

## Impurity Effects on $^{14}\text{N}$ NQR in Mixed Systems ; $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$ and $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$

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X-ray diffraction and  $^{14}\text{N}$  NQR have been investigated at room temperature in mixed systems,  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$  and  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$ , grown by evaporating mixed solutions. The results of x-ray pattern in both systems show that introducing  $[\text{KNO}_3$  or  $\text{SC}(\text{NH}_2)_2$ ] impurity into  $(\text{CH}_2)_6\text{N}_4$  leads to a formation of impurity cluster in the cubic phase of  $(\text{CH}_2)_6\text{N}_4$ . The spin-lattice relaxation time ( $T_1$ ) of  $^{14}\text{N}$  NQR in  $(\text{CH}_2)_6\text{N}_4$ -matrix in two mixed systems were measured. In both systems  $T_1$  tends to increase with impurity content. The change of  $T_1$  due to impurity is explained by the increase in the activation energy for reorientational motion of  $(\text{CH}_2)_6\text{N}_4$  molecules. Impurity effects of local molecular dynamics in two mixed systems are also discussed and compared to those obtained from the hydrated HMT.

### I. INTRODUCTION

In molecular crystals, NQR relaxations are often induced by the reorientational motion of molecular groups. In  $(\text{CH}_2)_6\text{N}_4$  (Hexamethylene tetramine : HMT), the temperature dependence of the  $^{14}\text{N}$ -NQR spin-lattice relaxation can also be interpreted in terms of the reorientational motion of the nitrogen ion in the tetrahedral HMT molecule in addition to the Raman-process [1]. From the initiating study by Alexander and Tzalmona [1] the relaxation mechanism in HMT is now well understood: the quadrupolar relaxation at low temperatures deviates increasingly from the relation,  $T_1^{-1} \propto T^2$ , with increasing temperature and above 250 K the relaxation is caused predominantly by the slow reorientational motion of the HMT molecule about one of its threefold axis.

On the other hand this motion may be directly affected by impurities and impurity induced lattice defects in crystals whose effects should be consequently reflected in NQR-relaxation spectra [2]. In this sense, NQR investigation of this motion in impurity doped crystals can offer fundamental grounds for the understanding of lattice dynamics. With regard to the impurity effect on the reorientational motion in HMT, a similar behavior was provided by the hydrated HMT, where  $T_1$  anomaly in the  $^1\text{H}$  NMR of HMT was observed [3]. This phenomenon was explained in terms of the diffusion of  $\text{H}_2\text{O}$  molecules through the HMT lattice, which, however, contribute negligibly to the spin-spin relaxation. Another

interesting fact on the effect of water molecule ( $\text{H}_2\text{O}$ ) on the  $^{14}\text{N}$  NQR relaxation was observed in the systematically hydrated HMT by Trepanier and Whitehead [4]. They showed that  $\text{H}_2\text{O}$  in the near of HMT molecule affects the  $^{14}\text{N}$  NQR relaxation in HMT.

This work presents the results of x-ray diffraction and  $^{14}\text{N}$  NQR investigation of the impurity effects in two kinds of mixed systems,  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$  and  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$ . From the results of measurements a correlation of the motion of impurity induced lattice defects to the reorientational motion in HMT was deduced. The influence of impurities on the  $^{14}\text{N}$  NQR relaxation in both mixed complex systems and hydrated HMT was also compared.

### II. EXPERIMENTS

The unit cell of HMT [5,6] is body centered cubic at room temperature with a tetrahedral symmetry of molecules. The crystal structure of both potassium nitrate [7-9] and thiourea [10] are orthorhombic at room temperature. Two kinds of mixed systems,  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$  and  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$  were prepared for experiment. All samples were grown by evaporation of mixed solutions at 40 °C for 5 weeks. Impurity concentration  $x$  in  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$  and  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$  (hereafter referred to as HK and HS, respectively) was determined by the atomic emission spectrometry (AES) and elemental analyzer (EA). X-ray diffraction patterns of the powder samples

