replacement of  $\text{Cl}^-$  ions by  $\text{Br}^-$  ions. Also, there was more scattering in the phase transition point values reported for mixed crystals than for pure  $\text{NH}_4\text{Cl}$ . According to these results, one can say that both the ordered and disordered states of  $\text{NH}_4\text{Cl}$  are affected by the presence of  $\text{Br}^-$  ions, i.e. the order-disorder transition process may be qualitatively changed by the addition of  $\text{Br}^-$  ions.

The activation energies of the mixed crystal systems were calculated according to the well-known resistivity-temperature exponential relation [16]. The dependence of activation energy on the concentration of  $\text{Br}^-$  ions is shown in Fig. 3. In general, the presence of  $\text{Br}^-$  ions in the mixed crystal system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  increases the activation energies within the concentration range  $0 < x \leq 0.5$ . But when the concentration of  $\text{Br}^-$  ions exceeds this

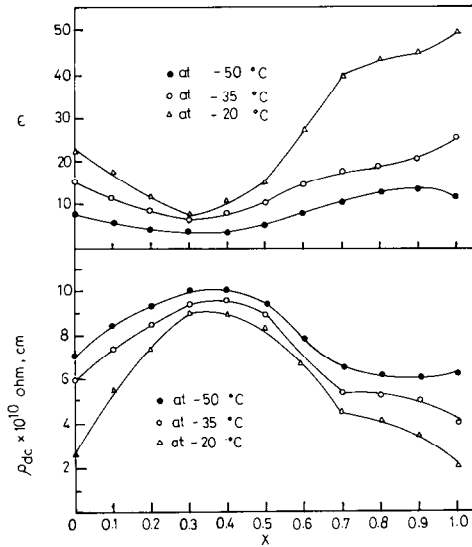


Fig. 2. Dependence of dielectric constant and d.c. resistivity on the concentration,  $x$ , of  $\text{Br}^-$  ions.

limit, the activation energies gradually decrease with approximately the same trend.

The electrical measurements were extended to include the spontaneous thermal current of the mixed crystal in the region of the order-disorder transition, as shown in Fig. 4. In general, the behaviour of the spontaneous thermal current is in good agreement with that expected from previous measurements. It can easily be seen that the partial replacement of  $\text{Cl}^-$  ions by  $\text{Br}^-$  ions in  $\text{NH}_4\text{Cl}$  causes a remarkable change in the spontaneous

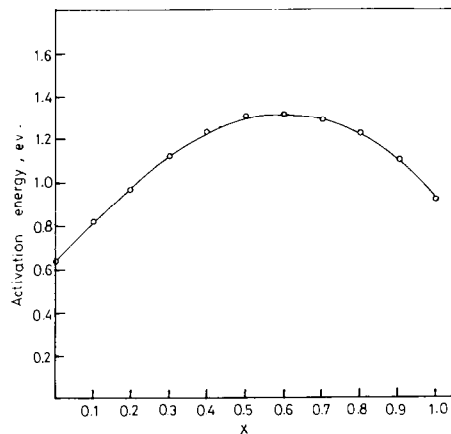


Fig. 3. Variation of the activation energy with the concentration of the  $\text{Br}^-$  ions.

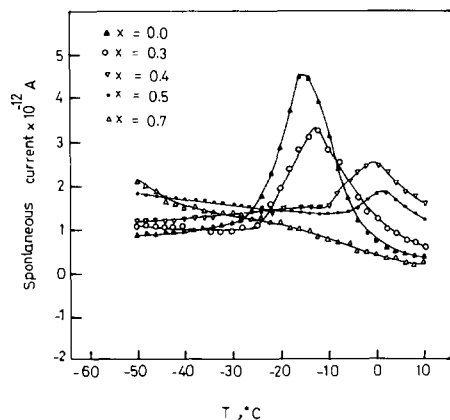


Fig. 4. Variation of spontaneous current with the concentration of  $\text{Br}^-$  ions.

current. When  $x$  exceeds 0.5, no current signal at all can be recorded. An increase in the concentration of  $\text{Br}^-$  ions has the same sort of effect as that of applying a negative polarizing electric field. Both changes, of course, cause a decay of the spontaneous current signal so that when  $x$  exceeds 0.5, the current signal disappeared completely in the region of the order-disorder transition.

