^{14}N NQR Study of Mixed Complexes $(NaNO_2)_{1-x}(ANO_3)_x$: (A = K, Na)*

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^{14}N nuclear quadrupole resonance of the system $(NaNO_2)_{1-x}(ANO_3)_x$ with A=K and Na in the x-range $0 \le x < 0.5$ and the temperature range $77\ K \le T < 360\ K$ has been studied. The ^{14}N NQR frequency of $NaNO_2$ and its line width do not change with x, the latter fact untrasting the results of other mixed systems such as $Na_{1-x}Ag_xNO_2$. This indicates that in $(NaNO_2)_{1-x}(ANO_3)_x$ highly mobile lattice defects exist. The dependence on x of the rate of change in the spin-lattice relaxation time T_1 near the transition temperature is discussed in terms of a correlated flipping motion of the NO_2^- ion groups.

Introduction

$NaNO_2$ is ferroelectric at room temperature. With increasing temperature the crystal undergoes an order disorder transition firstly to an antiferroelectric phase at 437 K and then to a paraelectric phase at $T_c = 438$ K. The transitions are driven by long range interactions of the NO_2^- dipoles. In the ferroelectric phase the NO_2^- ions are aligned in the bc plane of the orthorhombic unit cell yielding a net polarization which points along one direction of the ferroelectric ***b*** axis (Figure 1 a). On approaching T_c, the NO_2^- dipoles became oriented with equal probability parallel and antiparallel to the direction of the ***b*** axis. The reversal occurs through flipping of the NO_2^- ions around the ***c*** axis (Figure 1 a, b).

In $NaNO_2$, the ^{14}N NQR spectra are mainly determined by torsional vibrations and critical flipping of the NO_2^- ions, from which the latter contribution to the ^{14}N quadrupole relaxation rate and the line width is characterized roughly by a logarithmic divergence around T_c [1]. In order to explain the critical effect on the ^{14}N NQR parameters, a modified Ising model was used for the critical reversing of the NO_2^- dipoles, according to which the reversing of the NO_2^- dipole is achieved by an angle not exactly π [1, 2]. In the antiferroelectric phase between 437 K and 438 K, the presence of the two components in the NQR frequency was quantitatively analyzed in terms of a spatial plane wave modulation of the local polarization indicative of an incommensurate structure at these temperatures [3, 4].

An outstanding feature of $NaNO_2$, especially below 150 K, is the sample preparation dependence of NQR spectra which seems to be related to impurities or lattice defects in the crystal [5]. For a full understanding of the impurity related lattice dynamics, an investigation of impurity doped crystals is necessary.

As an extension of the previous study on NQR in the $Na_{1-x}Ag_xNO_2$ system [6], ^{14}N NQR in the ferroelectric phase of $(NaNO_2)_{1-x}(ANO_3)_x$ has been measured in the temperature and concentration ranges $77\ K < T < 360\ K$ and $0 < x < 0.50$.

The two starting materials of $(NaNO_2)_{1-x}(ANO_3)_x$ are not isostructural, and therefore on mixing various kinds of lattice defects are formed, while in the compositionally similar systems $Na_{1-x}Ag_xNO_2$ a smooth fit of Ag^+ ions into the site of the counterpart Na^+ is possible.

Sample Preparation and Experiment

The samples were prepared by evaporating a stoichiometrically mixed solution of $NaNO_2$ and ANO_3. The ANO_3 concentration and the crystal structure of the sample were checked and controlled by atomic emission and X-ray diffraction analysis. The NQR measurements were carried out using a pulsed NQR spectrometer (RITEC).

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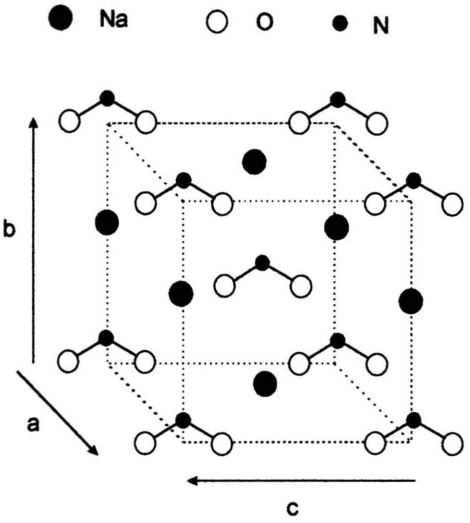


Fig. 1a. Unit cell of $NaNO_2$.