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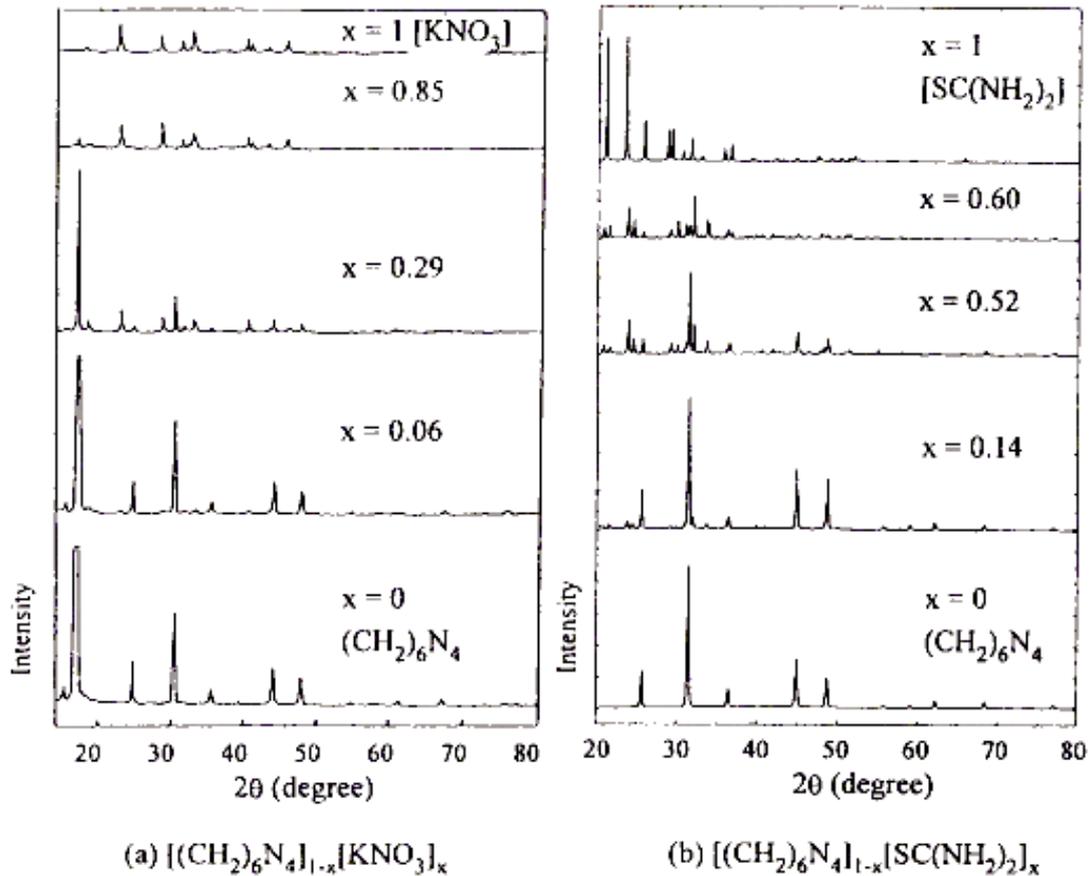


Fig. 1. X-ray diffraction patterns of two sample systems, (a)  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$  and (b)  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$ .

were obtained at room temperature using a Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ) x-ray diffractometer.  $^{14}\text{N}$  NQR spectra were measured by employing a pulsed NQR at room temperature. Spin-lattice relaxation time ( $T_1$ ) measurement was made by the inversion recovery  $180^\circ - \tau - 90^\circ$  with varying  $\tau$ .

### III. RESULTS AND DISCUSSION

#### 1. X-ray Diffraction

Figure 1 shows x-ray diffraction patterns for two mixed systems. X-ray data show that both host and impurity structure, HMT- and  $\text{KNO}_3$ -matrix (or  $\text{SC}(\text{NH}_2)_2$ -matrix) respectively exist together without any shift of their peaks implying that the lattice constants of both matrices remain unchanged with varying impurity content. The presence of both structure indicates that the impurity can not fit smoothly into the host crystal (HMT). Thus it is easily expected that many kinds of defects may be produced during the mixing of impurity.

