

^{14}N NQR Studies of Impurity Effects on the Local Structure of NaNO_2 -based Mixed Systems

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The influence of impurities on the ^{14}N NQR lineshape of $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ and $[\text{NaNO}_2]_{1-x}[\text{BNO}_3]_x$ ($\text{B} = \text{Na}, \text{K}$) at room temperature has been investigated. Carrying out spectral analysis in conjunction with classification of the local field inhomogeneities according to the structurally isomorphic, $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$, and anisomorphic $[\text{NaNO}_2]_{1-x}[\text{BNO}_3]_x$ systems, enabled an understanding of the microscopic nature of impurity-induced local disorder. The iso- and anisomorphic systems reveal their own unique features of the impurity induced local disorder. They are characterized by a static, random distribution of impurities in the isomorphic system and a fast motion of the impurity-induced mobile point defects in the anisomorphic system. However, for both systems, neither a change of the ^{14}N NQR frequency nor a multisplitting of the lines is observed because of the relatively low symmetry.

Key words: NQR; Lineshape; Iso- and Anisomorphic Systems; Local Disorder.

1. Introduction

Recently we became interested in crystalline solids with long range disorder, such as glassy matter, mixed solutions, and impurity doped/beam irradiated crystals, because the presence of the short range order, despite the lack of long range order, enables one to study by NQR the local environments of structurally disordered solids [1].

NaNO_2 is ferroelectric at room temperature, with the spontaneous polarization being parallel to the b -axis (Figure 1) [2]. It undergoes an order disorder transition to a sinusoidal antiferroelectric phase just below the Curie temperature at 437 K, above which the crystal becomes paraelectric. Above the Curie temperature the random orientation of NO_2^- ions parallel and antiparallel to the direction of the b -axis allows for a third mirror plane perpendicular to b -axis with zero average dipole moment. NaNO_2 has been widely investigated using NQR in an attempt to elucidate the local nature and related critical behavior in this material [3].

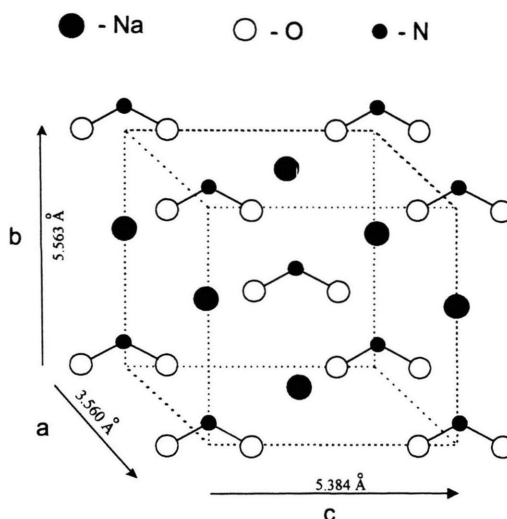


Fig. 1. Unit cell of NaNO_2 .

In this work, we carried out the ^{14}N NQR lineshape analyses with respect to the local field inhomogeneity for the two kinds of NaNO_2 -based mixed systems;

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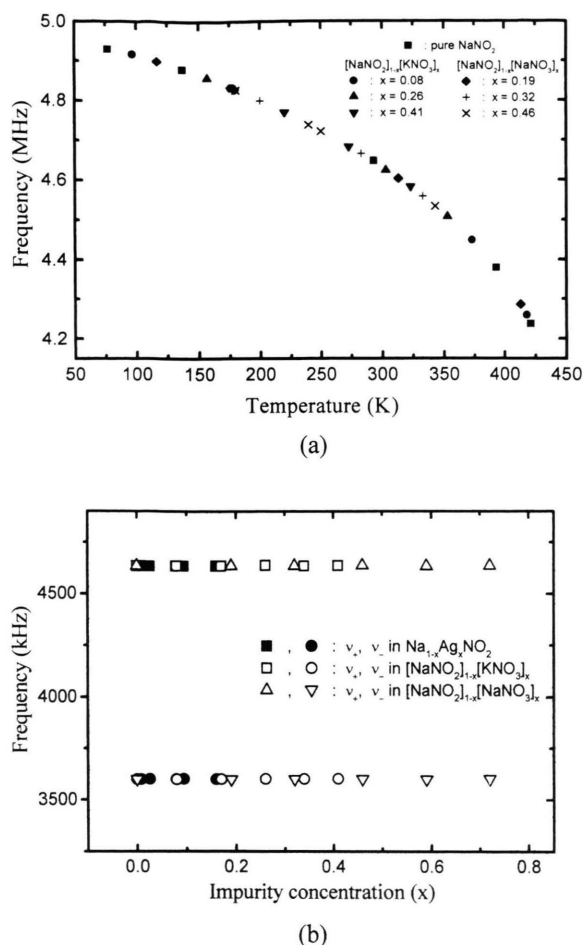


