Powder Zeeman NQR Study on the Absorption Forms for Nuclear Spin 5/2*

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For nuclei which have a nuclear spin of 5/2 and exhibit a small asymmetry parameter of the electric field gradient (η) at the nuclear site, line shapes of the Powder Zeeman NQR (PZNQR) spectra based on the transition between the energy levels $m_I = \pm 1/2$ and $\pm 3/2$ (the lower frequency line) were studied by means of computer simulations and experiments. (i) When an η value is very small (type 1; $\eta = 0$), the line shape exhibits two shoulders like the style of the American football player. (ii) While an η value is small (type 2; $0 < \eta <$ around 0.01) but not zero, the line shape has two small peaks which are symmetrically located on the shoulders, as in the case of the small η type of spin 3/2. (iii) When an η value is not small (type 3; around $0.01 < \eta$), the line shape has two symmetrical dips in stead of the peaks, which are also similar to the case of not small η type of spin 3/2. As the η value increases from around 0.01, the two dips grow and reach the maximum at the η value of 0.349, and then become smaller and obscure in the range of η larger than 0.349.

The observations of PZNQR spectra were performed for several compounds including the ^{127}I and/or ^{121}Sb nuclei to estimate the η values, and gave the results as follows: very small for ^{127}I (207.683 and 209.133 MHz, at 77 K) in SnI_4; very small for ^{127}I (176.496 and 177.438 MHz, at 77 K) in GaI_3; small for ^{127}I (265.102 MHz, at 77 K) in CH_3I; 0.33 for ^{127}I (247.69 MHz, at 77 K) in C_2H_5I; 0.27 for ^{121}Sb (58.23 MHz, at 290 K) in $SbCl_3$. The estimated η values were compared to those obtained from the frequencies of two NQR lines for spin 5/2. They were in good agreement with each other for the small region of η, though somewhat large disagreements were seen in the cases of not small η values.

Key words: NQR; Nuclear Quadrupole Resonance; Zeeman effect; Powder Zeeman NQR; Spin 5/2.

1. Introduction

The Zeeman effect on NQR for powder specimens (PZNQR) has been studied theoretically and/or experimentally [1–9]. In the case of nuclear spin 3/2, an asymmetry parameter of electric field gradient (η) at the nuclear site cannot be determined only from the NQR frequency, so that the Zeeman NQR method using single crystal (SZNQR) has usually been adopted. When a single crystal is not be available, the PZNQR method is quite advantageous in estimating η values. However, the PZNQR methods based on the detection in a differential form sometimes led to noticeable errors in estimating η values, compared to the method using SZNQR. We have observed the PZNQR spectra in simple integral forms using a bridge circuit and obtained the η values for several nuclei with spin 3/2, which are in good agreement with those evaluated from SZNQR [10–14].

In this paper we report an experimental and simulation study on PZNQR for nuclear spin 5/2. Although η values are approximately obtained only from the frequencies of two NQR lines for nuclear spin 5/2, it is obvious that the PZNQR method is another useful way to estimate small η values.

2. Experimental and Simulation

The PZNQR signals based on the transition between the energy levels $m_I = \pm 1/2$ and $\pm 3/2$ for the nuclear spin of 5/2 were observed using a super-regenerative oscillator and a Helmholtz coil. An oscillating magnetic field (Hr), generated in a sampling coil of the super-regenerative oscillator, and a static magnetic field (Ho), produced by the Helmholtz coil, were kept coaxially in the same direction. The S/N values of the PZNQR signals, which

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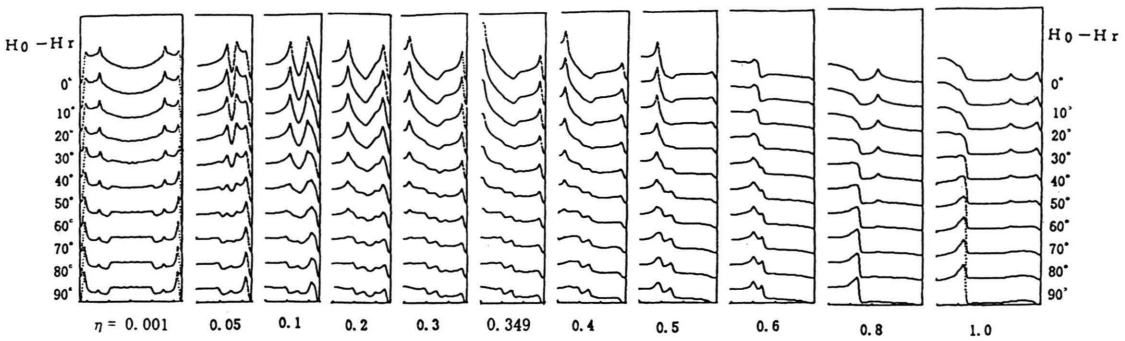


Fig. 1. Simulated PZNQR absorption curves as a function of both η and the angle between Ho and Hr.

