External Influences on the ^{14}N NQR of Ferroelectric $NaNO_2$

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External influences on the ^{14}N NQR of ferroelectric $NaNO_2$, such as changes of the temperature, electric field, stress, gamma-ray irradiation, and impurity doping are reviewed. They normally cause either a frequency shift or a broadening of the ^{14}N NQR lines and are strongly related to the change of the spontaneous polarization.

Key words: ^{14}N NQR; Ferroelectric $NaNO_2$; Spontaneous Polarization; External Effects; Impurity.

1. Introduction

$NaNO_2$ is a famous ferroelectric material with spontaneous polarization (P_s) along the crystallographic b-axis, which undergoes an order-disorder transition at T_c = 437 K [1 - 3]. The P_s, arising from the ordering of NO_2^- and the accompanying shift of Na^+, is sensitive to the environment. Information on the local structure in $NaNO_2$ has been obtained by employing ^{14}N NQR [4 - 5]. A change of the local structure can be achieved by changing the external conditions. The influences of those are reflected in the ^{14}N NQR. External influences, such as changes of the temperature [6], electric field [7 - 8], stress [9], gamma irradiation [10], and impurity doping [11 - 13], on the ^{14}N NQR in $NaNO_2$ were studied for a long time in our laboratory. A substitutional impurity A in $Na_{1-x}A_xNO_2$ (A = Ag, K) disturbs the electric field gradient (EFG) at the ^{14}N site, resulting in line broadening and intensity weakening of the ^{14}N NQR line [13]. This trend is similar to the effect of gamma irradiation on $NaNO_2$. The ^{14}N NQR spectra obtained in the presence of an external electric field, stress, or a change of temperature show a frequency shift or line broadening. In this work, the results of previous investigations are reviewed and explained in terms of the spontaneous polarization of $NaNO_2$.

The spontaneous polarization in ferroelectric $NaNO_2$ was derived by Yamada et al. [14] as

$$P_s = \tanh[(T_c/T)(P_s + P_s^3 \Delta)], \quad (1)$$

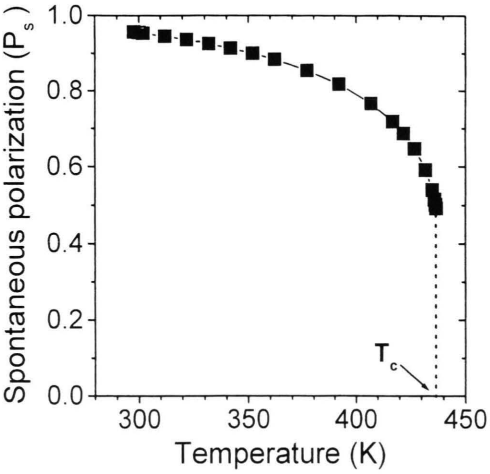

Fig. 1. Temperature dependence of the spontaneous polarization in $NaNO_2$.

where Δ is an anomalous volume expansion parameter which was found to be 0.39. P_s decreases with increasing temperature and goes to zero at T_c, as shown in Figure 1.

2. Experimental Results and Discussion

The employed spectrometers were a CW NQR spectrometer of Robinson type and a pulse NQR spectrometer (Ritec). The CW NQR spectrometer was efficiently employed to measure precisely the change of the lineshape as a function of temperature, elec-

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tric field, stress, and gamma irradiation. Meanwhile, a pulsed spectrometer was suitably used for impurity doped samples.

A) Temperature Dependence

For ^{14}N (I = 1) in $NaNO_2$ ($\eta \neq 0$), the ^{14}N NQR spectra consist of two resonance lines,

$$\nu_{\pm} = (3e^2qQ/4h)(1 \pm \eta/3), \tag{2}$$

where $e^2qQ/h = 2(\nu_+ + \nu_-)/3$ is the quadrupole coupling constant and η the asymmetry parameter. It was shown that the temperature dependence of the quadrupole coupling constant of ^{14}N is directly related to the spontaneous polarization:

$$(e^2qQ/h)_{\mathrm{exp}} = [5.2 - 0.6P_s^2 - 0.17 f_B(T)]\,\mathrm{MHz}, \tag{3}$$

where $f_B(T)$ represents the effect of lattice vibrations, based on the Bayer theory, given as $f_B(T) = 2/[\exp(h\omega_c/kT) - 1]$ with $\omega_c = 153\ \mathrm{cm}^{-1}$ [15]. Consequently, the changes of the quadrupole coupling constant and ^{14}N NQR frequencies originate from the change of spontaneous polarization due to the temperature by (3) and (1).

