

^{23}Na NMR and ^{14}N NQR in Mixed Crystals $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ *

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The ^{23}Na ($I=3/2$) NMR powder pattern for the $m=1/2 \leftrightarrow m=-1/2$ transition, broadened by the second-order quadrupole interaction, was investigated in mixed crystals $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ ($x \leq 0.16$). From the intensity loss of the ^{23}Na NMR line caused by the Ag^+ -impurity, the range of the quadrupole interaction in the ^{23}Na NMR central line was estimated. The range comprises ionic charges approximately up to the first nearest neighbour Na^+ site from the ^{23}Na nucleus, showing a large difference compared with that obtained from the ^{14}N NQR investigation in the same system.

1. Introduction

The quadrupole perturbed nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) depend on the charge configuration around the resonant nucleus, thus providing information on the local structure around the site of the resonant nucleus. Sodium nitrite (NaNO_2) is advantageous for this study because of its relatively strong signal intensity of ^{23}Na ($I=3/2$) NMR and ^{14}N ($I=1$) NQR. Therefore this crystal has extensively been studied by NMR [1–3] and NQR [4–6] techniques. Yagi and Tatsuzaki measured ^{23}Na NMR lines in γ -ray irradiated NaNO_2 crystal [7] and explained the irradiation effect in terms of the quadrupole interaction at the ^{23}Na site, to which a large number of surrounding ions contribute. However, the range of this quadrupole interaction was not determined quantitatively. Also, it was reported that the inhomogeneous distribution of the impurities within a certain volume induced the distribution of the EFG in the irradiated crystal, resulting in satellite line broadening.

Recently, a ^{14}N NQR investigation on NaNO_2 crystals mixed with AgNO_2 , isomorphous with NaNO_2 , was reported [8]. As an extension of this study, the impurity effects on the ^{23}Na NMR powder pattern of the $m=1/2 \leftrightarrow m=-1/2$ transition have been investigated at room temperature. The results of the ^{23}Na NMR study show that the Ag^+ -impurity in NaNO_2 leads to a weakening of the intensity of the ^{23}Na NMR central line compared to that of the pure crystal without any appreciable line broadening. By applying

the “all or nothing” model [9–11] to the intensity loss, we have roughly estimated the range of the quadrupole interaction on the ^{23}Na NMR central line and have compared it with that determined by ^{14}N NQR.

2. Experimental

The mixed crystals of $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ were obtained by evaporating mixed solutions for 4 weeks. Details on the growing technique and sample preparation are reported in [8]. The ^{23}Na NMR line was measured with a pulsed NMR (Bruker MSL 200). The resonance line was Fourier transformed to obtain the signal in the frequency domain.

3. Results and Discussion

A) ^{23}Na NMR

The ^{23}Na ($I=3/2$) NMR powder pattern of the $m=1/2 \leftrightarrow m=-1/2$ transition in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$, was measured at room temperature. The observed line is broadened by the second-order quadrupole perturbation to the central Zeeman line. Due to this perturbation, the central line is shifted according to the formula [12–13]

$$\Delta\nu_{1/2}^{(2)} = \frac{3\nu_Q^2}{16\nu_L} (1 - 9\cos^2\theta)(1 - \cos^2\theta), \quad (1)$$

where ν_L is the Zeeman frequency of the ^{23}Na nucleus, ν_Q the nuclear quadrupole frequency, and θ the angle between the applied magnetic field and the principal z -axis of the EFG tensor. The measured powder pattern as a function of the impurity fraction x in

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$\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ is presented in Figure 1. The zero point of the x -axis in Fig. 1 corresponds to the resonance frequency, 52.902 MHz, of the ^{23}Na nucleus at the static magnetic field of $B_0 = 4.700$ T.

