

Magnetic Resonances of ^{23}Na and ^{14}N Nuclei in Single and Multi-Domain Crystals of Ferroelectric NaNO_2

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1. Introduction

Betsuyaku [1] and Kanashiro et al [2] reported that the two satellite lines of ^{23}Na NMR in a ferroelectric NaNO_2 crystal were asymmetric, and that even the central line for $B_0//a$ deviates appreciably from the first derivative of the Gaussian line shape. Kanashiro et al [2] tried to explain this effect in terms of the nuclear dipole coupling between the Na atoms. Hughes and Pandey [3] also studied the same effect, and attempted to explain it by means of the magnetic dipolar third moments. They concluded that the asymmetry arises from the perturbation of the magnetic dipolar coupling, and this is the intrinsic property of NaNO_2 crystal from the similarity of experimental results obtained with two different crystals.

In connection with these reports [1-3], the present work is focused on the ^{23}Na NMR line shape as well as the electric field gradient (e.f.g.) at ^{23}Na and ^{14}N sites in NaNO_2 crystal by employing the NMR and NQR technique. Two NaNO_2 crystals prepared here have different domain states each other: one has a multi-domain and the other has a single domain state, respectively.

2. Experimental

A. Procedure

The NaNO_2 is body centered orthorhombic and its space group is $C_{2v}^{20}-Im2m$ in the ferro-

electric phase at room temperature [4]. The used sample crystals were grown from the melt. Virgin crystals of NaNO_2 turned out to be in the multi-domain state (herein named by S_m). The crystal of single domain (S_s sample) was prepared by applying an external electric field of 3 kV/cm along the ferroelectric axis of a virgin crystal for 8 hrs near its T_c of 163.5°C. Their domain states were confirmed by employing optical polarizing microscopy and etching technique [5].

The NMR signals for ^{23}Na nucleus were observed with an rf-frequency of 6 MHz by using the cw-NMR (Varian WL-112). They were recorded by setting the magnetic field modulation at 35 Hz with an approximate amplitude of less than one-third of the resonance line width. The pulse-NMR (Bruker MSL 200) system was also employed to investigate the exact line shape of ^{23}Na with an inversion recovery sequence, and NQR measurements were made by using the Robinson type spectrometer [6]. All the measurements were made at room temperature.

B. Results

Since the ^{23}Na nucleus has a spin of $I=3/2$, three resonance lines are typically observed: one central and two satellite lines. The line shape of ^{23}Na NMR in two single crystals of NaNO_2 had been measured [7] by using the cw-NMR spectrometer. In the S_s sample, as shown in Fig. 1, the asymmetric satellite lines were observed for $B_0//a$ and $B_0//c$, consistent with the previous reports [1-3]. However, in the S_m , the observed satellite lines was nearly symmetric (see Fig. 2).

