Powder Zeeman Study of the Nuclear Quadrupole Resonance Lower Transition Spectrum for *I* = 5/2; Application to Orthoperiodic Acid

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Dedicated to Prof. Dr. Alarich Weiss on the Occasion of his 60th Birthday

The Zeeman effect of the nuclear quadrupole resonance (NQR) lower transition ($\pm 3/2 \leftrightarrow 1/2$) spectrum for $I = 5/2$ in crystalline powder has been studied and the frequency splittings of the $\pm 3/2 \leftrightarrow \pm 1/2$ transition line have been plotted as a function of the asymmetry parameter η and the external magnetic field H. The experimental Zeeman frequency splittings of the ^{127}I lower transition line in crystalline powder of H_5IO_6 have been compared with the theoretical values in order to evaluate η. The present value of η agrees with the earlier values reported from the two transition frequencies and also from a single crystal Zeeman study on the $\pm 3/2 \leftrightarrow \pm 1/2$ transition line.

Introduction

Pure quadrupole resonance spectroscopy is insufficient to determine both the quadrupole coupling constant (e^2qQ) and the asymmetry parameter (η) of the electric field gradient (EFG) when dealing with a nuclear species with spin 3/2, and therefore an independent experiment must be performed to measure η. Application of a magnetic field results in the observation of four transitions, and a study of these transitions with single crystals [1–4] or powder samples [5–7] will allow for the determination of η. Morino and Toyama [5] have first developed the Zeeman NQR line shape theory for polycrystalline samples with spin 3/2 when the radio frequency field is parallel to the static field H. Subsequently, others [6, 7] have employed the method to measure η in polycrystalline materials.

In the case of spin 5/2 systems, there are two transition frequencies corresponding to $\pm 5/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 1/2$, and therefore one could obtain e^2qQ and η separately from the two resonance frequencies. However, for the knowledge of the directions of the principle axes of the EFG tensor one has to carry out Zeeman studies on single crystals.

Quite strong EFGs prevail at the ^{127}I nuclei in covalently bonded iodides [8] and coupling constants between 1500 MHz and 2000 MHz are found in these systems. On the other hand, low coupling constants of 20 MHz to 40 MHz for ^{127}I have been found for ionic systems like $NaIO_4$ and KIO_4 [9]. This implies that the lower transition line of ^{127}I in ionic systems will be observable around 3 to 6 MHz, and the higher transition line in covalent systems around 450 to 600 MHz. It will be sometimes difficult to detect both the lower and higher transitions of ^{127}I in ionic or covalent systems due to the limitations of the spectrometer. However, even if one of the two transition lines could be detected, a detailed Zeeman study on single crystals on the detected line would enable one to determine η and e^2qQ precisely. The main problem, however, arises when a single crystal specimen can not be obtained, in which case a powder Zeeman study has to be carried out in order to evaluate η.

2. Theory

In this section we present the method of calculating the frequency splittings of the $\pm 3/2 \leftrightarrow \pm 1/2$ transition line for spin 5/2 systems in an external magnetic field.

When electric quadrupole and nuclear Zeeman interactions are present, the Hamiltonian is given by

$$\varkappa = \varkappa_Q + \varkappa_m \,, \tag{1}$$

where

$$\varkappa_Q = \frac{e^2qQ}{4I(2I-1)}\,[3I_z^2 - I^2 + \eta(I_x^2 - I_y^2)] \tag{2}$$

and

$$\varkappa_m = -\hbar\gamma H\,(I_z \cos\theta + I_x \sin\theta \cdot \cos\varphi + I_y \sin\theta \cdot \sin\varphi)\,. \tag{3}$$

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Here I is the nuclear spin, θ and φ give the orientation of the steady field H in the principal axes system. The magnetic field is regarded as weak i. e. $e^2 qQ \gg \hbar\gamma H$. The solution of the resulting secular equation yields, to first order in the field strength, the energy levels as

$$E_{\pm m} = E^0_{\pm m} \pm \hbar\gamma H \left\{ A\cos^2\theta + \frac{\sin^2\theta}{4} \cdot (B + 2C\cos 2\varphi)\right\}^{1/2}, \qquad (4)$$

where $E^0_{\pm m}$ are the degenerate energy values in the absence of the magnetic field. Values A, B and C for $0.1 \leqq \eta \leqq 1.0$ in η intervals of 0.1 for the spins 5/2, 7/2 and 9/2 have been given by Cohen [10]. The transitions between these energy levels correspond to four different frequencies.

