Chlorine-35 NQR Studies on $[(NH_4)_{0.01}K_{0.99}]_2SnCl_6$ Mixed Crystals *

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The temperature dependence of ^{35}Cl NQR frequencies was measured on the mixed crystal $[(NH_4)_{0.01}K_{0.99}]_2SnCl_6$. Two phase transitions have been located at $T_{c1} = 259$ K and $T_{c2} = 252$ K, which are lower by 3 K than the corresponding transition temperatures of the pure K_2SnCl_6 crystal. The DSC experiments showed that the NH_4^+ concentration dependence of T_{c2} almost parallels that of T_{c1}. The impurity effect resulting from the inclusion of a small amount of $NH_4^{\oplus}$ ions in K_2SnCl_6 crystals is discussed in relation to the microscopic viewpoint of the phase transitions.

Introduction

At room temperature, K_2SnCl_6 forms anti-CaF_2 type cubic crystals with the space group Fm3m. The crystal undergoes two phase transitions: cubic ⇌ orthorhombic at $T_{c1} = 262$ K [1] and orthorhombic ⇌ monoclinic at $T_{c2} = 255$ K [1, 2]. $(NH_4)_2SnCl_6$ has the same crystal structure and nearly the same lattice constant as the potassium salt at room temperature. However, the ammonium salt retains its cubic structure down to liquid He temperature [3].

Recently, extensive studies on the mixed crystals of $[(NH_4)_xK_{1-x}]_2SnCl_6$ have been carried out by various experimental methods: differential scanning calorimetry (DSC) [4], Raman spectroscopy [4], X-ray [4] and neutron diffraction [5], and NQR spectroscopy [6–8]. These investigations have clarified that T_{c1} of the pure potassium salt shifts to a lower temperature with increasing concentration of ammonium ions in the mixed crystals. However, the phase transition corresponding to T_{c2} of the pure salt has not been reported in the mixed crystals $[(NH_4)_xK_{1-x}]_2SnCl_6$. Therefore we carried out measurements of the temperature dependence of ^{35}Cl NQR frequencies for the mixed crystals with the concentration $x = 0.010$ to examine the impurity effect on the NQR frequencies, and also of DSC for several mixed crystals with different $NH_4^{\oplus}$ concentrations in the range of $0 \leqq x \leqq 0.032$ to obtain information about the concentration dependence of T_{c2}.

Experimental

A modified Dean-type, superregenerative spectrometer was employed for the determination of ^{35}Cl NQR frequencies. The temperature was determined by use of a chromel-alumel thermocouple. DSC experiments were performed with a calorimeter from Rigaku Denki Co.

Potassium and ammonium hexachlorostannates (IV) were prepared by a known method [9]. To obtain high S/N ratios of the NQR spectra, K_2SnCl_6 was prepared from solutions with various acidity of hydrochloric acid. At room temperature, a single resonance line with the S/N ratios of ca. 20, 30, and 45 was observed for the crystals obtained from the 4*N*, 6*N*, and 8*N* solutions of hydrochloric acid, respectively. Annealing of the samples at 200 °C improved the S/N ratio of the lines by a factor of two. A similar tendency was observed for the ammonium salt. Presumably, hydrolysis of the complex anion takes place in solutions of weak acidity [10] which may lead to a weakening of the NQR signal intensity. Therefore, we prepared the mixed crystal from solution of 8*N* hydrochloric acid and we

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annealed the samples. The concentration of the ammonium ion in the crystals was determined by a colorimetric method using Nessler reagent. Here, we assumed that the $NH_4^{\oplus}$ ions added were homogeneously dispersed in the crystal of K_2SnCl_6. This was confirmed by taking X-ray powder patterns for the samples prepared with different $NH_4^{\oplus}$ concentrations, which indicated a smooth increase of the lattice constant with increasing concentration of $NH_4^{\oplus}$ ions.

Results

A temperature dependence of the ^{35}Cl NQR frequencies in K_2SnCl_6 has been reported by several authors [6, 11–13]. In the present study we measured the resonance frequency also for the pure compound as accurately as possible in order to obtain the precise frequency effect of the ammonium ions added as impurity in the crystal of K_2SnCl_6.

Figure 1 shows the temperature dependence of the ^{35}Cl NQR frequencies observed for K_2SnCl_6 and for the mixed crystal $[(NH_4)_{0.01}K_{0.99}]_2SnCl_6$. The same transition points were determined for the pure crystal as those already reported [1, 2]. The mixed crystal gave rise to three ^{35}Cl lines at 77 K. Their frequencies were nearly the same as those of the pure salt. When the temperature was increased, the frequency shift with respect to the pure salt became appreciable at about 230 K. With further increasing temperature, the two lines of higher frequencies approached each other and clearly became weak near ca. 250 K, where two completely different new lines appeared in the same frequency region. On the other hand, the lowest line of the triplet of the mixed crystal showed no appreciable change in the line shape and also decreased its frequency continuously with increasing temperature. However, a discontinuity in $(d\nu/dT)$ was observed at 252 K as indicated in Figure 1. Above 252 K three resonance lines of equal intensity were observed. They became weak at 258 K and disappeared at 259 K. At nearly the same temperature or a little above, a very strong and sharp line appeared and was observed up to 350 K. This temperature was higher by ca. 8 K than the fade-out temperature of the line of the pure salt observed in the present study. For the mixed crystal with $x = 0.01$, the same temperature dependence was found when the temperature was lowered, and the same transition temperatures $T_{c1} = 259$ K and $T_{c2} = 252$ K were determined. This suggests that these phase transitions bear a 2nd order nature to some degree. The present T_{c1} of the mixed salt was shifted by 3 K from the pure salt. This agrees well with the results already reported for the same $NH_4^{\oplus}$ concentration [6].