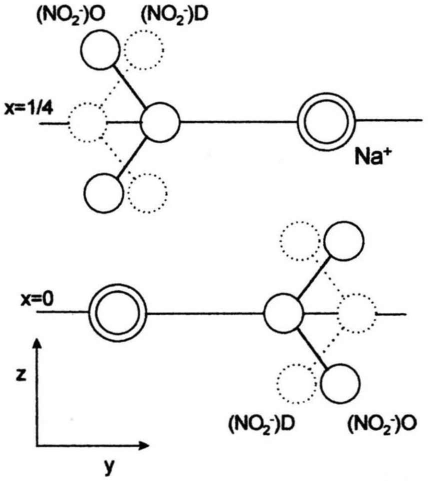


Fig. 1b. Two equivalent sites of the NO_2^- ion in the paraelectric phase.

Results and Discussion

– *NQR Frequency*

The ^{14}N NQR frequency in ferroelectric $NaNO_2$ at low temperatures follows the Bayer type temperature behaviour. As the temperature approaches the ferro-antiferroelectric transition temperature 437 K, a progressive deviation of the NQR frequency from the Bayer theory occurs due to the onset of large amplitude flipping of NO_2^- [7, 8].

The results of ^{14}N NQR frequency measurements show that there is no difference in the temperature dependence of the resonance frequency between pure $NaNO_2$ and the mixed complexes (Figure 2). This implies that the impurities influence negligibly the time averaged static EFG at the site of the ^{14}N nuclei, which is determined mainly by the local environment around the ^{14}N nuclei.

– *Line Width*

The width of the ^{14} NQR line in the $NaNO_2$ matrix at room temperature does not change with increasing ANO_3 concentration (Figure 3). This indicates the presence of highly mobile lattice defects, whose characteristic frequency seems to be much larger than the NQR frequency. The inhomogeneous line broadening caused by impurities, which was observed in the similar mixed systems $Na_{1-x}Ag_xNO_2$ [6], appears to be suppressed by the fast motion of the lattice defects produced by the substitution of ANO_3 into $NaNO_2$.

– *Spin-Lattice Relaxation Times*

In the temperature range 77 K$\leq T<$220 K there is no apparent difference in the temperature dependence of T_1 between pure and impurity doped crystals (Figure 4b). At these temperatures the motion of impurities and lattice defects does not influence the relaxation.

However, above 270 K the rate of decrease in T_1 with increasing temperature tends to diminish with increasing ANO_3 content (Figure 4a). Above 270 K, the possible contributions to the relaxation in $(NaNO_2)_{1-x}(ANO_3)_x$ are as follows:

1) sudden rotation of the NO_2^- ions,
2) contribution from the torsional lattice vibrations about the *a, b,* and *c* axes in the unit cell,
3) impurity induced lattice defects which undergo a fast diffusional motion,
4) contribution from impurities and lattice defects which are static or undergo a slow motion.

Among these relaxation mechanisms, the impurity effect on the lattice vibration can be neglected in view of the small contribution of charges outside NO_2^- under consideration to the EFG at the ^{14}N site compared with the local one. The fast motion of the lattice defects, which causes line narrowing, can also be ruled out because of its high frequency compared with the NQR frequency.

On the other hand, the flipping of NO_2^- is a thermally activated motion having an exponential temperature de-