$$\nu = \nu_Q(m_1 \leftrightarrow m_2) \pm \frac{\gamma H}{2}\{(m_1) \pm (m_2)\}, \qquad (5)$$

where

$$(m) = \left[A\cos^2\theta + \frac{\sin^2\theta}{4}(B + 2C\cos 2\varphi)\right]^{1/2}, \qquad (6)$$

and $\nu_Q(m_1 \leftrightarrow m_2)$ is the single quadrupole frequency in the absence of the magnetic field. The pair with larger frequency separation $\frac{\gamma H}{2}\{(m_1) + (m_2)\}$ is called β pair and the pair with smaller frequency separation $\frac{\gamma H}{2}\{(m_1) - (m_2)\}$ is called α pair. Both pairs are functions of θ and φ as seen from (4). When a polycrystalline specimen is employed, the crystallites with different orientations with respect to the field will have different resonant frequencies and therefore the frequency separations should be averaged over θ and φ. If we write $f_1(\theta, \varphi)$ for $\{(m_1) + (m_2)\}$ and $f_2(\theta, \varphi)$ for $\{(m_1) - (m_2)\}$, then the frequency separations of α and β pairs for a polycrystalline sample are

$$\Delta\alpha = \pm \frac{\gamma H}{(2\pi)^2} \int_0^{\pi/2} \int_0^{2\pi} f_2(\theta, \varphi) \sin\theta \, d\theta \, d\varphi, \qquad (7)$$

and

$$\Delta\beta = \pm \frac{\gamma H}{(2\pi)^2} \int_0^{\pi/2} \int_0^{2\pi} f_1(\theta, \varphi) \sin\theta \, d\theta \, d\varphi. \qquad (8)$$

The frequency splitting between α and β lines is $(\Delta\beta - \Delta\alpha) = \Delta\nu$. Using the values A, B and C for $I = 5/2$ [10], the $\Delta\nu$ for the lower transition line has been numerically calculated using (7) and (8) for various values of η. The influence of θ being more

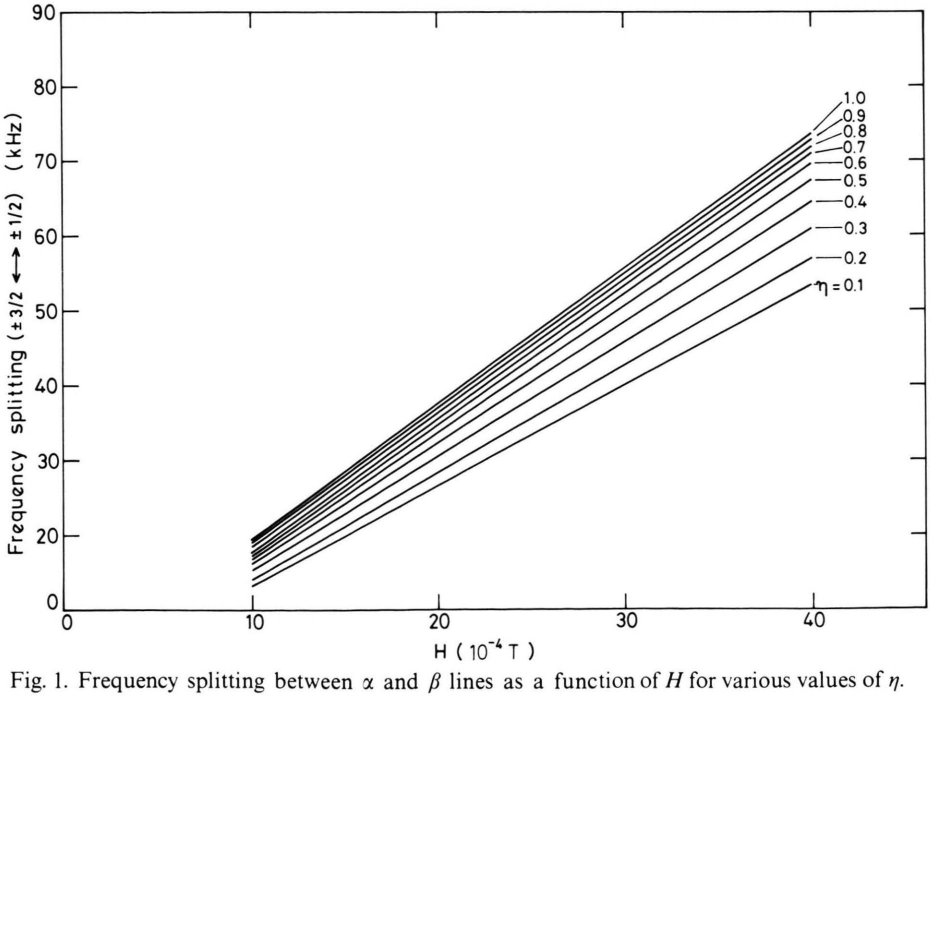

Fig. 1. Frequency splitting between α and β lines as a function of H for various values of η.