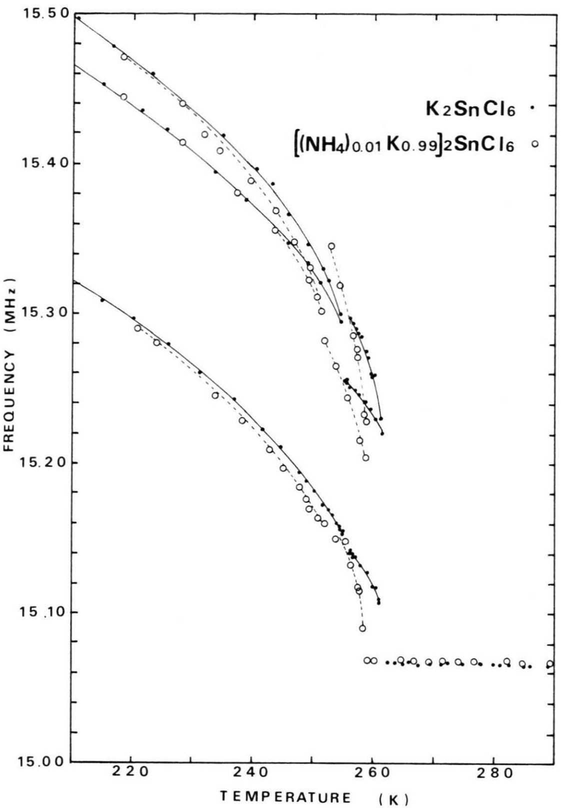

Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies of K_2SnCl_6 (●) and $[(NH_4)_{0.01}K_{0.99}]_2SnCl_6$ (○).

At room temperature we observed faint waves of the base line around the cubic phase resonance line. We disregarded these base-line waves, which, however, may correspond to the other resonance lines described by Dimitropoulos et al. [6, 7].

The transition temperatures T_{c1} and T_{c2} determined from the DSC measurements are given in Fig. 2 as a function of the $NH_4^{\oplus}$ concentration x. The curve for T_{c1} shows good agreement with the results already reported [4, 6, 8]. The heat of transition arising from the transition orthorhombic → cubic has been determined as 239 J/mol, almost indepen-

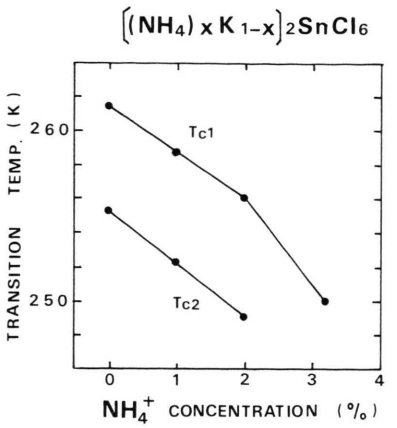

Fig. 2. Phase transition temperatures T_{c1} and T_{c2} in $[(NH_4)_xK_{1-x}]_2SnCl_6$ shown as a function of impurity concentration x.

dent of x. The transition enthalpy involved in the monoclinic to orthorhombic transition was smaller by ca. one order of magnitude than that of the former transition. With increasing x, both endothermic peaks became broad and at $x = 0.032$ no peak corresponding to T_{c2} was observed.

The DSC measurements were performed on polycrystalline samples, not ground into powder. The sample of K_2SnCl_6, pulverized using an agate mortar, showed only a single very broad endothermic anomaly corresponding to T_{c1}. After annealing the pulverized sample at 200 °C for 10 hours, the DSC peak recovered its original sharpness and the small peak of T_{c2} was observed again.

Discussion

Among the various kinds of crystals having K_2PtCl_6 type structure, K_2SnCl_6 is one of the compounds whose phase transitions have been investigated extensively and discussed with the model of a librational soft mode [14]. Through these investigations it has been clarified that the phase transition at T_{c1} is associated with an antiferro-distortive rotation of the complex anions and that the phase transition at T_{c2} is accompanied with an in-phase rotation of the complex anions [14].

For the hexahalometallates(IV) it has been well established that the increase in the ionic radius of the spherical cations stabilizes the cubic phase [15]. Armstrong and van Driel [16] have calculated the zone-averaged rotary mode frequency of the complex anions in the crystals of hexahaloplatinates(IV). Their calculation indicates that the average frequency has a higher value for the compounds which favor the cubic form. They have also shown that the frequency of the rotary lattice mode in K_2PtBr_6 crystals decreases significantly when the temperature decreases towards the transition point from the cubic to a lower symmetry crystal.