B) Electric Field Effect

The NQR line measurements with an applied external electric field were made at 77 K in order to obtain a good signal to noise ratio and to reduce the discharge current across the sample due to the high voltage. The apparatus and method were described in [7 - 8]. The electric field was applied either parallel or antiparallel to the direction of spontaneous polarization of the ferroelectric $NaNO_2$.

For the single domain $NaNO_2$ single crystal with spontaneous polarization along the b-axis, a frequency shift of the ν_+ and ν_- lines of ^{14}N NQR due to the electric field was observed [7 - 8]. For the multidomain crystal [7 - 8] and the powder [8], a broadening of the ν_+ and ν_- lines due to the external electric field was detected. While the direction of P_s is alternately reversed with a phase difference of 180° between domains in the case of multidomain, the direction of P_s of individual particles is ramdomly oriented with respect to the applied electric field in the powder sample.

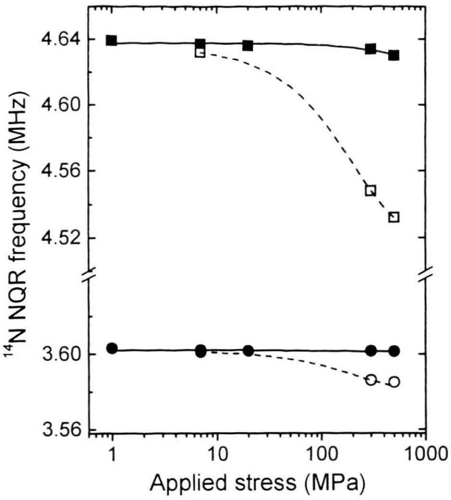

Fig. 2. The stress dependence of two pairs for $NaNO_2$, $\nu_{\pm}$ (ν_+: ■, ν_-: ●) and $\nu'_{\pm}$ (ν'_+: □, ν'_-: ○).

The frequency shift or line broadening due to the external electric field was explained with the fact that the direction of spontaneous polarization in a domain is related to the direction of the applied electric field. Consequently the shift and broadening of ^{14}N NQR line was well understood with the change of the spontaneous polarization due to the electric field.

C) Stress Effect

The stress effect on the ^{14}N NQR in $NaNO_2$ powder was investigated by the application of external pressure. In the samples, two extra NQR lines, $\nu'_{\pm}$, were observed in addition to the two normal NQR lines, $\nu_{\pm}$. The frequency of these four lines was found to decrease with increasing applied stress, as shown in Fig. 2, although hardly detectable in the case of ν_- [9]. The quadrupole coupling constants(Q_{cc} and Q'_{cc} arising from two sets of lines $\nu_{\pm}$, and $\nu'_{\pm}$, respectively, were found to decrease with increasing applied stress [9]. This anomaly and shift in NQR frequency, and the quadrupole coupling constant of ^{14}N may be attributed to the change of the spontaneous polarization caused by deformation of the ions due to the external stress.

D) Irradiation Effect

The $NaNO_2$ fine powder samples used here were irradiated at room temperature up to a maximum of

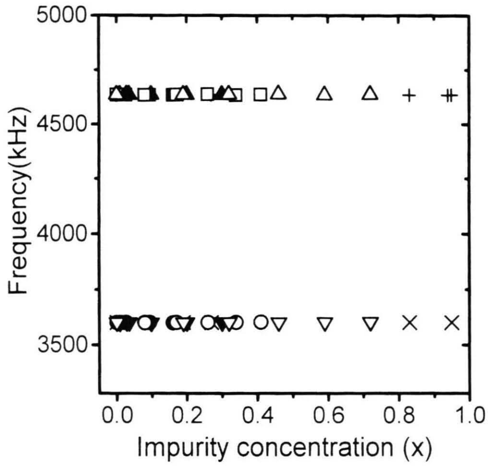

Fig. 3. ^{14}N NQR frequencies as a function of x in $Na_{1-x}Ag_xNO_2$ (ν_+: ■, ν_-: •), $Na_{1-x}K_xNO_2$ (ν_+: ▲, ν_-: ▼), $[NaNO_2]_{1-x}[KNO_3]_x$ (ν_+: □, ν_-: ○), $[NaNO_2]_{1-x}$-$[NaNO_3]_x$ (ν_+: Δ, ν_-: ∇), and $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$ (ν_+: +, ν_-: ×).

