Proc. JSSF-2, Kyoto, 1980
J. Phys. Soc. Jpn. 49 (1980) Suppl. B, pp. 169–171.

Phase Transitions in $NH_4Cl_{1-x}Br_x$ Mixed Crystals

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Critical phenomena accompanying β-δ, β-γ phase transition in $NH_4Cl_{1-x}Br_x$ mixed crystals have been studied by thermal and ultrasonic measurements. The critical anomaly of the specific heat on the low temperature side of the β-δ transition can be represented by a power equation, but in the case of β-γ transition it is represented by two different equations (crossover effect). Large critical softening in bulk modulus occurs both at β-δ, β-γ transitions, but that in shear modulus occurs only at β-γ transition.

§1. Introduction

Ammonium chloride undergoes a cubic-to-cubic ($\beta-\delta$) phase transition of the first order at 242 K. The tetrahedral NH_4^+ ions in ammonium halides can take two different positions in a cell. In β-phase NH_4^+ ions are in a disordered state, and in δ-phase they are oriented in a parallel arrangement. Ammonium bromide undergoes a cubic-to-tetragonal (β-γ) phase transition of the second order at 235 K. In γ-phase NH_4^+ ions are oriented in an antiparallel arrangement in the *ab* plane and in a parallel arrangement along the *c*-axis. The antiparallel ordering of NH_4^+ ions is incorporated with the displacement of halogen ions from the high-symmetry site. The γ-phase of ammonium bromide changes into the δ-phase at 78 K.

Two competing interactions between NH_4^+ ions exist in ammonium halide crystals. While the direct octupole-octupole interaction between NH_4^+ ions stabilizes the parallel ordering (δ-phase),[1] the indirect interaction between NH_4^+ ions through the displacement of halogen ions stabilizes the antiparallel ordering (γ-phase).[2]

Utilizing the fact that the dielectric constant of ammonium halides changes at the transition temperature, the phase diagram of the $NH_4Cl_{1-x}Br_x$ mixed crystal was determined previously.[3] Two different types of multicritical point exist in this mixed crystal system at ordinary pressure. One is a triple point ($x=0.06$) where three different phases, β, γ, δ coexist, and the other a tricritical point ($x=0.26$) where the order of the β-γ phase transition changes from the first to the second. In the present work, critical phenomena accompanying the β-δ, β-γ phase transitions in $NH_4Cl_{1-x}Br_x$ mixed crystals were studied by thermal and ultrasonic measurements.

§2. Measurement of Specific Heat

The specific heat, C_p, of $NH_4Cl_{1-x}Br_x$ mixed crystals was measured by an AC calorimeter. Figure 1, representative of the results, shows the temperature variation of C_p obtained for mixed crystals with $x=0.04$ and 0.25. By subtracting the part of specific heat due to the lattice vibration which was assumed to be $a+bT+cT^2$, where constants a, b, c were determined experimentally, the critical anomaly of specific heat, ΔC_p, accompanying the phase transition was estimated. Figure 2 shows the plot of log ΔC_p in the low temperature region of the transition as a function of log (T_0-T),

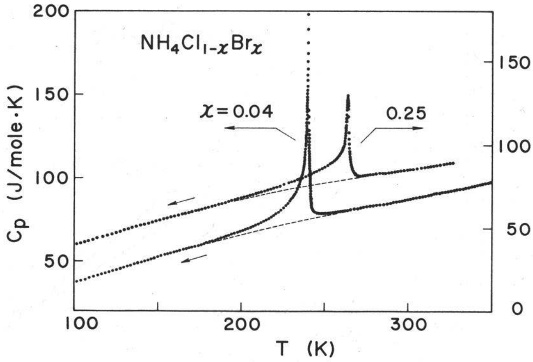

Fig. 1. Representative results of the temperature variation of specific heat, C_p, of $NH_4Cl_{1-x}Br_x$ mixed crystals.

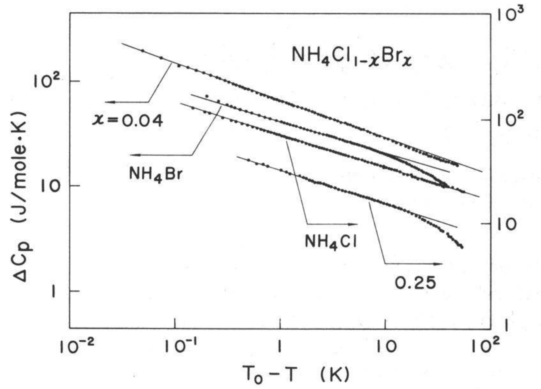

Fig. 2. Log-log plot of anomalous specific heat, ΔC_p, and T_0-T for $NH_4Cl_{1-x}Br_x$ mixed crystals, NH_4Cl and NH_4Br.