As can be seen in Fig. 1, the relative integrated intensity (normalized with respect to that in the pure host crystal) of the central line decreases with increasing concentration of the Ag^+ -impurity without any appreciable line broadening. This change of relative intensity as a function of the impurity fraction x in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ is displayed in Fig. 2, where the line intensity is taken by integrating the area of the ^{23}Na central NMR line. The intensity loss of the ^{23}Na NMR line may well be caused by the shift of the NMR line due to the second order quadrupole interaction of the Ag^+ -impurity near the resonant nucleus. Thus it is represented in terms of the probability that an Na^+ ion is replaced by an Ag^+ impurity ion, as given by [9–11]

$$I/I_0 = (1-x)^n \quad \text{or} \quad \ln(I/I_0) = n \ln(1-x), \quad (2)$$

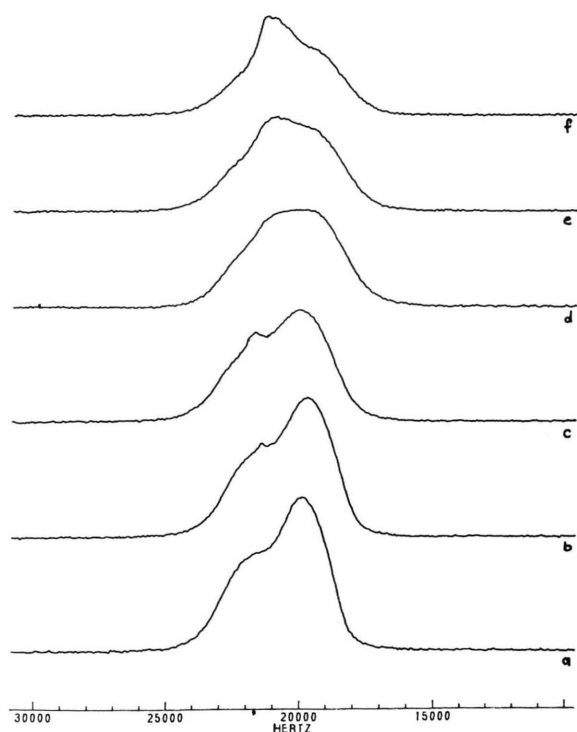


Fig. 1. The central transition ($+1/2 \leftrightarrow -1/2$) of the ^{23}Na NMR lines for the various impurity fractions x in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$: a) $x=0$, b) 0.0084, c) 0.026, d) 0.079, e) 0.094, and f) 0.16.

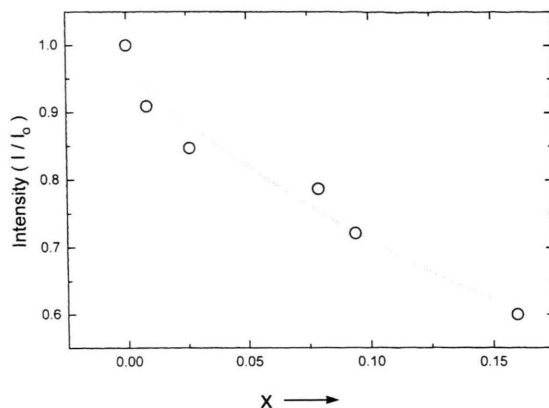


Fig. 2. The relative integrated intensity $[I_{\text{int}}(x)/I_0]$ of the ^{23}Na NMR line as a function of the impurity fraction x in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$.

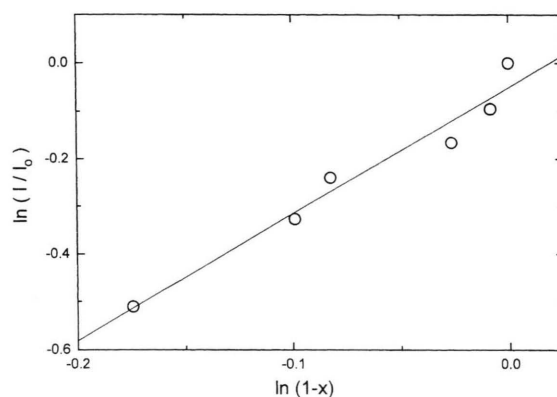


Fig. 3. Log-log plot of the relative integrated intensity vs. $(1-x)$ in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$.

where I_0 is the ^{23}Na NMR central line intensity of the pure crystal with the normalized sample volume. This yields a critical volume around a resonant nucleus, which contains n Na^+ sites. This volume is characterized such that only the impurity ions inside it diminish the NMR line intensity.