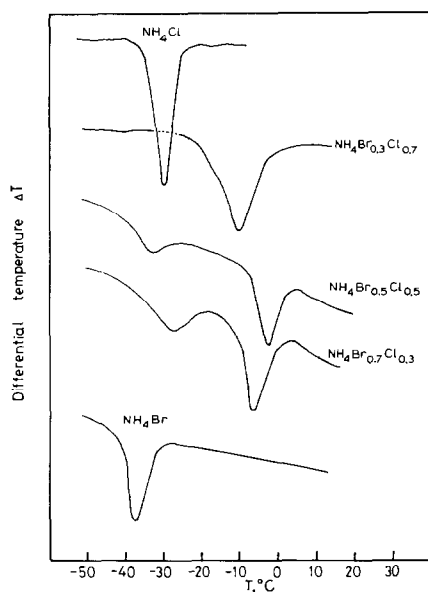


Fig. 5. Some DTA thermograms for the system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  recorded during order-disorder transition.

*Differential thermal analysis of  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$*

A set of DTA thermograms for the system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  was recorded during the order-disorder transition for different concentration of  $\text{Br}^-$  ions. Some of them are shown in Fig. 5, in which  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  thermograms are also presented for comparison. It is clear that the dilution of  $\text{Cl}^-$  concentration (i.e. its replacement by  $\text{Br}^-$  ions) systematically reduced the maximum differential temperature  $\Delta T_{\text{max}}$  of the DTA thermogram, in accordance with  $x$ . This is attributed to the decrease in transformation enthalpies, as is clear from Table 1. Also, the thermograms showed endothermic effects over the whole composition range. The order-disorder transition temperatures shifted regularly to higher values, see Table 1 and Fig. 6 (at  $x = 0.3$ ,  $T_{\text{tr}} = -10^\circ\text{C}$ , and at  $x = 0.5$ ,  $T_{\text{tr}} = -2^\circ\text{C}$ ), provided that  $x$  does not exceed the critical concentration 0.5. For higher values of  $x$ , the transition point decreased to  $-38^\circ\text{C}$  at  $x = 1$  which is the phase transition point of  $\text{NH}_4\text{Br}$ . Also, as  $x$  exceeds 0.5, the transformation enthalpies increased to  $62 \text{ cal mol}^{-1}$  at  $x = 1$ .

The dependence of the transition temperature and enthalpies of the order-disorder transition on  $x$  is shown in Fig. 6. However, the anomalous behaviour of the transition point for different concentrations of bromine observed here, confirms the previous predictions from electrical measurements.

*Dilatometric analysis of  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$*

Observation of the thermal expansion of the system of the two mixed halides was made by accurate dilatometric measurements during the

TABLE 1

Transformation enthalpies  $\Delta H$  of the system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  during the order-disorder transition III  $\rightarrow$  II

$x$	$T_c$ ( $^\circ\text{C}$ )	$\Delta H$ ( $\text{cal mol}^{-1}$ )
0.0	-30	84
0.1	-25	80.5
0.2	-17	73
0.3	-10	59
0.4	-7	47
0.5	-2	41.3
0.6	-5	45
0.7	-7	49
0.8	-15	58
0.9	-27	58
1.0	-38	62

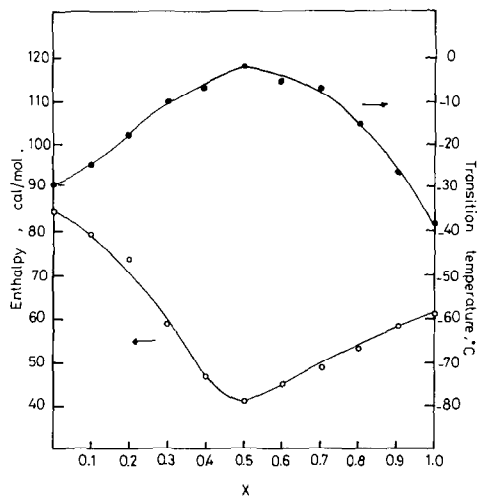


Fig. 6. Variation of enthalpies  $\Delta H$  and of the transition point of the system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  with the concentration of the  $\text{Br}^-$  ions.