Fig. 2. a) Temperature dependence of the ^{14}N NQR frequency (ν_+) of pure NaNO_2 and NaNO_2 -based mixed crystals. b) ^{14}N NQR frequency as a function of impurity concentration at room temperature.

the structurally isomorphous $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ and anisomorphous $[\text{NaNO}_2]_{1-x}[\text{BNO}_3]_x$ ($\text{B} = \text{Na}, \text{K}$) one. The method of sample preparation and experimental techniques for ^{14}N NQR are described in [4 - 6]. The ^{14}N NQR spectra of the mixed systems studied here exhibit a systematic trend according to whether the starting material is isostructural or not. In the isomorphous system the impurity effects are characterized by the static, random distribution of impurities, while in the anisomorphous system dynamic secondary impurity effects are dominant. A prototype of such a study has been the Cl NQR investigations in the mixed and metal-ion doped hexachlorometallate systems [7]. The results of the ^{14}N NQR investigations in the NaNO_2 -based mixed systems closely resem-

ble those obtained from the hexachlorometallate systems. One pronounced difference in the NQR spectra between the NaNO_2 -based mixed systems and the corresponding hexachlorometallate systems is as follows: in the latter case, the line spectra of the isomorphous system are characterized by multisplitting of the line. This effect is attributed to the formation of the local structural order, while in the former case, the corresponding isomorphous system $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ lacks it.

2. Theory

The quadrupole interaction Hamiltonian consists of the nuclear quadrupole moment coupled by the efg at the nuclear site:

$$\mathcal{H} = \mathbf{Q} \cdot \nabla E, \quad (1)$$

where \mathbf{Q} is the tensor of the nuclear quadrupole moment determined by the electric charge distribution within the nucleus in question and ∇E is the efg-tensor that describes the configuration of the efg at the nuclear site produced by the electronic and ionic charge clouds around the nucleus. The NQR spectra reveal the distribution of the efg, reflecting the local structure around the resonant nucleus. Motion directly affects the eigenstates of the Hamiltonian and the energy level spacing. This results in the temperature dependence of the NQR frequency. The local disorder observed by NQR manifests itself by homogeneous or inhomogeneous line broadening, corresponding to the fast motion and slow motion, respectively.

Homogeneous Line Broadening

In the case of the fast motion compared to the period of resonant frequency, the local field is spatially homogeneous. This leads to the motional narrowing and the collapse of the multicomponent structure. The homogeneous line broadening resulting from the local disorder is caused mainly by random motions. The lineshape function L is described approximately by a symmetric Gaussian or Lorentzian function. In this case the position of the central peak remains unchanged. This implies that the temperature dependence of the NQR frequency does not change in the presence of local disorder, as observed experimentally (Figure 2a).

Inhomogeneous Line Broadening

The homogeneous field, averaged over the NQR-period, becomes inhomogeneous if the temporal fluctuation is not so fast compared to the period of the resonant frequency. For the inhomogeneous line broadening, the lineshape may be represented in terms of the local field distortion, u , which was developed by Blinc for the description of modulated local fields in incommensurate systems [8], and later applied to the lineshape analyses of glassy solutions by Wolfenson *et al.* [9]. For a small u compared to the stable part of the local field, as is the case in most molecular crystals, the NQR frequency of a resonant nucleus in the presence of the local field deformation can be described by a linear dependence on u ,

$$\nu = \nu_0 + \alpha u, \quad (2)$$

with a proportionality constant α and the static NQR frequency ν_0 being free from the perturbation u . The deformation field u describes the spatial variation of the local field and is thus given by a function of position r , i. e., $u = u(r)$.

