Strong Quadrupole Interaction in ENDOR Spectroscopy *

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If the nuclear quadrupole interaction $\hat{H}_Q$ of the ligands exceeds the magnetic hyperfine $\hat{H}_{HF}$ and nuclear Zeeman $\hat{H}_{NZ}$ interaction ($\hat{H}_Q \gg \hat{H}_{HF} + \hat{H}_{NZ}$), ENDOR spectra show the same behaviour as Zeeman field perturbed NQR spectra. The angular dependence of the transition frequencies and the transition probabilities of such ENDOR spectra for axial symmetry are calculated and applied to analyze the $^{35,37}Cl$ distant ENDOR spectra of gamma-irradiated $NaClO_3$ single crystals.

1. Introduction

For paramagnetic ions and defects in magnetically diluted solids (single crystals, powders, glasses) electron nuclear double resonance (ENDOR) spectroscopy can be used to determine quadrupole couplings. The hyperfine interaction between the unpaired electron and the nuclear spin of the neighbours is dependent on the distance between them. The ENDOR spectra of nuclei ($I \geqq 1$) in the first coordination sphere of the paramagnetic defect can be analyzed on the assumptions that the electron Zeeman term, $\hat{H}_{EZ}$, is the dominant one in the spin Hamiltonian and that the sum of the hyperfine coupling, $\hat{H}_{HF}$, and the nuclear Zeeman interaction, $\hat{H}_{NZ}$, greatly exceeds the quadrupole coupling, $\hat{H}_Q$. In that case the ENDOR spectrum of a single nucleus coupled with a paramagnetic ion or defect centre with the electron spin $S = 1/2$ consists of $2 \cdot 2 \cdot I$ lines if the hyperfine structure in the EPR spectrum is not resolved [1].

The quadrupole coupling of nuclei in higher coordination spheres can exceed the sum of the hyperfine and nuclear Zeeman interaction. This results in complicated ENDOR spectra with additional lines and angular-dependent transition probabilities [2]. If $\hat{H}_{HF} + \hat{H}_{NZ}$ is very small in comparison with $\hat{H}_Q$, the detected ENDOR spectra will show the same behaviour as in the nuclear quadrupole resonance experiment in a weak magnetic field: the resonance frequencies are almost constant upon rotation whereas their intensities are strongly angular dependent [3].

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2. Calculation of ENDOR Spectra in the Case of Strong Quadrupole Interaction and Axial Symmetry

In the analysis of ENDOR spectra the standard spin Hamiltonian for a single nucleus ($I \geqq 1$) coupled with one unpaired electron is used:

$$\hat{H} = \hat{H}_{EZ} + \hat{H}_{HF} + \hat{H}_Q + \hat{H}_{NZ},$$
$$= \beta \tilde{\boldsymbol{B}}_0 \mathbf{g} \tilde{\hat{\boldsymbol{S}}} + \hat{\boldsymbol{S}} \mathbf{A} \hat{\boldsymbol{I}} + \tilde{\hat{\boldsymbol{I}}} \mathbf{Q} \hat{\boldsymbol{I}} - g_n \beta_N \tilde{\boldsymbol{B}}_0 \hat{\boldsymbol{I}}. \quad (1)$$

The terms of (1) successively denote the electron Zeeman term, the hyperfine term, the nuclear quadrupole and Zeeman term of one neighbouring nucleus. Each interaction is represented by a symmetric second-rank tensor ($\mathbf{g}$, $\mathbf{A}$, $\mathbf{Q}$).

If the quadrupole term $\hat{H}_Q$ in the spin Hamiltonian (1) exceeds the sum of the hyperfine and the nuclear Zeeman term, then the theory of Zeeman splitting of pure quadrupole resonance spectra can be used in the explanation of the line positions in ENDOR spectra.

However, in the case of the ENDOR spectroscopy the magnetic field at the nucleus is equal to the effective magnetic field depending on the electron spin quantum number M_s and the hyperfine coupling tensor [4],

$$\boldsymbol{B}_{eff}(M_s) = \boldsymbol{B}_0 + \boldsymbol{B}_{loc}(M_s) = \boldsymbol{B}_0 - \frac{1}{g \cdot g_n \beta_N} \tilde{\boldsymbol{u}} \cdot \mathbf{g} \cdot \mathbf{A} \cdot M_s. \quad (2)$$

Here $\boldsymbol{u}$ is the unit vector directed along the field $\boldsymbol{B}_0$ of the laboratory magnet and g is the effective g-factor for this direction $\boldsymbol{u}$,

$$g = (\tilde{\boldsymbol{u}} \mathbf{g} \tilde{\mathbf{g}} \boldsymbol{u})^{1/2}. \quad (3)$$

For a paramagnetic system with the electron spin $S = 1/2$ the effective magnetic fields belonging to

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$M_s = 1/2$ and $M_s = -1/2$ have both different magnitudes and orientations if the anisotropic hyperfine coupling is non-zero. Therefore one observes twice as many lines in an ENDOR spectrum as in an NQR one.