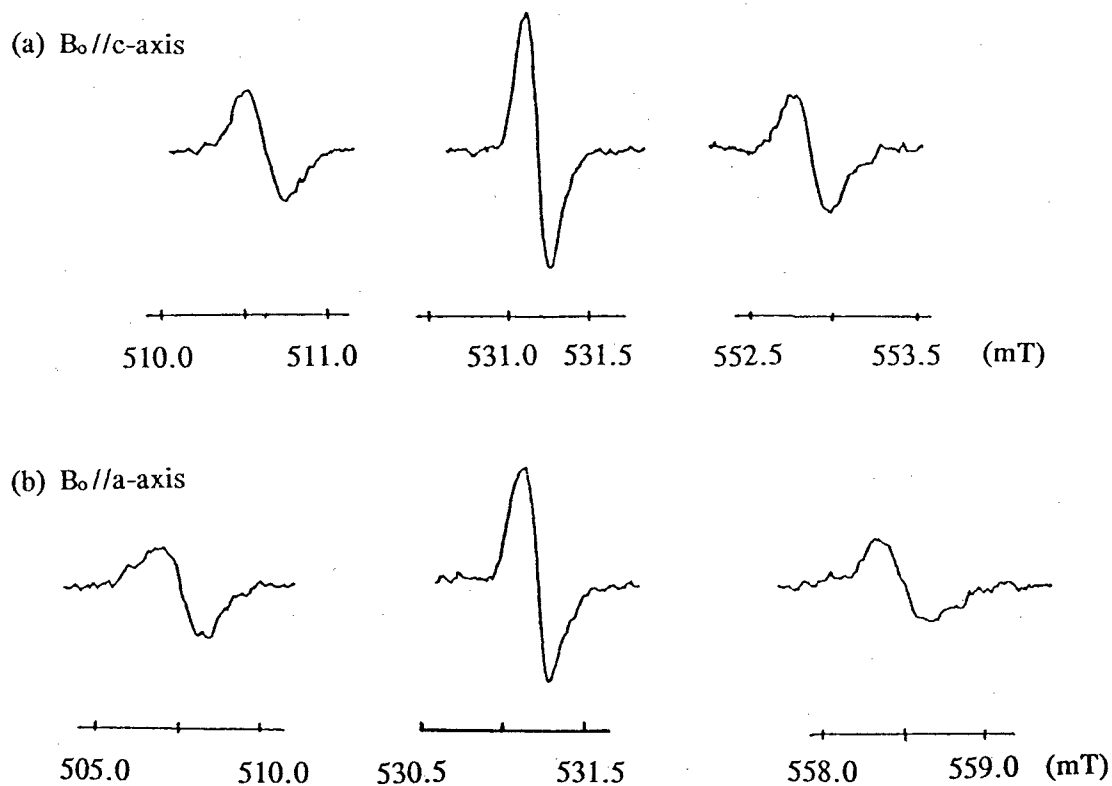


Fig. 1. In the S_s sample, asymmetric satellite lines were observed for (a) $B_0//c$ and (b) $B_0//a$ with the cw-NMR spectrometer.

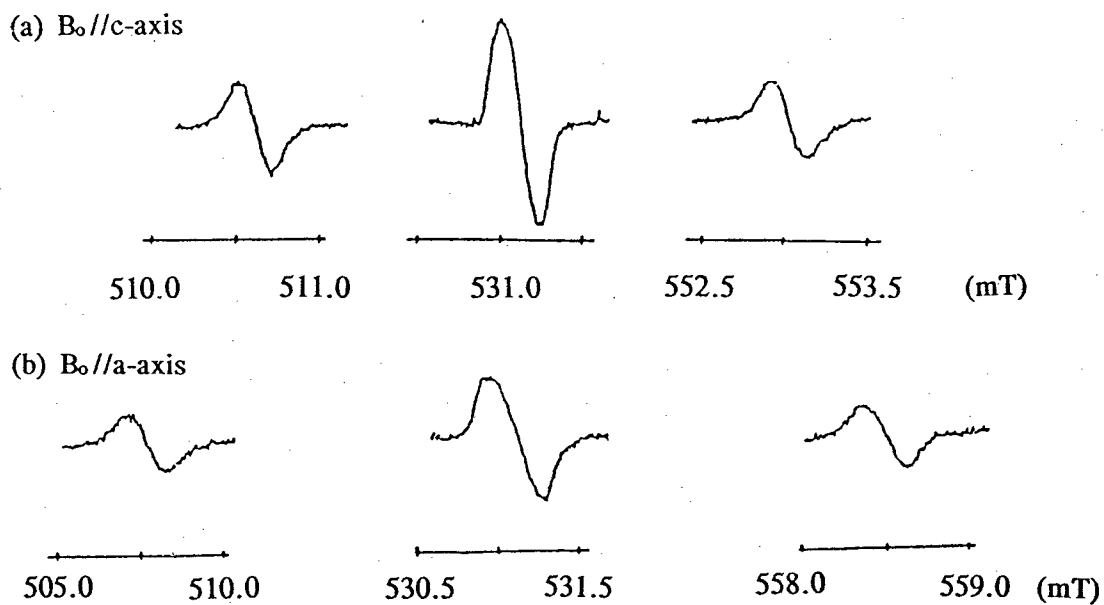


Fig. 2. In the S_m sample, symmetric satellite lines were observed for (a) $B_0//c$ and (b) $B_0//a$ with the cw-NMR spectrometer.