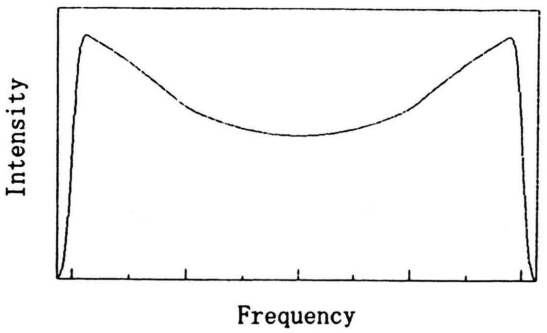


Fig. 2. PZNQR absorption curve simulated for $\eta = 0$ (Hr // Ho).

were detected in integral forms employing a bridge circuit, were improved with a signal averaging device.

In order to compare with the observed signals, the intensity simulations for the PZNQR absorption curves were performed using the equation

$$T_{kl} = \sum_{i,j=x,y,z} Hr_i \; Hr_j \; J_{ij} \; (E_k, \; E_l), \qquad (1)$$

where T_{kl} were the relative transition probabilities, H_{ri} and H_{rj} $(i, j = x, y, z)$ were the radio frequency field components producing the transitions, and J_{ij} (E_k, E_l) were the intensity parameters represented in terms of the matrix elements: $\langle \xi_l | I_i | \xi_k \rangle$, $\langle \xi_l | I_j | \xi_k \rangle$, and so forth, as given by Brooker and Creel [5].

Varying the angle between Hr and Ho from 0 (Hr // Ho) to 90° (Hr ⊥ Ho), PZNQR absorption curves were simulated as a function of η. The results are shown in Figure 1, where only halfs of the curves are exhibited except for the curves of small η (for example $\eta = 0.001$). For the very small η ($\eta = 0$), the simulation curve for Hr // Ho is shown in Figure 2. In Figs. 1 and 2, the abscissa and ordinate of each curve represent a reduced frequency and an absorption intensity, respectively. When the angle between Hr and Ho is 0° or relatively small, the shapes of the curves drastically change as η increases, in the following manner. (i) When an η value is very small (type 1; $\eta = 0$), the line shape exhibits two shoulders like the style of the American football player. (ii) While an η value is small (type 2; $0 < \eta <$ around 0.01) but not zero, the line shape has two small peaks which are symmetrically located on the shoulders, as seen in the case of the small η type for a nuclear spin of 3/2 [13]. (iii) When an η value is not small (type 3; around $0.01 < \eta$), the line shape has two symmetrical dips in stead of the peaks, as also seen in the case of not small η type for a spin of 3/2. With an increase of η, the two dips grow deeply and widely in the range of $0.01 < \eta < 0.349$, attain the maximum size at an η value of 0.349, and then become smaller and obscure at η values larger than 0.349.

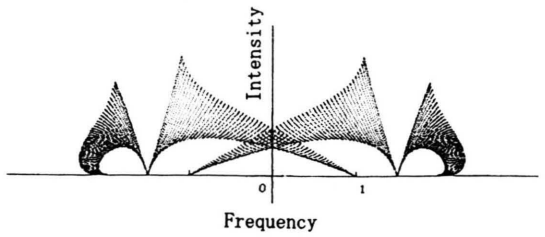
In the region of $0.01 < \eta < 0.349$, η can be estimated according to the equation

$$\left(3 - \frac{10}{27}\eta^2\right)(\overline{AC} + \overline{DF}) = 8\,\eta\,(2\,\overline{BE}), \qquad (2)$$

where $\overline{AC}$, $\overline{DF}$, and $\overline{BE}$ denote the horizontal distances between the points A, B, ..., F on a recorded chart. These symbols are given in Fig. 3, in which the PZNQR absorption curve is simulated for a spin of 5/2 and on the η value of 0.1.

At the η value 0.349, the point C and point D exchange their positions. The ratio $\overline{AB}/\overline{BC}$ becomes larger than 0.89, in the region of $\eta > 0.349$. Moreover, the dips become obscure and undistinguishable around $\eta = 0.4$, so that the η value is estimated according to the following equation, within the limits ($0.349 < \eta <$ around 0.4):

$$\left(3 - \frac{10}{27}\eta^2\right)(\overline{AD} + \overline{CF}) = 8\,\eta\,(2\,\overline{BE}). \qquad (3)$$



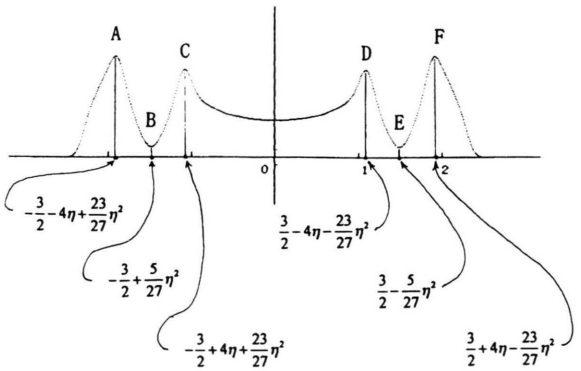


Fig. 3. Simulated distribution of PZNQR absorption intensities (upper) and PZNQR absorption curve from the distribution (lower), for $\eta = 0.1$ (Hr//Ho).