order-disorder transition from III to II. At  $x = 0$ , normal expansion behaviour was observed until the transition point  $-30^{\circ}\text{C}$  when the trend of expansion changed; a sudden expansion occurred over a very short temperature interval (about  $2^{\circ}\text{C}$ ), see Fig. 7. After that, normal expansion behaviour

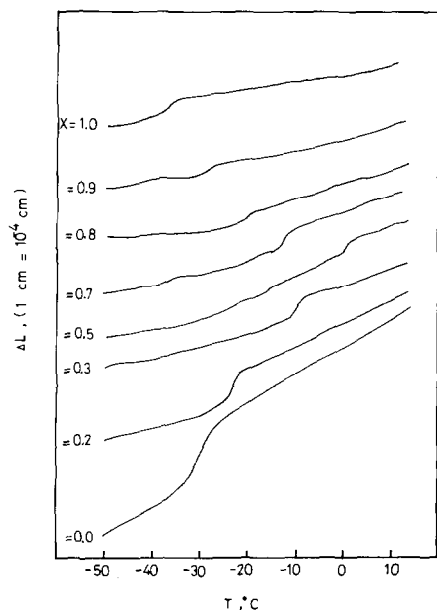


Fig. 7. Variation of thermal expansion with the concentration of  $\text{Br}^-$  ions.

TABLE 2

Relative expansions in the ordered phase III and disordered phase II for the system  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$

Composition	Relative expansion (ordered phase III)	Relative expansion (disordered phase II)
$\text{NH}_4\text{Cl}$	$6.88 \times 10^{-3}$	$7.6 \times 10^{-3}$
$\text{NH}_4\text{Br}_{0.2}\text{Cl}_{0.8}$	$6.64 \times 10^{-3}$	$7.39 \times 10^{-3}$
$\text{NH}_4\text{Br}_{0.3}\text{Cl}_{0.7}$	$6.38 \times 10^{-3}$	$7.09 \times 10^{-3}$
$\text{NH}_4\text{Br}_{0.5}\text{Cl}_{0.5}$	$5.29 \times 10^{-3}$	$6.15 \times 10^{-3}$
$\text{NH}_4\text{Br}_{0.7}\text{Cl}_{0.3}$	$5.69 \times 10^{-3}$	$6.29 \times 10^{-3}$
$\text{NH}_4\text{Br}_{0.8}\text{Cl}_{0.2}$	$6.16 \times 10^{-3}$	$6.61 \times 10^{-3}$
$\text{NH}_4\text{Br}_{0.9}\text{Cl}_{0.1}$	$6.36 \times 10^{-3}$	$6.95 \times 10^{-3}$
$\text{NH}_4\text{Br}$	$0.82 \times 10^{-3}$	$7.44 \times 10^{-3}$

returned, but the relative expansions in the ordered and disordered phases were different, as is clear from Table 2. In the presence of  $\text{Br}^-$  ions, the relative expansion is reduced for both ordered and disordered states until it reaches the critical composition  $x = 0.5$ . But when  $x$  exceeds 0.5, the relative expansion increased. Also, the fractional sudden change of length just at the order-disorder transition point, depends on  $x$  over the whole composition range, see Fig. 8, which has a clear kink at the critical value of  $x$ . The detailed analysis of the fractional change of length in the ordered phase III and disordered phase II are given in Table 3. However, dilatometric results

TABLE 3

Fractional change of length (in units of  $10^{-3}$ ) of  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  samples in the ordered phase I and disordered phase II

$T$ ( $^{\circ}\text{C}$ )	$x = 0.0$	$x = 0.2$	$x = 0.3$	$x = 0.5$	$x = 0.7$	$x = 0.8$	$x = 0.9$	$x = 1.0$
	$T_c = -30^{\circ}\text{C}$	-17	-10	-2	-7	-15	-27	-38
-50	6.77 *	6.56 *	6.29 *	5.22 *	5.63 *	6.11 *	6.31 *	6.78 *
-40	6.83 *	6.61 *	6.32 *	5.25 *	5.65 *	6.19 *	6.35 *	6.85 *
-30	7.29	6.65 *	6.42 *	5.28 *	5.68 *	6.17 *	6.41 *	7.02
-20	7.52	6.72 *	6.51 *	5.32 *	5.72 *	6.22 *	6.54	7.29
-10	7.59	7.10	6.92	5.37 *	5.78 *	6.31	6.71	7.37
0	7.62	7.37	7.04	5.83	6.12	6.44	6.91	7.44
10	7.65	7.43	7.1	6.14	6.23	6.51	6.99	7.49
20	7.67	7.45	7.13	6.21	6.30	6.56	7.06	7.52
30	7.69	7.46	7.15	6.24	6.34	6.60	7.11	7.54
40	7.70	7.47	7.16	6.25	6.36	6.64	7.16	7.55
50	7.71	7.48	7.27	6.26	6.37	6.62	7.19	7.56

\* The values with asterisks are those obtained for the ordered phase while the others are for the disordered phase.