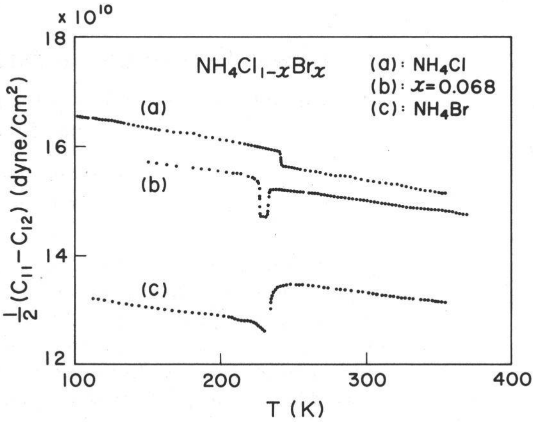

Fig. 4. Temperature variation of $1/2(C_{11}-C_{12})$ for $NH_4Cl_{1-x}Br_x$ mixed crystals.

yielding the critical index, α', in an equation

$$\log \Delta C_p \backsim \log (A'/\alpha') - \alpha' \log (T_0/T-1).$$

The constants, A', T_0 were estimated so that ΔC_p can be expressed by a straight line with minimum error. The value T_0 obtained is roughly equal to the temperature corresponding to the peak of C_p within the experimental error. It is seen from these results that in the case of β-δ transition in the specimens with $x=0$ (NH_4Cl) and $x=0.04$ (near the triple point), the critical anomaly, ΔC_p, can be represented by a power equation over a wide temperature region. On the other hand, in the case of β-γ transition in the specimens with $x=0.25$ and $x=1$ (NH_4Br), deviation from a linear relation is seen in the temperature region $T_0-T>10$. For this region ΔC_p is better represented by a logarithmic equation

$$\Delta C_p \backsim A_1' \log (T_0/T-1)$$

as shown in Fig. 3. Therefore, ΔC_p is governed by two different type laws, a power equation for the temperature region near the transition and a logarithmic equation for the region remote from the transition (crossover effect).

The critical anomaly, ΔC_p, in the high temperature region of the phase transition is also expressed by a power equation satisfactorily in the case of NH_4Cl, but in other specimens the temperature region where ΔC_p can be expressed by a simple power equation becomes narrow.

§3. Ultrasonic Measurement

Ultrasonic measurement on $NH_4Cl_{1-x}Br_x$ mixed crystals of a longitudinal wave at 10 MHz

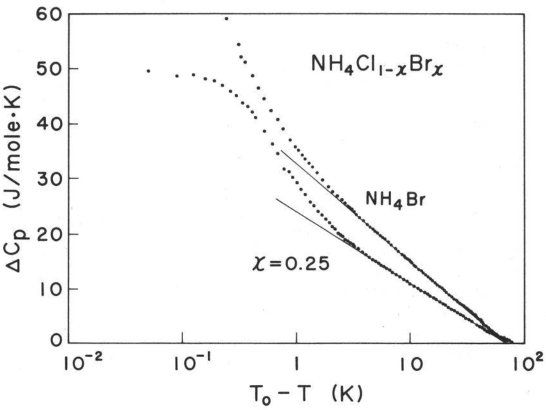

Fig. 3. Semi-logarithmic plot of ΔC_p and T_0-T for $NH_4Cl_{1-x}Br_x$ mixed crystals.

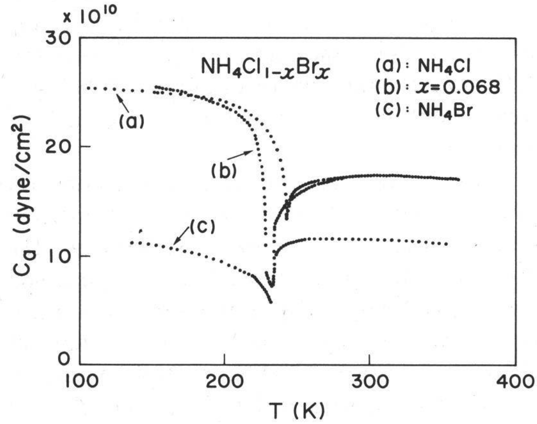

Fig. 5. Temperature variation of bulk modulus, C_a, for $NH_4Cl_{1-x}Br_x$ mixed crystals.

propagating along the *a*-axis was reported previously.[4,5] Figure 4 shows the results of ultrasonic measurement of a transversal shear wave at 10 MHz propagating along [110] direction and vibrating in the *ab* plane. Figure 5 shows the bulk modulus, $C_a = C_{11} - 2/3(C_{11} - C_{12})$ as a function of temperature. From these results it is found that very large critical softening of C_a is seen both at β-δ and β-γ transitions. It amounts to about 60% at the transition in the case of the mixed crystal with $x = 0.068$. On the other hand, the critical softening of shear modulus is seen only at the β-γ transition. This anomaly diminishes with the decrease of mole fraction of Br in the mixed crystal.

It is also found from the present experimental results that a linear relation holds between the inverse of anomalous shear modulus and $\Delta C_p/T$ in the high temperature region of the β-γ transition in NH_4Br,[6] but that it does not hold in the case of β-γ transition in the mixed crystal with $x = 0.068$.

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