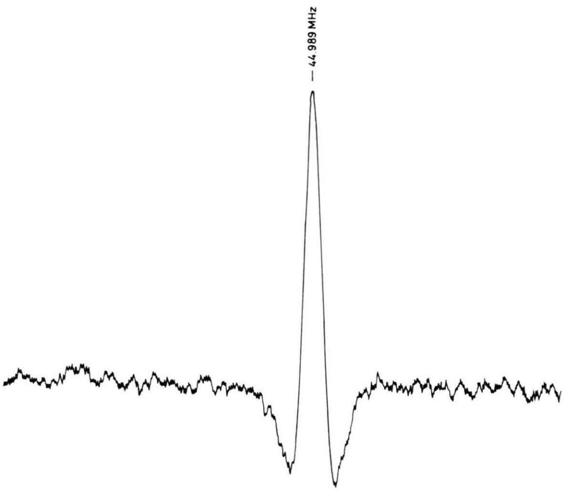

Fig. 2. ^{127}I NQR spectrum of the lower transition line at 294 K. $H = 0$.

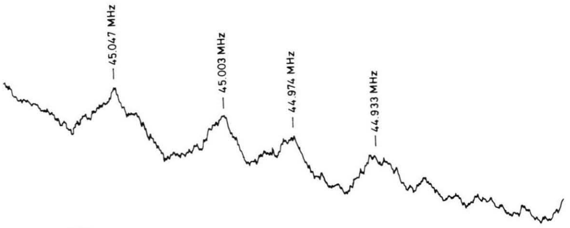

Fig. 3. ^{127}I NQR spectrum of the lower transition line at 294 K. $H = 22.727 \cdot 10^{-4}$ T parallel to the r.f. coil axis.

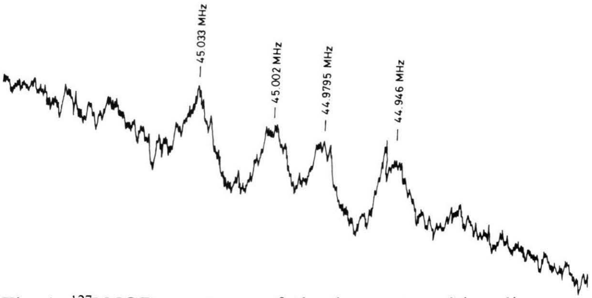

Fig. 4. ^{127}I NQR spectrum of the lower transition line at 294 K. $H = 30.157 \cdot 10^{-4}$ T parallel to the r.f. coil axis.

Table 1. Zeeman NQR data on the $\pm 3/2 \leftrightarrow \pm 1/2$ transition line of ^{127}I in H_5IO_6 at 294 K.

H 10^{-4}T	Experimental splittings [kHz]	η^{a}
22.727	32.0	0.185
30.157	42.5	0.190

[a] $\eta = 0.237$ [12], 0.25 [13] (previous values).

important than that of φ, in evaluating the integrals the increments 3° and 10° have been chosen for θ and φ, respectively. Figure 1 shows the variation of $\Delta\nu$ for the lower transition line with respect to H for various values of η.

3. Experimental Study

The experimental work has been done at Darmstadt using the NQR spectrometer along with the magnetic field assembly described by Nagarajan et al. [11]. Frequency modulation was employed with application of the Zeeman field along the r.f. coil axis. The magnetic field was measured to an accuracy of 0.1% at $300 \cdot 10^{-4}$ T and the frequency to an accuracy of ± 0.005 MHz. H_5IO_6 was obtained from E. Merck, Darmstadt. Figure 2 shows the ^{127}I NQR spectrum of the lower transition line at 44.989 MHz recorded at 294 K. With the application of the Zeeman field along the r.f. coil axis, the spectrum shows splittings as shown in Fig. 3 ($H = 22.727 \cdot 10^{-4}$T) and Fig. 4 ($H = 30.157 \cdot 10^{-4}$T).

4. Results and Discussion

The pure quadrupole resonance frequencies of the two transition of ^{127}I in H_5IO_6 were studied by Rama Rao and Weiss [12] from 77 K to 398 K, and the value of η reported by them at 296 K is 0.237. The Zeeman study on the $\pm 3/2 \leftrightarrow \pm 1/2$ transition line occurring at 44.976 MHz at 296 K obtained in single crystals of H_5IO_6 [13] using the Zero locus method [14] has given an average value 0.25 for η. The present powder Zeeman NQR data on the $\pm 3/2 \leftrightarrow \pm 1/2$ transition line of ^{127}I in H_5IO_6 at 294 K are shown in Table 1, and a value of 0.19 for η is obtained by comparing the experimental and theoretical Zeeman splittings, which agrees with the previous values.

From Fig. 1 it can be seen that at higher fields the accuracy of the determination of η is better. However, the disappearance of the signal at higher fields is handicap in locating the pairs.

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