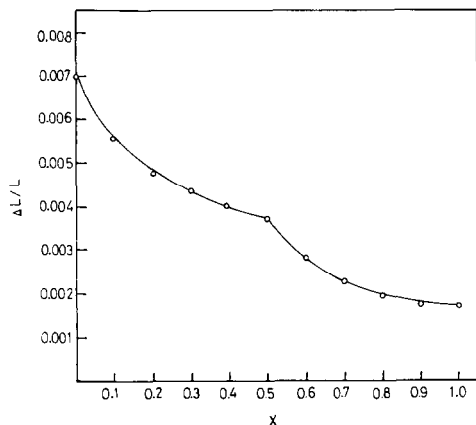


Fig. 8. Fractional change of length, adjacent to the order-disorder transition region as a function of the concentration of the  $\text{Br}^-$  ions.

strongly supported the previous results of the electrical and differential thermal analysis measurements.

## DISCUSSION

According to the experimental results obtained here, there are a number of grounds for believing that for both  $\text{NH}_4^+$  ions and  $\text{Cl}^-$  ions, there are significant contributions to the processes of ordering and disordering. Since ammonium halides display a very general type of order-disorder phase change, it has been thought that a wide variety of information on ordering and disordering in  $\text{NH}_4\text{Cl}$  crystals can be obtained by studying some of the different mixed crystal systems  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$ . It is clear that the order-disorder phase transition point  $T_t$  is a well behaved regular function of  $x$  (within the limit  $0.5 \geq x > 0$ ), at atmospheric pressure. The surprising increase in the value of  $T_t$  ( $T_t = -2^\circ\text{C}$  at  $x = 0.5$ , while  $T_t = -30^\circ\text{C}$  at  $x = 0$ ), is probably due to the presence of  $\text{Br}^-$  ions which in turn affect the hydrogen bonding. This change in the hydrogen bonding strength occurs primarily in the composition region  $0 < x \leq 0.5$ . The reason for this behaviour is not obvious, but one might speculate about the effects of local halide configurations on hydrogen bonding. When there are many halogen ions around any given  $\text{NH}_4^+$  ion, it seems that the lattice is not able to relax significantly about the  $\text{Br}^-$  ion impurity, and without such relaxation, the  $\text{Br}^-$  ion cannot get sufficiently close to  $\text{NH}_4^+$  to form strong hydrogen bonds. Below  $x = 0.5$ , the ion-ion repulsion between the  $\text{Br}^-$  ions becomes less important and the lattice can relax more freely about the  $\text{Cl}^-$  ion, thus leading to an increase in the effective hydrogen bonding and, hence, to an increase in the order-disorder transition point. The dependence of the phase

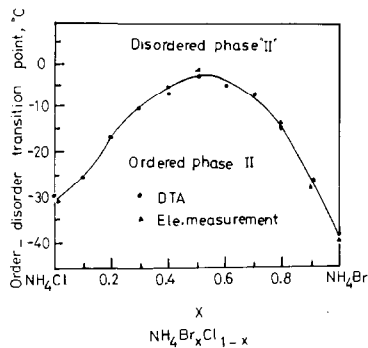


Fig. 9. Phase diagram for the mixed crystal systems  $\text{NH}_4\text{Br}_x\text{Cl}_{1-x}$  and  $\text{K}_y(\text{NH}_4)_{1-y}\text{Cl}$  at atmospheric pressure.

transition on the percentage composition is a predictable behaviour especially in the case of a disordered crystal lattice.

According to previously described results of electrical and thermal analysis of the mixed system, a phase diagram was obtained which is shown in Fig. 9. It is obvious that the low temperature order-disorder phase transition III  $\rightarrow$  II is probably a well-behaved regular function of the bromide concentration  $x$ .

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