It is useful to consider the case of half-integral and integral spins separately.

Half-Integral Spins

In the absence of the hyperfine and the nuclear Zeeman interaction energies there are $(I+1/2)$ doubly degenerate energy levels E_{MI} of the quadrupole operator $\hat{H}_Q$. The effective magnetic field $\boldsymbol{B}_{\text{eff}}(M_s)$ removes this degeneracy, and for the nuclear spin quantum numbers $M_I > 1/2$ there are two energy levels:

$$E_{\pm MI} = (Q_3/2) \cdot [3M_I^2 - I(I+1)] \mp M_I \beta_N g_n B_{\text{eff}}(M_s) \cdot \cos\theta(M_s) \quad (4)$$

with

$$Q_3/2 = e^2 q Q/(4I[2I-1]) \quad (5)$$

(the parameter Q_3 is the largest diagonal element of the quadrupole tensor).

$\theta(M_s)$ is the angle between the effective magnetic field and the symmetry axis of the quadrupole tensor. The perturbation theory leads to zero-order mixing of the $\psi_{\pm 1/2}$ states with the energies given by

$$E_{\pm} = Q_3/2\,[3/4 - I(I+1)] \mp (f/2)\,\beta_N g_n B_{\text{eff}}(M_s) \cos\theta(M_s), \quad (6)$$

where

$$f = [1 + (I+1/2)^2 \tan^2\theta(M_s)]^{1/2}. \quad (7)$$

The energy levels of a paramagnetic centre interacting with one nucleus $(I = 3/2)$ are shown in Figure 1.

The $\Delta M_I = \pm 1$ transitions between the $\pm M_I$ and $\pm (M_I + 1)$ levels lead to the frequencies $\omega^+_{MI}(M_s)$ and $\omega^-_{MI}(M_s)$:

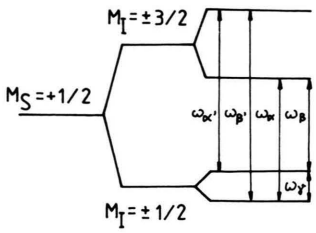
$$\omega^{\pm}_{MI}(M_s) = (2|M_I| + 1)\frac{3Q_3}{\hbar} \mp \omega_{\text{eff}}(M_s) \cdot \cos\theta(M_s). \quad (8)$$

The ENDOR frequencies of the transitions between the mixed states and the states $\psi_{\pm 3/2}$ are

$$\omega_{\alpha,\alpha'}(M_s) = \frac{3Q_3}{\hbar} \mp \frac{3-f}{2}\omega_{\text{eff}}(M_s)\cos\theta(M_s), \quad (9)$$

$$\omega_{\beta,\beta'}(M_s) = \frac{3Q_3}{\hbar} \mp \frac{2+f}{2}\omega_{\text{eff}}(M_s)\cos\theta(M_s), \quad (10)$$

$$\hbar\,\omega_{\text{eff}}(M_s) = g_n \beta_N B_{\text{eff}}(M_s). \quad (11)$$



$$\beta \cdot \tilde{\underline{B}} \cdot \underline{g} \cdot \hat{\underline{S}} + \tilde{\hat{\underline{I}}} \cdot \underline{Q} \cdot \hat{\underline{I}} - g_n \cdot \beta_N \cdot \tilde{\underline{B}} \cdot \hat{\underline{I}} + \tilde{\hat{\underline{S}}} \cdot \underline{A} \cdot \hat{\underline{I}}$$

Fig. 1. Energy level diagram for $S = 1/2$, $I = 3/2$ system showing ENDOR transitions in the presence of strong quadrupole coupling.

These lines are symmetric about the pure quadrupole frequency $\omega_Q = 3Q_3/\hbar$ for each value of the spin quantum number M_s. Further, the transition between the mixed states can also be observed in the ENDOR experiment. The two frequencies belonging to the different M_s values lie in the low frequency part of the spectrum:

$$\omega_\gamma(M_s) = f\,\omega_{\text{eff}}(M_s)\cos\theta(M_s). \quad (12)$$

The transition probabilities of the lines $\alpha, \alpha', \beta, \beta'$ depend on the angles $\theta(M_s)$ between the effective magnetic field and the symmetry axis of the quadrupole tensor. In the case of the anisotropic hypefine interaction the angles $\theta(1/2)$ and $\theta(-1/2)$ are unequal. Therefore ENDOR lines with different intensities were observed in the experiment for the spin quantum numbers $M_s = \pm 1/2$.