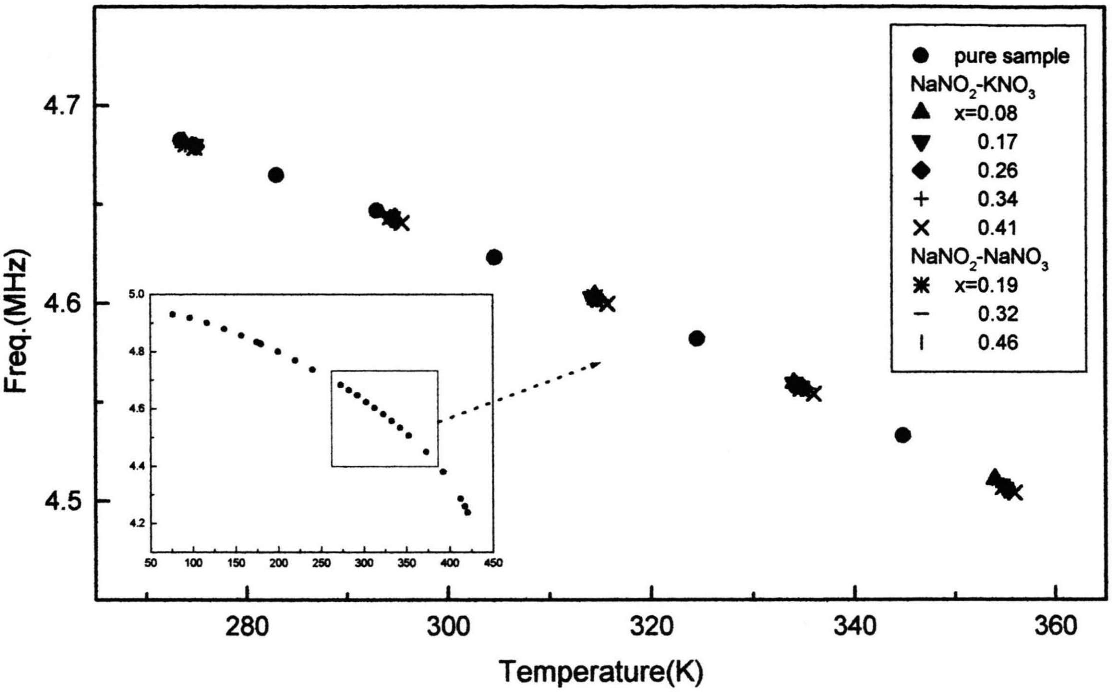


Fig. 2. ^{14}N NQR frequency of the $NaNO_2$ matrices in $(NaNO_2)_{1-x}(ANO_3)_x$: A=K, Na.

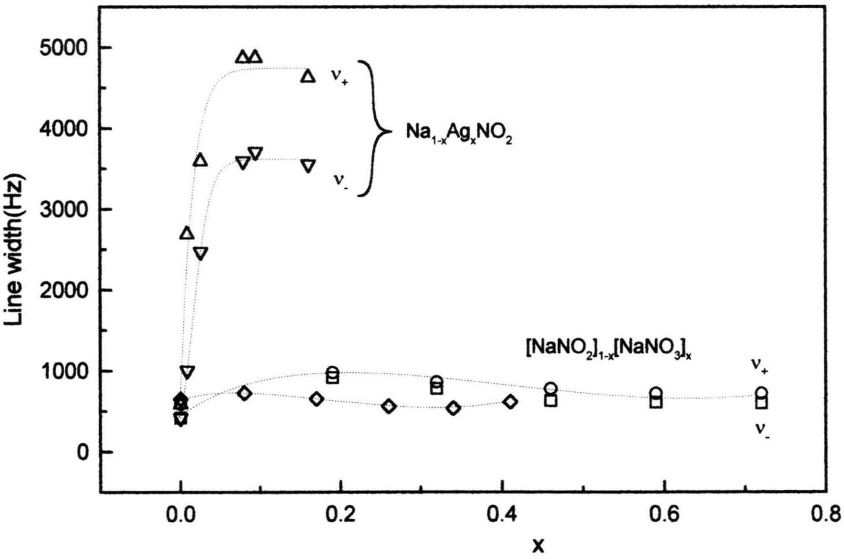
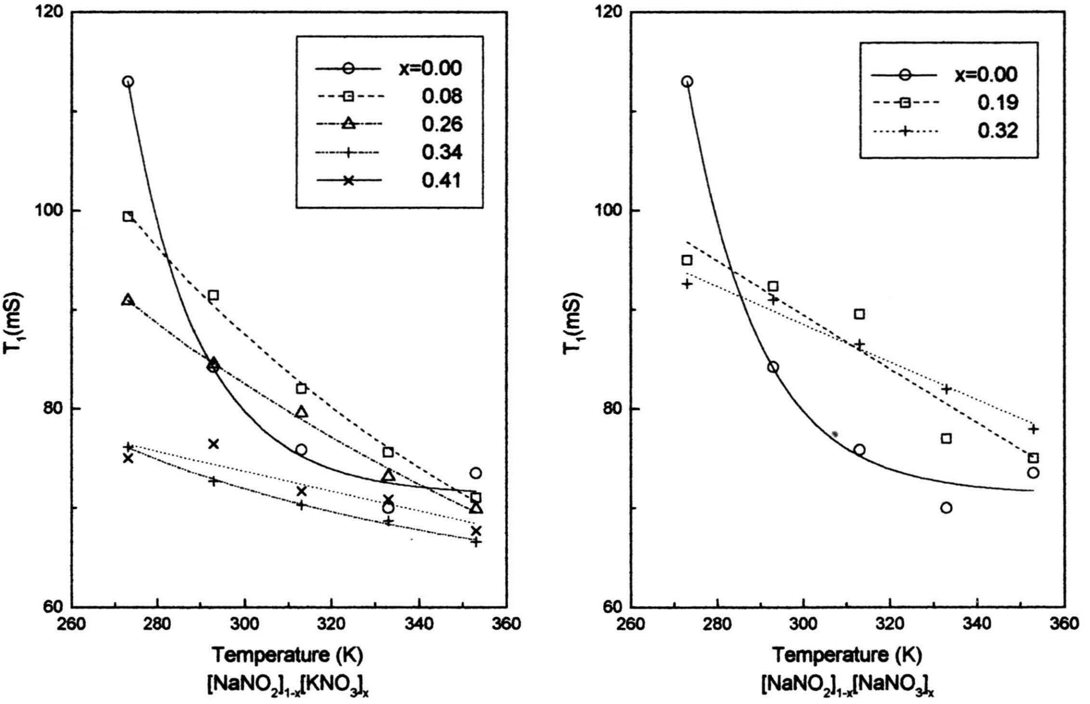