Fig. 4. PZNQR absorption curves for ν_1 and ν_2 due to ^{127}I in SnI_4 (Hr//Ho).

Fig. 5. PZNQR absorption curves for ν_2 and ν_3 due to ^{127}I in GaI_3 (Hr//Ho).

Fig. 6. PZNQR absorption curve for ^{127}I in CH_3I (Hr//Ho).

Fig. 7. PZNQR absorption curve for ^{127}I in C_2H_5I (Hr//Ho).

Fig. 8. PZNQR absorption curve for ^{121}Sb in $SbCl_3$ (Hr//Ho).

3. Result and Discussion

At 77 K, tin tetraiodide (SnI_4) has two NQR absorption lines at 207.683 (ν_1) and 209.133 (ν_2) MHz, which are due to the ^{127}I nuclei. Under the condition of Hr // Ho, the observed PZNQR absorption curves have two shoulders of type 1, as seen in Figure 4. Therefore, their η values are both estimated to be very small (almost 0). These η values are in good agreement with the values 0.00905 for ν_1 and 0.0 for ν_2 determined by Livingston and Zeldes [15], and with 0.0092 for ν_1 and 0.0040 for ν_2 by Robinson et al. [16], respectively.

Gallium triiodide (GaI_3) shows three NQR lines due to the ^{127}I nuclei at 77 K. Two lines (ν_2 and ν_3) are closely located on the higher frequency side, and a single line (ν_1) is separately situated on the lower side. PZNQR absorption curves of type 1 were observed for the two lines (ν_2 and ν_3) of ^{127}I in GaI_3 (Figure 5). Therefore, their η values were estimated to be very small (almost 0). These values are slightly smaller than the values 0.009 (for ν_2; 176.496 MHz) and 0.028 (for ν_3; 177.438 MHz) by Segel and Barnes [17].

At 77 K, methylioide (CH_3I) has a single absorption line at 265.102 MHz, which is due to ^{127}I. The PZNQR absorption curve of type 2 was observed for ^{127}I (Fig. 6) and its η value was estimated to be small ($\eta <$ around 0.01). It is in good agreement with the values 0.0279 of Robinson et al. [16] and 0.025 of Kojima et al. [18].

At 77 K, ethylioide (C_2H_5I) has a single absorption line at 247.69 MHz resulting from ^{127}I. The PZNQR absorption curve (type 3) observed for ^{127}I is shown in Figure 7. An η value of ^{127}I in ethylioide is evaluated to be 0.33 from (2). The η value thus obtained is larger than the η value of 0.016 evaluated by Kojima et al. [18] and that of 0.020 by Petukhov et al. [19].

At 290 K, antimony trichloride ($SbCl_3$) has a single absorption line at 58.23 MHz, resulting from ^{121}Sb. The PZNQR absorption curve (type 3) observed for ^{121}Sb is shown in Fig. 8, and its η value is evaluated to be 0.27 from (2). The η value is larger than the η value of 0.159 by Gotou [20].

Table 1. NQR frequencies, η values, and coupling constants for ^{127}I and ^{121}Sb in several compounds.

Compound	Nucleus	Frequency (MHz)	η	e^2Qqh^{-1} (MHz)	Temperature (K)
SnI_4	^{127}I	207.683 [16]	very small	1384.22	77
		209.133 [16]	very small	1394.22	77
GaI_3	^{127}I	176.496 [17]	very small	1176.64	77
		177.438 [17]	very small	1182.92	77
CH_3I	^{127}I	265.102	small	1767.35	77
C_2H_5I	^{127}I	247.69	0.33	1475.68	77
$SbCl_3$	^{121}Sb	58.23	0.27	359.56	290

Table 1 summarizes the resonance frequencies, the η values, and the coupling constants for the compounds examined in this work. The coupling constants in Table 1 were calculated assuming $\eta = 0$ when it was either small or very small.

In the case of the spin 5/2, the extremely small variation in η is sensitively reflected on the line shape of the PZNQR spectrum. This is not the case for the spin 3/2. Moreover, if there exist inequivalent nuclei, in the PZNQR method for spin 5/2, it is not necessary to assign a pair of resonance lines (lower and higher frequency lines) due to the equivalent nuclei in order to evaluate η values.

Accordingly, the PZNQR method for the nuclear spin 5/2 is very useful especially in estimating small η values.

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