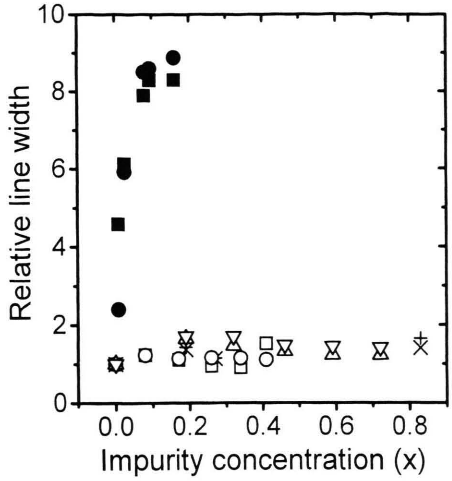

Fig. 4. Relative linewidth of the ^{14}N NQR line as a function of x in $Na_{1-x}Ag_xNO_2$ (ν_+: ■, ν_-: •), $[NaNO_2]_{1-x}[KNO_3]_x$ (ν_+: □, ν_-: ○), $[NaNO_2]_{1-x}[NaNO_3]_1$, (ν_+: Δ, ν_-: ∇), and $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$ (ν_+: +, ν_-: ×).

1.2×10^9 roentgens (r) at 6 different dosages. The employed radiation source was ^{60}Co with a gamma-ray activity of 10 kCi. Effects of gamma-ray irradiation on ^{14}N NQR in the samples were also investigated. The irradiation caused an intensity loss and broadening of ^{14}N NQR line without any detectable line shift [10], which was similar to the case of presence of impurities [11, 13]. It is suggested[10] that the effect of the gamma-ray irradiation on ^{14}N NQR in $NaNO_2$ powder is mainly due to a gradual change of surroundings as a result of the lattice distortion by point defects created by irradiation.

Meanwhile, the Curie temperature, T_c, obtained by measuring the dielectric constant, was decreased with the increasing amount of irradiated dose [16]. Equation (1) implies that a decrease of T_c causes a decrease of P_s. Thus the decrease of T_c observed in gamma-ray irradiated $NaNO_2$ crystal is due to the reduction of spontaneous polarization by point defects created by irradiation.

E) Impurity Effect

^{14}N NQR spectra in $NaNO_2$ are usually affected by doping impurities. In this study, impurity effects on ^{14}N NQR in isomorphic mixed systems $Na_{1-x}A_xNO_2$ (A = Ag, K) and anisomorphic mixed systems $[NaNO_2]_{1-x}$ $[BNO_3]_x$ (B = K, Na) and $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$, were investigated and compared to each other. All mixed systems investigated here were obtained by slow evaporation of aqueous mixed solutions. The sample preparation, characterization, and measurement were described in detail [11].

In the isomorphic systems $[NaNO_2]$-$[ANO_2]$ (A = Ag, K) and anisomorphic systems $[NaNO_2]$-$[BNO_3]$ (B = K, Na) and $[NaNO_2]$-$[(CH_2)_6N_4]$, the ^{14}N NQR frequencies ν_+ and ν_- of the $NaNO_2$-matrix were measured. For both iso- and anisomorphic mixed systems, the resonance line positions remained unchanged independent of the concentration and kinds of impurity, as shown in Figure 3. This implies that introducing impurities into $NaNO_2$ host crystal do not cause any ordered change in the EFG-configuration at the ^{14}N-site [11 - 13].

Figure 4 shows a comparison of the relative line width (normalized with respect to that in the pure host crystal) obtained with three kinds of mixed systems, $[NaNO_2]$-$[AgNO_2]$ [11], $[NaNO_2]$-$[BNO_3]$ (B = K, Na) [12], and $[NaNO_2]$-$[(CH_2)_6N_4]$ [13]. The line width is the full width at half maximum (FWHM) of the NQR line. The line width for the isomorphic mixed systems increases rapidly with increasing $AgNO_2$ concentration. This implies that the substitutional Ag impurity ions at Na ion sites are static in nature.