The line width of the satellite lines (ΔB_s) in S_s was found to be broader than that in S_m , whereas the central line in these two samples is symmetric and its line shape is nearly the same; it was 0.29 mT (0.21 mT) for $B_o//a$ ($B_o//c$). Meanwhile, the quadrupole coupling constant (Q_{cc}) and asymmetry parameter (η) for ^{23}Na of these two samples are nearly the same within the experimental accuracy ($\Delta Q_{cc} : \pm 0.003$ MHz, $\Delta\eta : \pm 0.003$) [7].

For the ^{14}N NQR measurements in the two samples, there were no detectable differences in their line widths ($\Delta\nu^+$ and $\Delta\nu^-$) and NQR parameters. The quadrupole parameters at the ^{23}Na and ^{14}N nuclei in the S_m and S_s samples are summarized in Table 1 together with the line width. The only difference between the S_m and S_s samples is in the line shape of ^{23}Na NMR and its line width.

The line shape of ^{23}Na NMR in the two samples obtained with the pulse-NMR is shown in Fig. 3 and 4, respectively. In both of two samples, the central line has one peak and its line shape is a Gaussian as well known [1-3]. So the central line is not shown in Fig. 3 and 4, where $\nu_L^{s(m)}$ ($\nu_H^{s(m)}$) is the satellite line of low (high) frequency, and superscript $s(m)$ stands for the single domain (multi-domain) state. In Fig. 3, (a) shows that each satellite line obtained with S_s has two peaks ($\nu_L^{s'}$ and ν_L^s , ν_H^s and $\nu_H^{s'}$), and (b) displays their first derivative curves. However, in the S_m sample, the satellite line (ν_L^m or ν_H^m) has only one peak and it is well fitted with a Gaussian line shape as shown in Fig. 4, which displays ν_L^m representatively since the two satellite lines all are symmetric. The inner set (ν_L^s and ν_H^s) of the two couples obtained with S_s [Fig.3 (a)] corresponds to those (ν_L^m and ν_H^m)

with the S_m sample (Fig. 4). The outer set ($\nu_L^{s'}$ and $\nu_H^{s'}$) in S_s is newly observed additionally.

3. Discussion

Betsuyaku and Kanashiro et al [1-2] had measured the NMR line shapes for $B_o//a$ and $B_o//c$. Their data for $B_o//a$ was distinctively asymmetric but those for $B_o//c$ was hardly asymmetric. They, by considering the dipolar interaction, argued that this effect arised from the geometrical arrangement of Na atoms in NaNO_2 crystal having two fold symmetry along the b-axis. Namely, the dipole coupling between the two Na nuclei along the a-axis contribute considerably to the asymmetry of the satellite lines because the interatomic distance along the a-axis is about two-thirds of that along the c-axis.

Kanashiro et al [2] determined the sign of the Q_{cc} at Na in NaNO_2 by comparing the line shape of the satellites for $B_o//a$ with the calculated line spectrum of two interacting $I = 3/2$ spins. However, Hughes et al indicated that there was some uncertainty in the determination by Kanashiro et al since the resonances showed a substantial inhomogeneous quadrupole broadening, and no steps were taken to confirm that the asymmetry was indeed associated with the dipolar interaction and not with the quadrupole broadening. Hughes et al confirmed the sign of Q_{cc} determined by Kanashiro et al by comparing the magnetic dipolar third moment with the observed asymmetry, and reported that the asymmetry due to the quadrupole broadening was dominant at some crystal orientations by measuring quantitatively the asymmetry of inhomogeneous

Table 1. The quadrupole parameters and the line widths at room temperature.

| samples | ^{23}Na NMR | | | | ^{14}N NQR | | | |
|---------|----------------------|------------|----------------------|----------------------|---------------------|------------|---------------------|---------------------|
| | Q_{cc} (MHz) | η (%) | $\Delta B_s(B_o//a)$ | $\Delta B_s(B_o//c)$ | Q_{cc} (MHz) | η (%) | $\Delta\nu^+$ (kHz) | $\Delta\nu^-$ (kHz) |
| S_m | 1.094 | 11.0 | 0.30 mT | 0.23 mT | 5.490 | 35.7 | 0.66 | 0.53 |
| S_s | 1.094 | 11.0 | 0.38 mT | 0.25 mT | 5.490 | 35.7 | 0.67 | 0.53 |