In Fig. 2 the angular dependence of both the ENDOR frequencies and the intensities is shown for a nucleus with $I = 3/2$. For $\theta_2(M_s) = 0°$, i.e. the effective magnetic field and the external field are parallel to the symmetry axis, the splitting of the components is

$$\Delta\omega_\alpha(M_s) = 2\,g_n \beta_N B_{\text{eff}}(M_s, \theta = 0). \quad (13)$$

The β, β' components have exactly twice the splitting of the component. But in this case the intensities of the

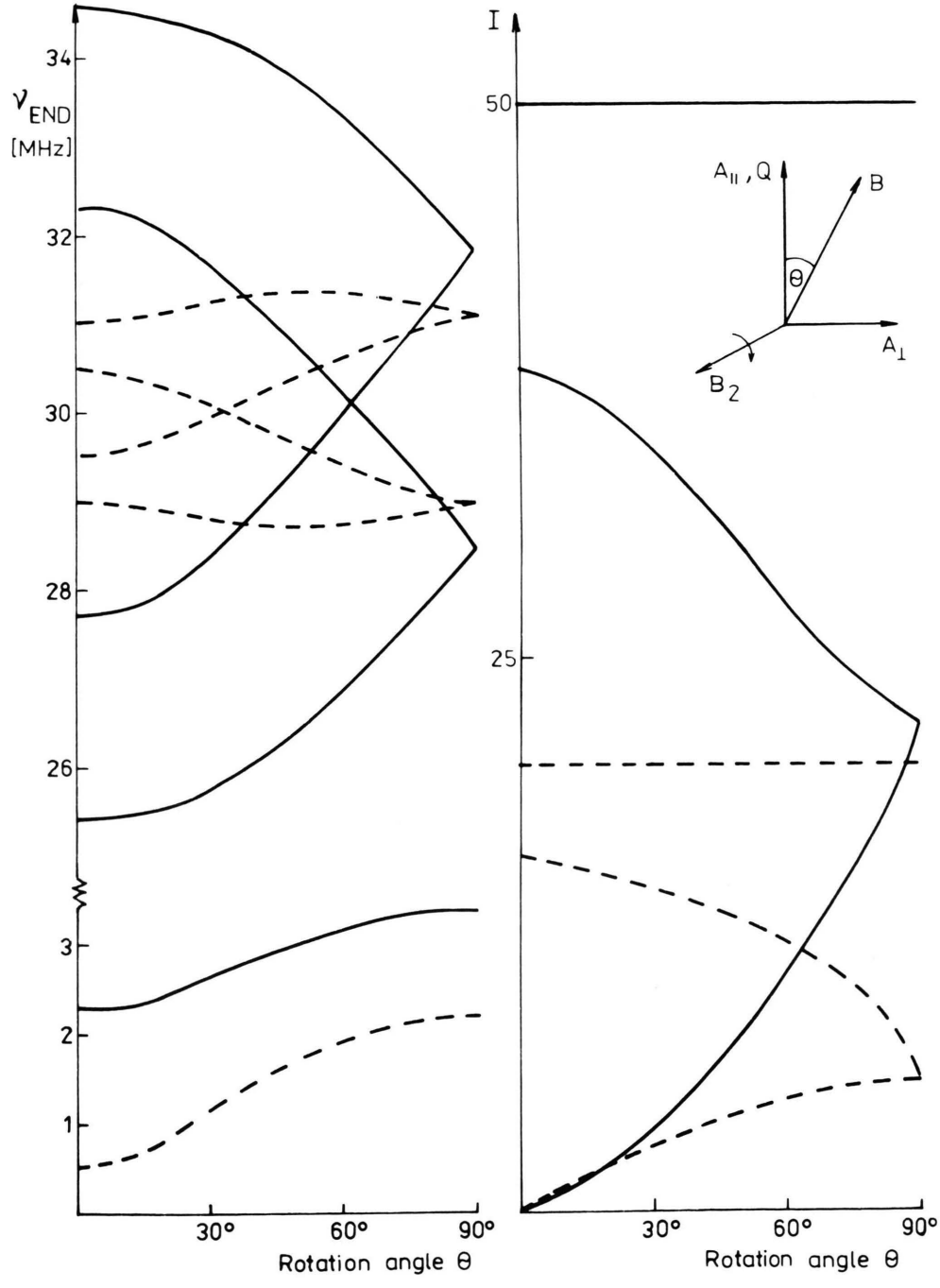


Fig. 2. Angular dependence of ^{35}Cl ENDOR transition frequencies and probabilities in case of strong quadrupole interaction (—— $M_s = +1/2$, – – – $M_s = -1/2$). The same symbols of angular frequencies are used in both M_s's for convenience.