On the other hand, the line width in anisomorphic mixed systems $[NaNO_2]_{1-x}[BNO_3]_x$ (B = K, Na) [12] and $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$ [13] is more or less constant regardless of the impurity concen-

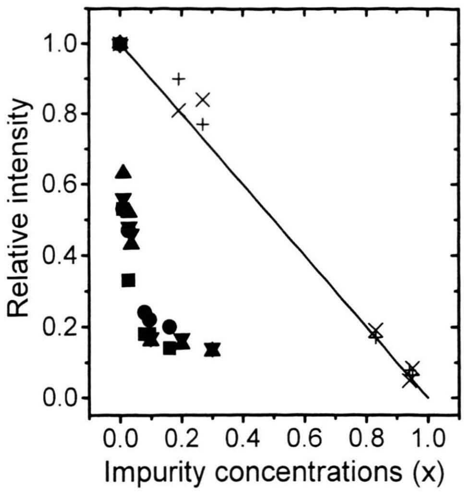

Fig. 5. Relative line intensity of ^{14}N NQR as a function of x in $Na_{1-x}Ag_xNO_2$ (ν_+: ■, ν_-: •), $Na_{1-x}K_xNO_2$ (ν_+: ▲, ν_-: ▼), and $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$ (ν_+: +, ν_-: ×).

tration. The result of x-ray diffraction in the anisomorphic systems shows the presence of both structures [13]. This implies that the mixing leads to a segregation of both parent crystals. In other words, the anisomorphic system is mainly composed of clusters of the host and impurity crystals. In these systems, the impurity molecules outside the cluster can not influence the ^{14}N NQR. The observed impurity effects are the secondary ones. They are caused by the lattice defects inside the cluster and are assumed to be small in concentration, which is responsible for the relatively weak impurity effects observed in this system. Though a detailed explanation for the process of forming defects is not simple, many of them are, at least, assumed to be produced at the cluster wall, where the static local field inhomogeneity dominates, by means of the charge compensation and the structural mismatching between the parent crystals. The defects may then diffuse into the matrix inside the cluster. The relatively narrow and constant line width of the observed ^{14}N NQR over the whole range of impurity concentration indicates that the defects are mobile point defects, the motion of which is fast enough with respect to the NQR frequency at room temperature.

The relative resonance line intensity (normalized with respect to that in the pure host crystal of the same sample volume) of ^{14}N NQR lines in two mixed systems is found to decrease with increasing amount of impurities, as shown in Fig. 5, where the line intensity is taken by integrating the area of the NQR line. In Fig. 5, the line intensity of the isomorphic systems $Na_{1-x}A_xNO_2$ (A = Ag, K) decreases much more rapidly than that of the anisomorphic system $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$ [13]. The line intensity in the anisomorphic system $[NaNO_2]_{1-x}[(CH_2)_6N_4]_x$ is found to decrease roughly in proportion to the content of the corresponding structure, as shown with the solid line in Fig. 5 [13]. Because of the fast motion of the lattice defects, the local field is spatially homogeneous within the cluster, leading to the motional narrowing. Thus the point defects do not smear the resonance line as the static impurities do in the isomorphic system.

The transition temperature(T_c) between the ferroelectric to paraelectric phase due to the Ag-impurity in the isomorphic mixed system $Na_{1-x}Ag_xNO_2$ is found to increase with x by measuring the ^{23}Na NMR spin-lattice relaxation [17]. Equation (1) shows that an increase of T_c causes an increase of P_s below T_c. The increase of P_s in $Na_{1-x}Ag_xNO_2$ may be caused by substitution of Ag^+ at the Na^+ site. The Ag^+ ion is larger in size and electronegativity than the Na^+ ion. The increase of T_c in $Na_{1-x}Ag_xNO_2$ with x contrasts the general trend of impurity effects in other systems and that observed in gamma-ray irradiated $NaNO_2$ crystal [16, 18].

Meanwhile, the decrease of T_c in an anisomorphic mixture $[NaNO_2]_{0.8}[KNO_3]_{0.2}$ was observed. The decrease of T_c in the mixed system can be explained by the decrease of P_s in (1). As already mentioned, the anisomorphic mixture is characterized by mismatch between the starting materials due to the absence of structural similarity. Thus the impurity effect in the anisomorphic mixture is associated with the fast motion of lattice defects produced by introducing impurities into the host crystal. Consequently, the decrease of P_s may be attributed to the fast motion of mobile defects in the mixture, disturbing the correlated motion.

3. Summary

The external effects on ^{14}N NQR in the ferroelectric $NaNO_2$ have been reinvestigated in terms of the spontaneous polarization. The frequency shift due to temperature, the line broadening and frequency shift due to electric field, the anomaly and frequency shift due to external stress, and the change of T_c as well as line intensity loss/line broadening due to gamma-ray irra-

diation and impurity doping have been observed. The examination of the results leads to a conclusion that the change of transition temperature, the line broadening and frequency shift of ^{14}N NQR line due to the external effects are originated from the change of the spontaneous polarization of the $NaNO_2$ system as a macroscopic quantity.

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