#### 2. $^{14}\text{N}$ NQR in HMT-matrix

$^{14}\text{N}$  NQR frequency  $\nu_0$  for HMT with  $\eta = 0$  is given by

$$\nu_0 = 3e^2qQ/4h, \quad (1)$$

where  $q$  is the largest electric field gradient (EFG) at  $^{14}\text{N}$  site and  $Q$  is the electric quadrupole moment of  $^{14}\text{N}$  nucleus. As shown in Fig. 2, the observed  $^{14}\text{N}$  NQR frequency in the mixed systems is the same as that in pure HMT. This is due to the fact that the local structure observed by NQR remains essentially unchanged in spite of the presence of the nearby impurity or impurity induced lattice defects. Figure 2 shows the change of the NQR line shape with varying impurity concentration for both HK and HS mixed systems at room temperature. Compared to the results in  $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$  [11], where the parents crystals are isostructural, the concentration independent line width in HK and HS mixed systems indicates that the corresponding temperature ( $\sim 300 \text{ K}$ ) belongs to the region of the motional narrowing. Namely, the motion of impurities and lattice defects are fast compared to the NQR periods. Figure 3 shows the  $^{14}\text{N}$  NQR

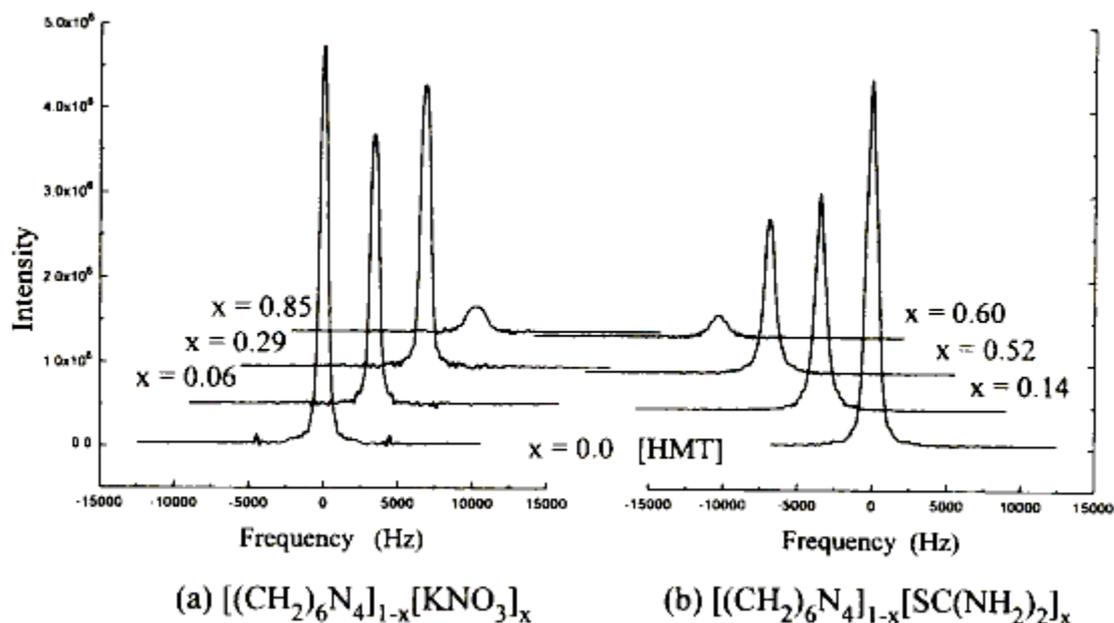


Fig. 2.  $^{14}\text{N}$  NQR line shapes in (a)  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{KNO}_3]_x$ , and (b)  $[(\text{CH}_2)_6\text{N}_4]_{1-x}[\text{SC}(\text{NH}_2)_2]_x$ .