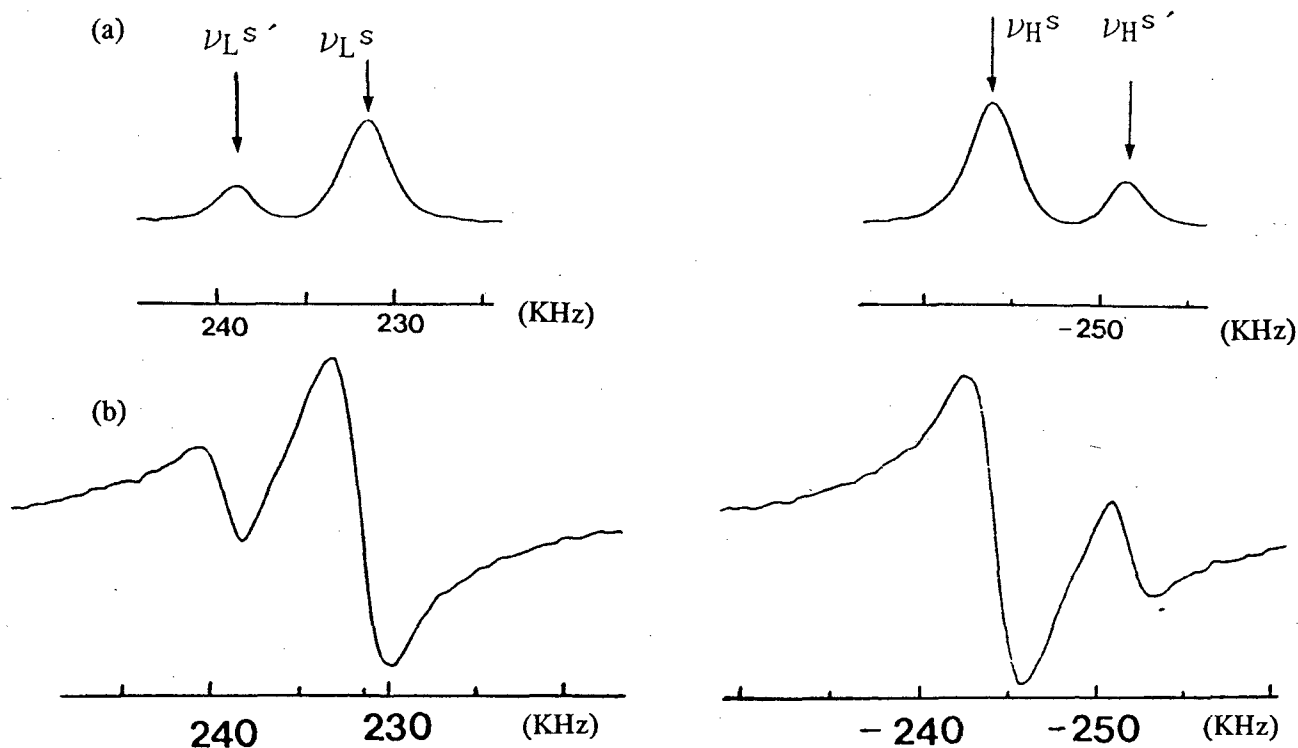


Fig. 3. The satellite lines of ^{23}Na NMR in the S_s sample observed for $B_0//c$ with the pulse-NMR spectrometer. (a) Each satellite line has two peaks. (b) the first derivative curve of (a)