The macroscopic inhomogeneous spectral distribution is

$$F(\nu) = \int L(\nu - \nu_s) \rho(\nu - \nu_s) d\nu_s, \quad (3)$$

where L is the elementary lineshape at the nuclear site s . A random distribution of u described by the Gaussian function with a half-width σ ,

$$f(u) = A \exp(-u^2/2\sigma^2), \quad (4)$$

yields the spectral density, $\rho(\nu)$:

$$\rho(\nu) = C \exp[-(\nu - \nu_0)^2/(2\alpha^2\sigma^2)], \quad (5)$$

where C is the normalized proportionality. Equations (2) and (5) show that the random distribution of the local deformation leads to a symmetric inhomogeneous line broadening being proportional to the Gaussian half-width σ without a displacement of the frequency of the spectral peak. The reason why the resonant frequency is not displaced is that the expected value of the random variable u is zero. And so $E(\nu_0 + \alpha u) = \nu_0$. The temperature dependence of the NQR frequency is expected in this case to be the same as that of the original line in the absence of local disorder.

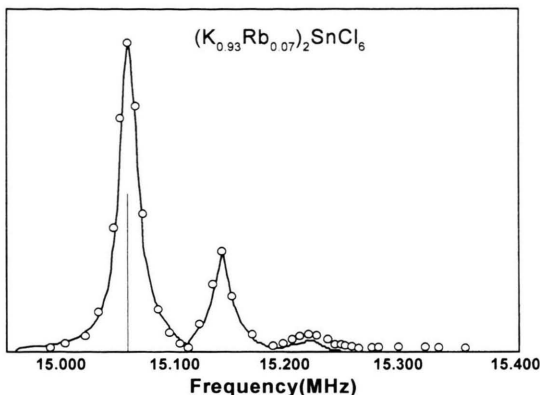


Fig. 3. Multisplitting of the resonance line caused by the local structure in $(\text{K}_{0.93}\text{Rb}_{0.07})_2\text{SnCl}_6$. The position of the original resonance line is indicated by a straight line.

The local deformation is in some cases spatially correlated, causing a multisplitting of the original resonance line, if impurities occupy particular lattice sites, all of which belong to the same local site symmetry with respect to a certain bonding axis. This occurs particularly in the isomorphic mixed crystals, $(\text{K}_{0.93}\text{Rb}_{0.07})_2\text{SnCl}_6$ (Fig. 3), where both parent crystals have the same structure [7]. The spatial extension of these ordered regions is assumed to be in most cases short range.

If a local structural order exists, the deformation field is no longer randomly distributed. The total spectral density, ρ_{total} , is then composed of a few number of elementary spectral densities ρ_i :

$$\rho_{\text{total}} = \sum_{i=1}^n \rho_i. \quad (6)$$

This yields the spectral distribution $F(\nu)$ corresponding to the number of the local site symmetry n .

$$F(\nu) = \sum_{i=1}^n \int L(\nu - \nu_c) \rho_i(\nu - \nu_i) d\nu_c \quad (7)$$

with ρ_i given by a Gaussian function.

Previous studies on the NaNO_2 -based mixed systems show that the impurity-affected local properties in this systems can be classified into two parts [4], isomorphic and anisomorphic systems. In the isomorphic system, the impurity effects are produced by the random distribution of the static impurities, whereas in the anisomorphic system dynamic secondary impurity effects are dominant above room temperature. According to the characteristics of both types of systems,