spin-lattice relaxation time in HMT matrix versus the impurity concentration. The general tendency is that  $T_1$  for both HK and HS system hardly increases at first with increasing concentration. In HK system the figure shows apparently an increase in  $T_1$  for large concentration of impurity. However the similar concentration dependence of  $T_1$  in both HK and HS systems for  $x$  below  $\sim 0.6$  suggests that  $T_1$  in HS system would increase also for large concentration of impurity. In HMT structure the relaxation at room temperature is mainly caused by slow reorientation of the tetrahedral nitrogen molecule. For each rotation of the nitrogen molecule, the resonant nucleus, which is a part of the molecule under consideration, feels a drastic change in the orientation of EFG at its sites. In this case, one can apply the “strong collision theory” [12], which yields a simple relation between  $T_1$  and the correlation time  $\tau_c$  of the rotational motion of the tetrahedral molecule.

$$T_1 \sim \tau_c = \tau_0 \exp(E_a/kT), \quad (2)$$

$\tau_0$  is defined as the characteristic time of the motion in the limit of infinite temperature ( $T = \infty$ ), where  $\tau_0$  is usually taken to be independent of the presence of impurities.  $E_a$  is the potential barrier for the reorientational motion. From Eq. (2) the increase in  $T_1$  means the increase in  $E_a$ , *i.e.*, the substitution of large concentration of impurity leads to an enhancement of the tetrahedral potential barrier  $E_a$ . A drastic decrease in the line intensity at high concentrations ( $x = 0.85$  for HK and  $0.60$  for HS, respectively) indicates the presence of lattice defects, which are located just near the tetrahedral local space around the resonant nucleus and appear to induce the

increase in  $E_a$ . In the systematically humidified HMT [4],  $T_1$  decreases even with increasing  $\text{H}_2\text{O}$  content implying a decrease in  $E_a$ . The decrease in  $T_1$  was ascribed to the increase in the cell dimension due to introducing water molecules to the host HMT. In this sense, the situation for the impurity related molecular dynamics in HK and HS differs from that in hydrated HMT. In our case, x-ray diffraction pattern shows that the size of the unit cell of both HMT and impurities  $[\text{KNO}_3$  and  $\text{SC}(\text{NH}_2)_2]$  does not change with adding impurities to the host HMT. The enhancement of  $T_1$  in the HK and HS mixed system can be explained in terms of the pinning effect of the im-

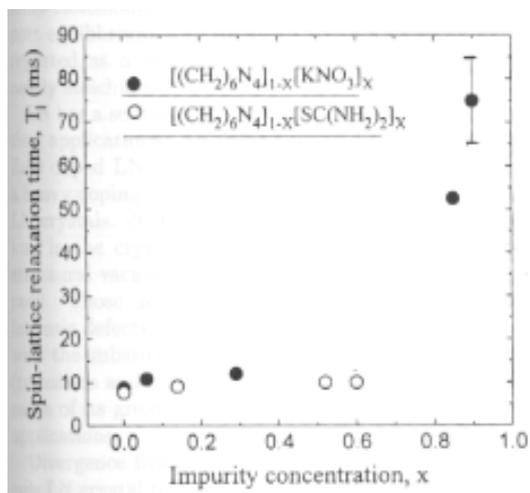


Fig. 3. Spin-lattice relaxation time,  $T_1$  versus impurity concentration  $x$ .

purity induced lattice defects for the rotational motion of the tetrahedral nitrogen molecule in the HMT crystal.

#### IV. SUMMARY

X-ray diffraction pattern reveals no apparent change in the lattice constant for both host and impurity structure. The presence of the macroscopic cluster of the starting materials indicates that a smooth fit of impurity to the host crystal cannot be expected without producing many kinds of lattice defects.

The independence of the  $^{14}\text{N}$  NQR frequency on the type and concentration of impurity confirms again that the NQR spectra reveal the local structure. In the case of hydrated HMT,  $T_1$  decreases slightly compared to that in pure HMT due to the increase in size of the unit cell, whereas  $T_1$  in HMT matrix in both HK and HS mixed systems tends to increase especially for a large concentration. This is accounted for the enhancement of the activation energy due to the presence of the lattice defects just near the tetrahedral local space around the resonant nucleus.

#### ACKNOWLEDGMENTS

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