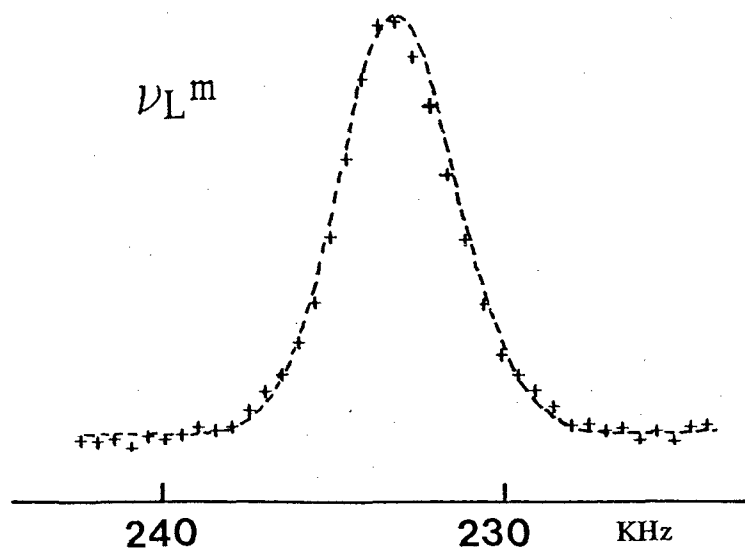


Fig. 4. The satellite line of ^{23}Na NMR in the S_m sample observed for $B_0//c$ with the pulse-NMR spectrometer. The satellite line has only one peak and is well fitted with a Gaussian line shape, where + denotes signal trace and the dashed line is a best fitted Gaussian line shape.

geneous quadrupole broadening. They also suggested that the asymmetry was the intrinsic property of this crystal by observing the similar quadrupolar broadening for two different crystals.

As can be seen in Fig. 1, our NMR results show that the satellite line shape in S_s is asymmetric, which is in accordance with the previous reports [1-3]. However, those in S_m is nearly symmetric (Fig. 2). The exact line shapes of Fig. 3 and 4 obtained with the pulse-NMR system may provide a decisive clue for the origin of the observed asymmetry. Fig. 3(a) shows that each satellite line in S_s has two peaks, and the line intensity of the inner set is stronger than that of the outer one. Fig. 3(b) displays their first derivative curves in Fig. 3(a). It can be expected to obtain the asymmetric satellite line of Fig. 1 by drawing a curve as an envelope of the satellite line made of two peaks of Fig. 3(b). Whereas, in the S_m sample, the satellite line has only one peak as shown in Fig. 4 and it is found to be well fitted with a Gaussian line shape.

Our experimental results shown in Fig. 4 suggest that the asymmetry due to the dipole coupling is quite small or very weak based on the fact that the satellite line in the S_m is well fitted with a Gaussian. Two peaks in the satellite line of Fig. 3 may imply that there are possibly two different absorption centers in the S_s sample: one is a normal set of the satellite lines corresponding to those in S_m and the other is a new one (ν_{L^s} and ν_{H^s}). Such a new set might have originated from the strained part of the crystal during the process of the polarization reversal to make the virgin crystal into a single domain state. Meanwhile, as listed in Table 1, the Q_{cc} and η for ^{23}Na in these two samples with the cw-NMR were the same within the experimental uncertainty [7]. NQR results such as line widths and quadrupole parameters of ^{14}N in S_m and S_s are also similar to each other. The appreciable difference between the S_m and S_s samples is only in the line shape of ^{23}Na NMR. These facts on the e.f.g. at ^{23}Na and ^{14}N sites supports the proposal of the existence of two absorption regions in the S_s sample. The asymmetry and broad line width of the satellites in

the S_s sample can be understood by means of the formation of a new region in the crystal due to the strain induced by the polarization reversal.

From our experimental results, one can propose that the asymmetric line shape of the satellite line of ^{23}Na is due to an imperfection caused by the applied electric field rather than the magnetic dipole coupling in the crystal. In general, crystal imperfection may be produced during the crystal growth [8] or by the external stress [9], and due to the external electric field as the present case [10].

4. Conclusion

We observed the symmetric line shape as well as the asymmetric one in the ^{23}Na NMR in the ferroelectric NaNO_2 crystal by employing the cw-NMR and pulse NMR technique. The pulse NMR spectrometer provided a better resolved resonance line shape than the cw-NMR. Each satellite line obtained with S_s has two peaks, while only one peak in the S_m sample. Thus the observable asymmetry might have originated from the existence of two absorption regions in the crystal such as a normal region and a new one abnormally induced in NaNO_2 crystal. Such a new region seems to be due to the internal strain induced during the process of polarization reversal by the external electric field. These results imply that the asymmetry is not the intrinsic property of an NaNO_2 crystal but due to a kind of crystal imperfection caused by strain.

Acknowledgements

This work is supported by the Korea Science and Engineering Foundation through the SRC of Excellence Program (1991-94). Authors are grateful to Professor R. Blinc of University of Ljubljana for his helpful discussion during his visit to Korea in February 1992.

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