Figure 3 shows the temperature dependence of the ^{35}Cl resonance frequencies of pure K_2SnCl_6 and the mixed crystal $[(NH_4)_{0.01}K_{0.99}]_2SnCl_6$ in the cubic phase. The frequency difference between the two complexes is almost constant below 300 K. When the temperature is increased, the pure salt shows a more marked decrease in the frequency and the frequency difference becomes larger. The greater frequency decrease observed in the pure compound means that the torsional oscillations of the complex anions involve larger anharmonicity.

We have estimated the oscillational frequency by Bayer's analysis. Around 340 K, the Bayer functions which fitted best the experimental data were determined and the torsional frequencies, 47 and 54 cm^{-1}, were obtained for the pure and mixed crystals, respectively. The NQR frequencies observed deviated at lower temperatures from the Bayer functions, which were determined by the data obtained in a high temperature region. This can be attributed to the change of the torsional frequency due to the phase transition at T_{c1} [16]. The torsional frequencies derived from the observed NQR frequencies near T_{c1} were smaller by ca. 6% than those evaluated from the above Bayer curves. Since the transformation is believed to result from the condensation of a soft phonon mode, the higher value of the torsional frequency in the mixed crystal explains well the greater stability of the cubic phase.

The effect of $NH_4^{\oplus}$ impurities on the transition temperatures shown in Fig. 2 is much more remarkable than that of $Rb^{\oplus}$ observed in $(Rb_xK_{1-x})_2SnCl_6$ [8]. Furthermore, the pure K_2SnCl_6 shows a small value of the positive pressure coefficient of T_{c1} [13]. Therefore, we can not explain the observed effect of the $NH_4^{\oplus}$ ions on T_{c1} as well as T_{c2} by the volume effect alone as was done by Dimitropoulos et al. [6, 8]. In the K_2PtCl_6 structure, the repulsive force acting between halogens and cations due to the overlapping electron clouds stabilizes the cubic

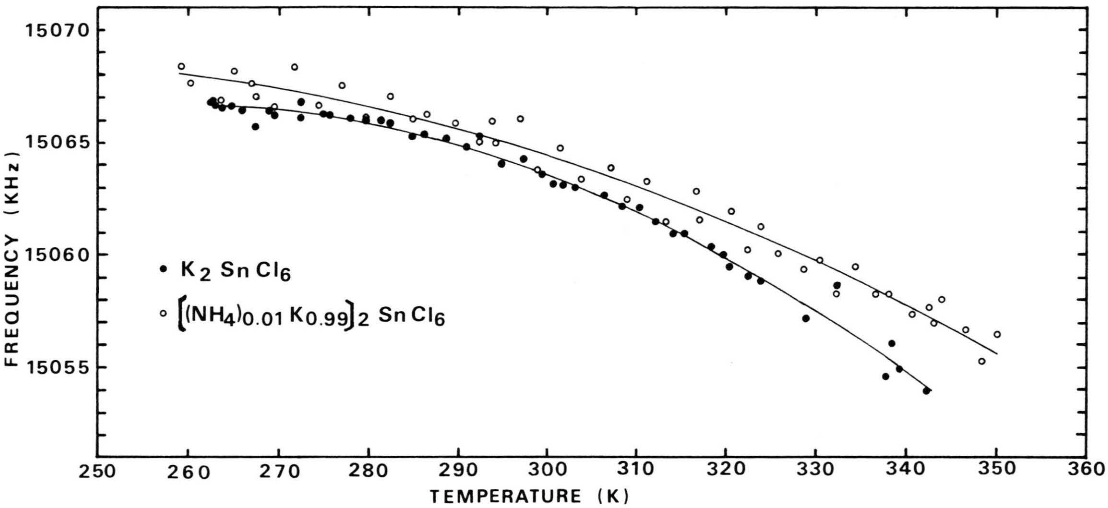

Fig. 3. Temperature dependence of the ^{35}Cl NQR frequencies of K_2SnCl_6 (●) and $[(NH_4)_{0.01}K_{0.99}]_2SnCl_6$ (○) in the cubic phase. The solid lines represent fitting curves to the observed values by a least squares method.

phase, whereas the anion-cation Coulomb forces and the halogen-halogen repulsion between the neighboring anions favor the rotation of the complex anions [13]. The stronger Coulomb interaction between $NH_4^{\oplus}$ and $SnCl_6^{2\ominus}$ ions such as due to hydrogen bond formation would explain the higher torsional frequency observed in the mixed crystal. However, such an interaction can not explain the stability of the cubic phase in the mixed crystal. Presumably, the overlap repulsion between $NH_4^{\oplus}$ and $SnCl_6^{2\ominus}$ ions plays an important part for the stabilization of the cubic phase in the mixed crystal.

The observed dependence of T_{c2} on the $NH_4^{\oplus}$ concentration almost parallels that of T_{c1}. This would suggest that the phase transition at T_{c2} also results from the rotation of the complex anions in the crystal.

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