Fig. 3. ^{14}N NQR line width vs. x in $Na_{1-x}Ag_xNO_2$ and $(NaNO_2)_{1-x}(ANO_3)_x$: A=K, Na. ◇-◇-◇ $(NaNO_2)_{1-x}(KNO_3)_x$.

pendence. If this motion is affected by impurities or impurity induced lattice defects, it may influence the time dependence of the EFG at the ^{14}N site, resulting in a change in T_1.

Below T_c, the individual random motion of NO_2^- ions changes progressively into the aligned motion of neighbouring NO_2^- ions with decreasing temperature and produce a net polarization. In the case of ^{23}Na NMR the relaxation probability W of ^{23}Na due to the thermal motion of NO_2^- modified by the order parameter S is given by [9]

$$W \propto (1-S^2)(1-S)\exp\frac{E_a}{kT},$$



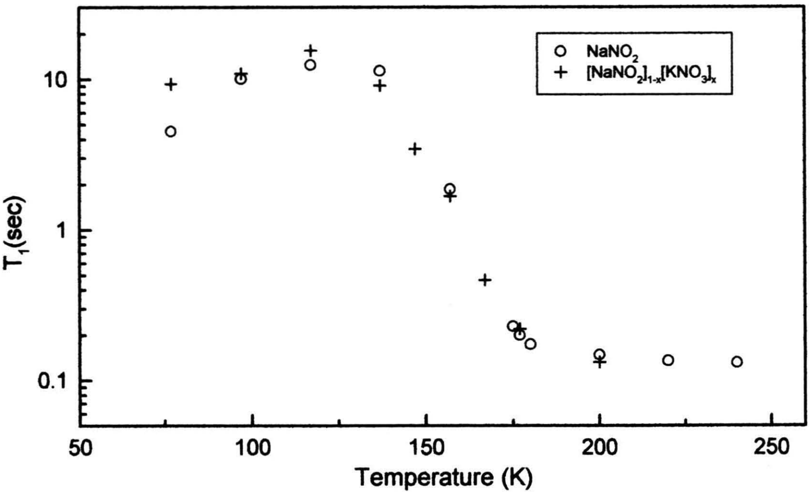


Fig. 4. Temperature dependence of the ^{14}N NQR spin-lattice relaxation time for mixed complexes $(NaNO_2)_{1-x}(ANO_3)_x$: A=K, Na in the temperature range of a) 260 K$<T<$360 K and b) 77 K$<T<$250 K. The lines in Fig. 4a are an exponential fits to the data obtained with the assumption of an exponential decay of T_1 on increase of temperature.

where E_a is the potential barrier for the flipping motion.

The temperature dependence of S was derived by Yamada et al. [10]:

$$S = \tanh\left[\frac{T_c}{T}(S + S^3 \Delta)\right], \Delta = 0.39$$

with $S = \dfrac{N_1 - N_2}{N_1 + N_2}$, where N_1 and N_2 are the number NO_2^- groups with parallel and antiparallel orientations.

If we assume that this equation holds for the ^{14}N NQR relaxation probability, the slight change of the temperature dependence of T_1 above 250 K may be attributed to the impurity induced modification of the temperature dependence of the order parameter S and the change in the potential barrier E_a.

Summary

In the $(NaNO_2)_{1-x}(ANO_3)_x$ mixed complexes the NQR spectra of ^{14}N of the $NaNO_2$ matrices are characterized by the influence of mobile lattice defects.

Substitution of ANO_3 (A=K, Na) impurities may induce a change in the temperature dependence of the order parameter and the potential barrier of the flipping of the NO_2^- ions.

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