β components vanish because there is no mixing between the pure $\psi_{+1/2}$ and $\psi_{-1/2}$ states, and the β, β' transitions are no longer allowed. For $\theta_2(M_s)=90°$ the splittings are given by

$$\Delta\omega_\alpha(M_s) = \Delta\omega_\beta(M_s) = (I+1/2)\, g_n\, \beta_N\, B_{\text{eff}}(M_s, \theta=\pi/2), \quad (14)$$

and again a single pair of lines is obtained. For

$$\theta_3(M_s) = \tan^{-1}[2\sqrt{2}/(I+1/2)], \quad (15)$$

the splittings are given by

$$\Delta\omega_\alpha(M_s) = 0, \quad (16)$$

$$\Delta\omega_\beta(M_s) = 6 g_n\, \beta_N\, B_{\text{eff}}(M_s, \theta_3)\cos\theta_3(M_s). \quad (17)$$

The lines α, α' coalesce into a single pair at the original pure quadrupole frequency.

Integral Spins

For integral spins, the lowest state is non-degenerate and the ENDOR frequencies are given by the formula

$$\omega_{MI\pm}(M_s) = (3/2h)\cdot Q_3(2|M_I+1|) \pm \omega_{\text{eff}}(M_s)\cos\theta(M_s). \quad (18)$$

If the magnetic field is not weak, i.e. $\omega_{\text{eff}}(M_s) \approx Q_3/2$, a first order treatment canot be used. Therefore the complete spin Hamiltonian must be diagonalized for the evaluation of the ENDOR frequencies and the transition probabilities. Due to the $\hat{I}_x$ and $\hat{I}_y$ terms then there are some mixings between adjacent nuclear states, and transitions are allowed between them. Additional lines in the ENDOR spectra can be detected.

In the case of ^{14}N ENDOR spectra of a paramagnetic centre with $S=1/2$, two sets of three ENDOR transitions belonging to the different electron spin quantum numbers M_s are observed [5, 6]. The transition frequencies within each set fulfil the relation

$$\nu_{13}(M_s) = \nu_{12}(M_s) + \nu_{23}(M_s). \quad (19)$$

In most cases ENDOR lines whose frequencies are smaller than 0.3 MHz cannot be detected in the experiment because their transition probabilities are very weak.

3. Distant ENDOR of ^{35,37}Cl Nuclei in $NaClO_3$:γ

In a distant ENDOR experiment, NMR transitions of nuclei whose distances from the paramagnetic centre are very large are detected. Their electron-nuclear interaction with an unpaired electron spin of a paramagnetic centre is smaller than the nuclear dipole-dipole interaction between the neighbouring nuclei. Since the magnetic hyperfine interaction of the detected nuclei is smaller than the square root of the second moments of their lines, distant ENDOR experiments produce typical wide-line NMR spectra with enhanced sensitivity due to the polarization of the nuclear spins by the unpaired electrons.

Because of the very small hyperfine coupling of the distant nuclei the effective magnetic field B_{eff} is equal to the external one and does not depend on the electron spin quantum number M_s. Therefore distant ENDOR spectra have the same structure as the wide-line NMR or Zeeman field perturbed NQR spectra. They can be analyzed using the formula given in Section 2.

It should be noted that attempts to detect distant ENDOR lines from nuclei with strong quadrupole interaction (^{14}N, ^{35,37}Cl) were unsuccessful [7]. Here we report the first results of our static distant ENDOR investigations of ^{23}Na (small quadrupole interaction) and ^{35,37}Cl nuclei (strong quadrupole interaction) in γ-irradiated $NaClO_3$.

The cubic unit cell of $NaClO_3$ contains four molecules. Each molecule consists of an Na^+ and a ClO_3^- ion, forming a pyramid with the chlorine atom at the apex. Because of the threefold symmetry around each Na and Cl atom the electric field gradient tensors are axially symmetric. Thus there are four quadrupole tensors with the same principal values but with four different directions of the symmetry axes (parallel to the different body diagonals) for each nucleus sort.