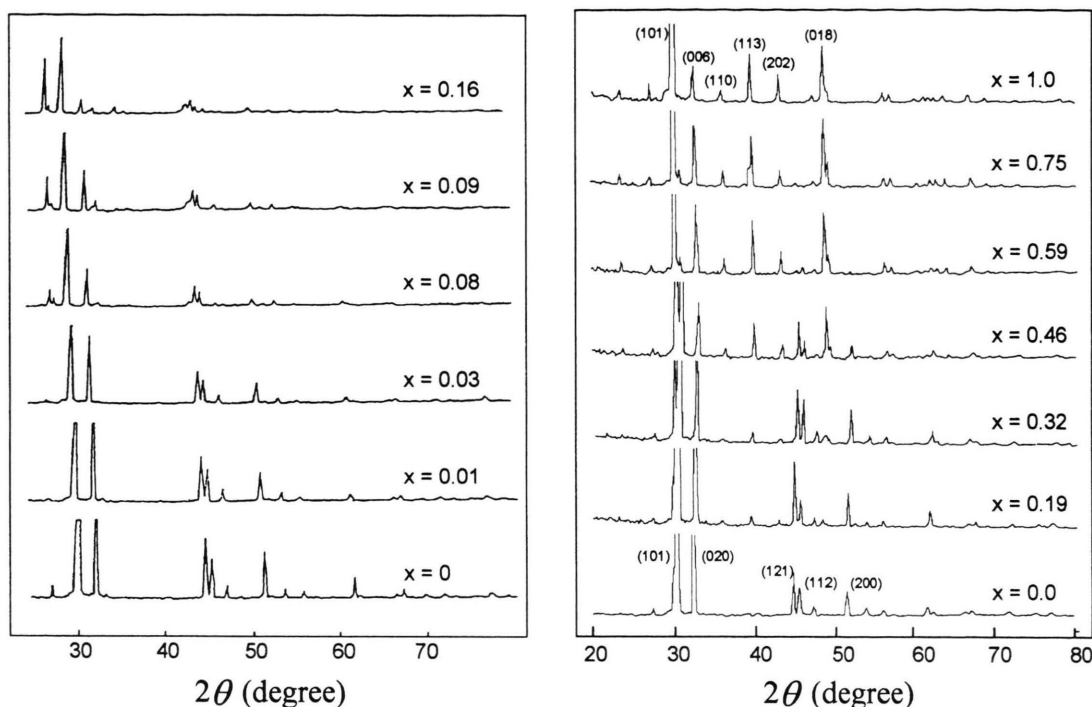


Fig. 4. X-ray diffraction patterns for the NaNO_2 -based mixed systems at room temperature. a) $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$, b) $[\text{NaNO}_2]_{1-x}[\text{NaNO}_3]_x$.

isomorphic and anisomorphic systems are subjected to inhomogeneous and homogeneous line broadening, respectively.

3. Results and Discussion

One common feature for both types of the mixed systems is that the ^{14}N NQR frequency of the NaNO_2 -structure and its temperature behavior is the same as those of pure NaNO_2 , regardless of the impurity concentration (Fig. 2 a and b). This result is expected from the concept of local deformation, if the displacement field u is small compared with the undisturbed field for the inhomogeneous line broadening without the presence of the local structural order described by (4) and (5), as well as for the homogeneous line broadening, where the related motion is usually much faster than the NQR time scale. Apart from the same impurity-related behavior of the NQR frequency, the overall impurity effects on the lineshape for both iso- and anisomorphic systems are different and resemble strongly to those observed from the ^{35}Cl NQR on the isomorphic and anisomorphic A_2BCl_6 -mixed systems [7].

The Isomorphic System $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$

X-ray diffraction patterns for the isomorphic system show a progressive increase of the lattice constant with increasing Ag concentration, without any change of the crystal structure (Figure 4a). The observed NQR spectra show that the line is symmetric and the linewidth increase rapidly with increasing concentration of impurities without a change of the NQR frequency and without the line splitting. The x-ray results and the rapid increase of the linewidth with impurity concentration imply that the most favorable impurity being responsible for the impurity effects is the Ag^+ ions which replace the Na^+ ions in the crystal. They are substitutional for the Na and static in nature. Thus the line broadening is inherently inhomogeneous in this system with a local deformation u that is assumed to be small compared to the undisturbed field. Then the lineshape is given by (3) and (7) for the presence of the local structural order, which is characterized by the dense distribution of elementary lines that are merged into one total line.