Fitting (2) to the integrated intensity data as a function of x , the number of lattice sites (n_{int}) within the critical volume (V_{int}) was determined to be $n_{\text{int}} = 2.6 \pm 0.4$, as shown in Figure 3. This number comprises the Na^+ sites up to the first nearest neighbours from the ^{23}Na nucleus. This implies that the perturbation of the quadrupole interaction by the Ag^+ -impurity within V_{int} is so strong that the ^{23}Na resonance line is shifted to the region beyond the observation, resulting in the intensity loss, while the impurity ions

outside V_{int} have no influence on the ^{23}Na NMR line. In other words, the external contribution to the quadrupole interaction of ^{23}Na NMR is mostly determined by the ionic charges up to the first nearest neighbour Na^+ sites from the ^{23}Na nucleus.

B) ^{14}N NQR

The position of the ^{14}N NQR lines [$\nu_{\pm} = 3e^2qQ \cdot (1 \pm \eta/3)/4h$] of $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$ was practically the same as that of pure NaNO_2 [8]. This implies that substitution of AgNO_2 impurities in NaNO_2 does not induce any macroscopic change in the EFG at the ^{14}N site.

However, the two differently defined line intensities (integrated intensity and peak height of lines) de-

creased with increasing concentration of Ag^+ , as shown in Figure 4. Applying these two results to (2), the number of lattice sites was obtained to be $n_{\text{int}} = 34 \pm 4$ and $n_{\text{peak}} = 56 \pm 7$, as shown in Fig. 5, where n_{int} and n_{peak} are lattice sites determined by the integrated intensity and the peak height, respectively, of the NQR lines. These numbers comprise the Na^+ sites up to the fifth (V_{int}) and sixth nearest neighbours (V_{peak}), respectively.

From ^{14}N NQR results, the position of the Ag^+ ions from the resonant nucleus could be classified into 3 regions. Firstly, for the case of the impurity ions located within V_{int} , the perturbation to the quadrupole interaction due to the impurity is so strong that ^{14}N NQR line is completely shifted to the region beyond the range of observation, resulting in the loss of integrated line intensity. Secondly, for the case of impurity ions located between V_{int} and V_{peak} , the perturbation such that the ^{14}N NQR line is slightly shifted to a region within the range of observation, resulting in the line broadening. Finally, for the case of impurity ions located outside V_{peak} , the quadrupole interaction due to the impurity ions has no influence on the ^{14}N NQR line. Thus, the whole range of the contribution to the quadrupole interaction in ^{14}N NQR comprises ionic charges up to the sixth nearest neighbour Na^+ sites from the ^{14}N nucleus.

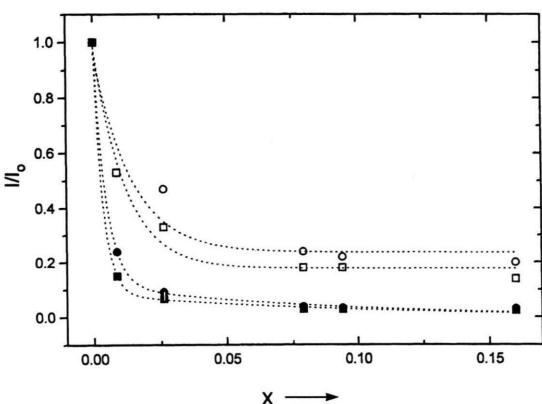


Fig. 4. The relative integrated intensity $I_{\text{int}}(x)/I_0$ (\square : ν_+ , \circ : ν_-) and peak height $I_{\text{peak}}(x)/I_0$ (\blacksquare : ν_+ , \bullet : ν_-) of the line as a function of the impurity fraction x in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$.

