$^{14}\text{N}$ NQR Study of Mixed Complexes
$(\text{NaNO}_2)_{1-x}(\text{ANO}_3)_x$: $(A=\text{K}, \text{Na})$


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$^{14}\text{N}$ nuclear quadrupole resonance of the system $(\text{NaNO}_2)_{1-x}(\text{ANO}_3)_x$ with $A=\text{K}$ and $\text{Na}$ in the $x$-range $0\leq x<0.5$ and the temperature range $77\,\text{K}\leq T<360\,\text{K}$ has been studied. The $^{14}\text{N}$ NQR frequency of $\text{NaNO}_2$ and its line width do not change with $x$, the latter fact contrasting the results of other mixed systems such as $\text{Na}_{1-x}\text{AgNO}_2$. This indicates that in $(\text{NaNO}_2)_{1-x}(\text{ANO}_3)_x$ 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 $\text{NO}_2$ ion groups.

Introduction

$\text{NaNO}_2$ is ferroelectric at room temperature. With increasing temperature the crystal undergoes an order-disorder transition firstly to an antiferroelectric phase at $437\,\text{K}$ and then to a paraelectric phase at $T_c=438\,\text{K}$. The transitions are driven by long range interactions of the $\text{NO}_2$ dipoles. In the ferroelectric phase the $\text{NO}_2$ ions are aligned within the bc plane of the orthorhombic unit cell yielding a net polarization which points along one direction of the ferroelectric $b$ axis (Figure 1a). On approaching $T_c$, the $\text{NO}_2$ dipoles became oriented with equal probability parallel and antiparallel to the direction of the $b$ axis. The reversal occurs through flipping of the $\text{NO}_2$ ions around the $c$ axis (Figure 1a, b).

In $\text{NaNO}_2$, the $^{14}\text{N}$ NQR spectra are mainly determined by torsional vibrations and critical flipping of the $\text{NO}_2$ ions, from which the latter contribution to the $^{14}\text{N}$ 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 $^{14}\text{N}$ NQR parameters, a modified Ising model was used for the critical reversing of the $\text{NO}_2$ dipoles, according to which the reversing of the $\text{NO}_2$ dipole is achieved by an angle not exactly $\pi$ [1, 2]. In the antiferroelectric phase between $437\,\text{K}$ and $438\,\text{K}$, 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 $\text{NaNO}_2$, especially below $150\,\text{K}$, 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 $\text{Na}_{1-x}\text{AgNO}_2$ system [6], $^{14}\text{N}$ NQR in the ferroelectric phase of $(\text{NaNO}_2)_{1-x}(\text{ANO}_3)_x$ has been measured in the temperature and concentration ranges $77\,\text{K}<T<360\,\text{K}$ and $0<x<0.50$.

The two starting materials of $(\text{NaNO}_2)_{1-x}(\text{ANO}_3)_x$ are not isostructural, and therefore on mixing various kinds of lattice defects are formed, while in the compositionally similar systems $\text{Na}_{1-x}\text{AgNO}_2$ a smooth fit of $\text{Ag}^+$ ions into the site of the counterpart $\text{Na}^+$ is possible.

Sample Preparation and Experiment

The samples were prepared by evaporating a stoichiometrically mixed solution of $\text{NaNO}_2$ and $\text{ANO}_3$. The $\text{ANO}_3$ 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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The results of $^{14}$N NQR frequency measurements show that there is no difference in the temperature dependence of the resonance frequency between pure NaN$_2$ 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 $^{14}$N QNR line in the NaN$_2$ matrix at room temperature does not change with increasing AN$_3$ 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$_x$NO$_2$ [6], appears to be suppressed by the fast motion of the lattice defects produced by the substitution of AN$_3$ into NaN$_2$.

### 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 AN$_3$ content (Figure 4a). Above 270 K, the possible contributions to the relaxation in (NaN$_2$)$_{1-x}$(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 dep-
Dependence. 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]

$$W \propto (1 - S^2)(1 - S) \exp \frac{E_a}{kT}.$$
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 $S = \frac{N_1 - N_2}{N_1 + N_2}$, 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 $E_a$.

Fig. 4. Temperature dependence of the $^{14}$N NQR spin-lattice relaxation time for mixed complexes (NaNO$_2$)$_{1\text{-}}$(AN$_3$)$_x$: (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.
Summary

In the \((\text{NaN}_2)_x(\text{AN}_3)_{1-x}\) mixed complexes the NQR spectra of \(^{14}\text{N}\) of the NaN\(_2\) matrices are characterized by the influence of mobile lattice defects. Substitution of AN\(_3\) (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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