Regarding to the lineshape in the $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ isomorphic system, it is useful to compare the line

spectra of this system with those of the ^{35}Cl NQR in the isomorphous $(\text{K}_{1-x}\text{Rb}_x)_2\text{SnCl}_6$ systems [7]. In the $(\text{K}_{1-x}\text{Rb}_x)_2\text{SnCl}_6$ systems a multisplitting of line was observed that consists of a few satellite lines, the maximum number of which is limited to 4, in addition to the original resonance line. From the characteristics of the lines, the origin of the line splitting is attributed to the formation of local structural order that is associated with the 4-fold symmetry along the B-Cl bonding axis in the crystal.

However, in the case of the $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ system, it is not expected to observe such a line splitting. The relatively low symmetry (body centered orthorhombic with space group C_{2v}^{20} at room temperature) in the crystal structure of the NaNO_2 compared to that of K_2SnCl_6 (face centered cubic with space group O_h^5 at room temperature), enables one to explain the absence of the multisplitting. Because of the weak features of the local site symmetry, the formation of the local structural order is unrealistic in the $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ system. Additionally, fast fluctuations with a large amplitude caused by the flipping of the NO_2^- ions would erase the local structures, if they exist at all.

The Anisomorphous System $[\text{NaNO}_2]_{1-x}[\text{BNO}_3]_x$ ($B = \text{Na}, \text{K}$)

X-ray diffraction patterns show the presence of both structures of the two starting materials without a change of the lattice constant (Figure 4b). This implies that the anisomorphous system has a segregated structure. In other words, the anisomorphous system is mainly composed of clusters of the host and impurity crystals, whose crystal structure and the unit cell size remain essentially unchanged from those of the corresponding parent crystals.

The intensity behavior of the resonance line indicates that the cluster size of the NaNO_2 -matrix is much larger than the size of its unit cell [4]. Thus any modification of the NQR spectra of the anisomorphous system is caused not directly by the impurities substituted, but by the impurity-induced lattice defects that are present inside the NaNO_2 -cluster. Inside the NaNO_2 -cluster the possibility of the formation of any local structural order is ruled out because of the irregular feature of the lattice defects.

The lattice defects are assumed to be produced by means of the charge compensation because of the structural mismatching between parent crystals. The relatively narrow and constant linewidth of anisomor-

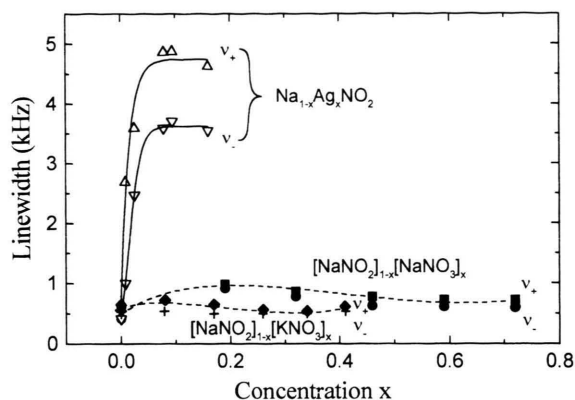


Fig. 5. ^{14}N NQR linewidth as a function of impurity concentration at room temperature.

phic systems over the whole range of impurity concentration compared to that of isomorphous mixed system (Fig. 5) indicates that the lattice defects are mobile point defects, the motion of which is fast compared to the period of the NQR frequency at room temperature. From the fast motion and the absence of the local structural order as mentioned above, the ^{14}N NQR line in the NaNO_2 -structure is expected to be symmetric as predicted by (7). The peak position and the temperature dependence of the NQR frequency remains also unchanged which is in agreement with the experiments (Figure 2).

4. Summary

Lineshape analysis has been done for the NaNO_2 -based isomorphous and anisomorphous mixed systems with regards to the local disorder features. The characteristics of the impurity effects in the NQR spectra for both, the isomorphous and anisomorphous systems have a strong resemblance to the corresponding isomorphous and anisomorphous A_2BCl_6 system: the static primary effects caused by the random occupation of impurities at the corresponding lattice sites of the counterpart ions in the isomorphous system and the dynamic effects caused by the impurity induced lattice defects in the anisomorphous system. The absence of local structure in the isomorphous $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ system is assumed to be due to the weak local site symmetry in the NaNO_2 -matrix.

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