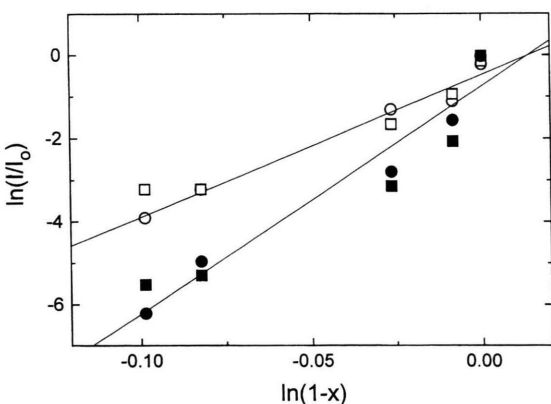


Fig. 5. Log-log plot of the relative integrated intensity (\square : ν_+ , \circ : ν_-) and peak height (\blacksquare : ν_+ , \bullet : ν_-) vs. $(1-x)$ in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$.

C) Comparison

The small critical volume (V_{int} =first neighbour Na^+ sites) obtained from $n_{\text{int}} = 2.6 \pm 0.4$ for ^{23}Na NMR compared to that (V_{int} =fifth neighbour Na^+ sites) for ^{14}N NQR implies that the range of influence of the impurity ions on the quadrupole interaction is much smaller for the ^{23}Na NMR than that for the ^{14}N NQR. This can be understood as follows. For the ^{23}Na NMR central line, the quadrupole interaction arising from the impurity ion around the resonant nucleus is considered as a second order perturbation ($\langle |H_Q|^2 \rangle$). Thus the quadrupole contribution due to the impurity falls off with a $1/r^6$ power dependence ($\langle |H_Q|^2 \rangle^2 \sim 1/r^6$) from the resonant nucleus. However, the situation is quite different for ^{14}N NQR. Here the main Hamiltonian is the quadrupole interaction. With a $\langle |H_Q| \rangle \sim 1/r^3$ dependence of the separation, the quadrupole contribution of impurity ions reduces slowly, compared to the case of ^{23}Na NMR. Therefore, the range of influence of the quadrupole interaction in ^{23}Na NMR is much smaller than that in ^{14}N

NQR. In this respect, the small critical volume in ^{23}Na NMR compared to that in ^{14}N NQR can be understood.

Furthermore, the intensity loss without appreciable line broadening in ^{23}Na NMR can also be explained as a result of second order quadrupole interaction. The shift of the NMR line position caused by the quadrupole interaction due to the impurity ions is proportional to v_Q^2 , as shown by (1), so that any impurity ions outside V_{int} produce no detectable line broadening. Meanwhile, in ^{14}N NQR the shift of the NQR line caused by the impurity ions decreases with a $1/r^3$ dependence, so that any impurity ions located outside V_{int} (between V_{int} and V_{peak}) cause a small shift of the NQR line resulting in the line broadening.

The appreciable broadening of ^{23}Na NMR satellite lines due to the impurity ions observed in Gamma-ray irradiated NaNO_2 crystal [7] may be explained as a result of first order quadrupole interaction with a $1/r^3$ dependence on the distance r from the resonant nucleus to the impurity ion. The line broadening may be similar to that originated from $1/r^3$ dependence in the case of ^{14}N NQR in $\text{Na}_{1-x}\text{Ag}_x\text{NO}_2$.

4. Summary

In the case of the central transition of ^{23}Na NMR, the Ag^+ -impurity ions within V_{int} around the resonant

nucleus cause an intensity loss due to a shift of the resonance line beyond the range of observation without any detectable line broadening, as a result of the second order quadrupole interaction. The results of ^{23}Na NMR show that the range of the quadrupole interaction to the ^{23}Na NMR comprises ionic charges approximately up to the first nearest neighbour Na^+ site from the resonant nucleus. In ^{14}N NQR, the effect of Ag^+ -impurity is an intensity loss or line broadening according to the extent of the line shift which depends on the distance of the impurity ion from the ^{14}N nucleus. The results of ^{14}N NQR show that the contribution of the nuclear quadrupole interaction is mostly determined by ionic charges up to the sixth nearest neighbour Na^+ sites from the resonant nucleus. The large difference of the critical volume between the ^{14}N NQR and ^{23}Na NMR, and the insensitivity of the ^{23}Na NMR line against the impurity concentration observed in this study clearly demonstrate that NQR is a more sensitive technique for the investigation of the static and dynamic phenomena associated with the local charge distribution in the crystal.

Acknowledgements

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