To produce paramagnetic centres in $NaClO_3$ with a concentration of about 10^{17} spins/cm^3, pure crystals were irradiated by γ-rays.

The distant ENDOR transitions of chlorine nuclei were detected in the frequency ranges 1.5–3.5 MHz and 25–35 MHz (Figure 3). The quadrupole coupling constants of the ^{23}Na and ^{35,37}Cl nuclei were estimated from the spectra; their values are in agreement with those measured by NQR [8].

The experimental points in the rotation pattern of Fig. 4 can be nicely fitted to the theoretical curves calculated by the exact diagonalization of the nuclear spin Hamiltonian with these parameters in Section 2.

Beside the ^{35,37}Cl ENDOR spectrum, a ^{23}Na distant ENDOR spectrum with weak quadrupole interaction was observed.

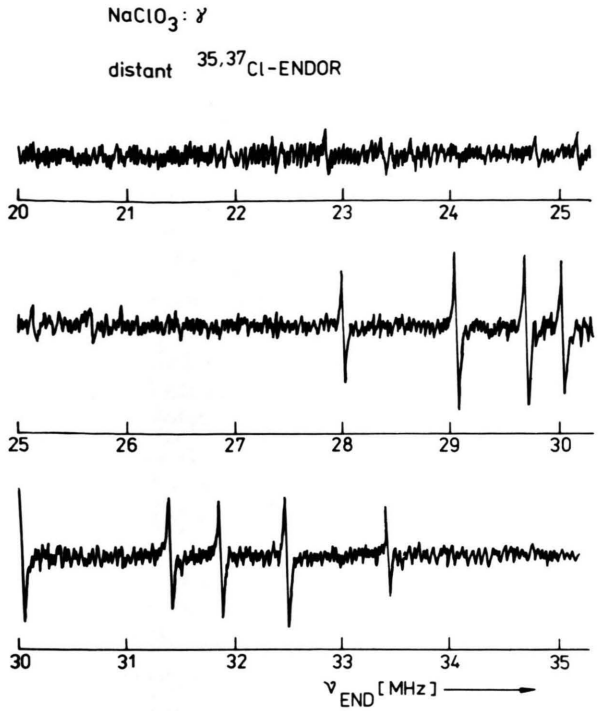


Fig. 3. Distant ENDOR spectrum of $^{35,37}Cl$ nuclei. The rotation axis of the crystal is the [001] axis. The angle between the static magnetic field and the [100] axis is about 35°.

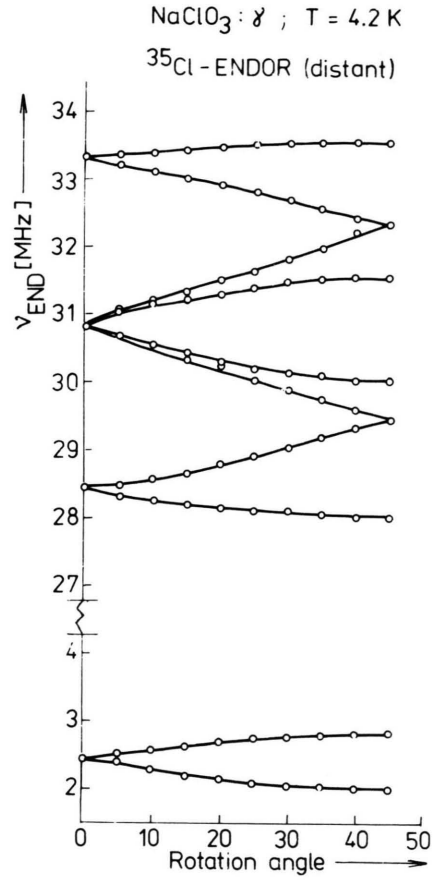


Fig. 4. Angular dependence of the α, α' and β, β' distant ENDOR transitions of ^{35}Cl nuclei in $NaClO_3:\gamma$. The rotation axis is the [001] axis, the rotation angle 0° corresponds to $B \parallel [100]$. Each series of experimental values is connected by a solid line.

As in other spectroscopic technique, for ENDOR a maximum of information is obtained from single crystal studies in which the paramagnetic centres are diamagnetically diluted in a host crystal. Polycrystaline material is of increasing technological interest and hence ENDOR in disordered solids is an area of increasing interest. In the case of paramagnetic systems with axially symmetric interaction tensors the determination of the principal values of the hyperfine and the quadrupole tensor is possible by ENDOR spectra measured in randomly oriented systems.

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