Effect of Lattice Disorder on the Line Shape of NMR Spin Echo Signals

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I. Introduction

As shown by OTSUKA 1, FUKAI 2, KANERT 3 et al. lattice distortions (point defects and dislocations) produce a variation of the quadrupole term in the Hamiltonian of the nuclear spin system. This results in a perturbation of the line shape of the NMR wide line signal. From an analysis of the line shape one obtains the type and the number of defects in the lattice (see for example: EBERT-SEIFERT 4).

The following is an investigation of the influence of lattice distortions on spin echo signals based on a general paper investigating the influence of perturbation in the quadrupolar Hamiltonian on the shape of spin echo signals (MEHRING 5).

II. Influence of Dislocations and Point Defects on the Quadrupolar Term of the Hamiltonian

The quadrupolar term of the Hamiltonian of a nuclear spin system with the spin I and the quadrupole moment Q has the well-known form (see ABRAGAM 6)

\[ H_q = a \hbar \left( I_z^2 - \frac{I(I+1)}{3} \right) \]  

where the quadrupole frequency \( a \) is given by

\[ a = \frac{3eQ}{4I(2I-1)} V_{zz} \]  

Here \( e \) is the electronic charge, \( \hbar = h/2\pi \) Planck's constant and \( V_{zz} \) the component of the electric field gradient (EFG) tensor \( \mathbf{V} \) in the direction of the external magnetic field \( H_0 \) which determines the nuclear Zeeman frequency \( \omega_0 \) of the spin system. According to KANERT 7 and MÜLLER 8 the EFG \( V_{zz} \) at the site of a nucleus with cylindrical coordinates \((r, \theta)\) relative to the dislocation line (given in an isotropic cubic lattice) may be written as

\[ V_{zz} = \frac{b}{2\pi} S_{44} h_i(\theta, h_i) \frac{1}{r} \]  

Here \( b \) is the modulus of the Burgers vector, \( S_{44} \) the corresponding element in the gradient-elastic matrix (SHULMAN 9 et al.), which connects the EFG tensor \( \mathbf{V} \) with the strain tensor \( \mathbf{e} \), and \( f_{ij}(\theta, h_i) \) an orientation function depending on the type of the dislocation (edge- or screw dislocation) and its position relative to the external magnetic field \( H_0 \) which is described by the direction cosines \( h_i \) of the dislocation frame \((u, v, w)\) relative to the direction of the field \( H_0 \). Now the quadrupole frequency \( a \) of a nucleus near a dislocation can be rewritten as

\[ a(r, \theta, h_i) = A f_{ij}(\theta, h_i) \frac{1}{r} \]  

where

\[ A = \frac{3eQ}{4I(2I-1)} h_i S_{44} \]  

According to FUKAI 2 the EFG \( V_{zz} \) at a distance \( r \) of a point defect is given by

\[ V_{zz} = \frac{3}{2\pi} S_{33} C \frac{1}{r} \left( z_i, h_i \right) \]  

Here \( C \) is the "strength" of the point defect which describes the degree of lattice distortion, and \( S_{33} \) is...
the corresponding element in the gradient-elastic matrix. The arguments \( z_i \) and \( h^+ \) \((i = 1, 2, 3)\) in the orientation function \( f_p(z_i, h^+) \) are the direction cosines of the distance vector \( \mathbf{r} \) and the field \( H_0 \) respectively, referred to the cube axes of the lattice. Therefore, the frequency \( a \) for a nucleus in the neighborhood of a point defect is

\[
a(r, z_i, h^+) = B f_p(z_i, h^+) \frac{1}{r^3}
\]

where

\[
B = -\frac{3cQ}{4I(2I-1)} \hbar S_{11} C.
\]

### III. The Quadrupolar Distribution Function
#### for Randomly Located Dislocations
and Point Defects respectively

In the following the distribution function \( p(a) \) of the frequencies \( a \) [see Eq. (3) and Eq. (5)] is derived under the assumption of randomly located dislocations and point defects respectively. In this case for dislocations according to \( \text{Kanert} \) \(7\) the distribution function \( p_d(a) \) has the form

\[
p_d(a) \, da = c A^2 2\pi \int_0^2 \frac{f_d^2 \exp\left\{-\tau c A^2 f_d^2 \right\} \, d\theta \, da}{2 |a|^2} \]

or with the normalized frequency \( s = a/A \sqrt{s}c \) in a normalized representation:

\[
p_d(s) \, ds = \frac{1}{2 \pi |s|^2} \int_0^2 f_d^2 \exp\left\{-f_d^2 |s|^2 \right\} \, d\theta \, ds.
\]

Both functions are normalized in the following way:

\[
\int_{-\infty}^{+\infty} p(a) \, da = \int_{-\infty}^{+\infty} p(s) \, ds = 1.
\]

The integration over the angle \( \theta \) can be done, if the functions \( f(b) \) are known. Fig. 1a and Fig. 1b give a few examples of the normalized function \( p_d(s) \) in the case of a different mixture of edge and screw dislocations distributed in the six possible slip planes. These calculations were done by means of the IBM 360/50 computer. By a similar calculation as given by \( \text{Mehring} \) \(10\), one obtains for the distribution function \( p_p(a) \) in the case of point defects:

\[
p_p(a) \, da = \frac{n B}{6 |a|^2} \int_0^2 \frac{f_p \exp\left\{-\frac{4\pi}{3} n \frac{B}{|a|^2} f_p \right\} \, d\Omega(z_i) \, da}{2}.
\]

where \( n \) is the density of the defects and \( d\Omega(z_i) \) is a solid angle element around the distance vector \( \mathbf{r} \). With the normalized frequency

\[
z = \frac{3a}{4\pi n B}
\]

a normalized form of \( p_p(a) \, da \) can be derived:

\[
p_p(z) \, dz = \frac{1}{8 \pi |z|^2} \int_0^2 f_p \exp\left\{-f_p |z| \right\} \, d\Omega(z_i) \, dz.
\]

Since the function \( f_p \) is known \( (\text{Fukai}^2) \), the integration over the angle \( \Omega(z_i) \) can be done. Eqs. (7) and (9) may be rewritten as

\[
\lim_{z \to \infty} F_d(s) = \lim_{z \to \infty} F_p(z) = \text{const.}
\]

### IV. Dependence of the Spin Echo Signal on the Quadrupol Distribution Function

As calculated by \( \text{Mehring}^5, \text{Butterworth}^11, \text{Bonera}^12 \) et al. the normalized spin echo signal \( E_n(t) \) at time \( t = 2\tau \) after a \( \pi/2 - \tau - \beta \) pulse sequence resulting from the nuclear spins in the lattice coupled by magnetic dipole and electric quadrupole interaction is given in the case of first order quadrupole perturbation by

\[
E_n(t) = D(t) A_M(\beta) + \sum_{m=-\frac{1}{2}}^{\frac{1}{2}} A_Q^{(m)}(\beta) Q^{(m)}(t).
\]

Here \( D(t) \) and \( Q^{(m)}(t) \) are the Fourier-transforms of the corresponding distribution function \( p(b) \) of the dipolar frequencies \( b = \gamma H_{dz} \) \((H_{dz} \) : component of the dipolar local field at a given nucleus in the direction of the external magnetic field \( H_0 \)) and the distribution function \( p(a) \) of the quadrupole frequencies \( a \):

\[
D(t) = \int_{-\infty}^{+\infty} p(b) \cos(bt) \, db \quad \text{with} \quad D(0) = 1,
\]

\[
Q^{(m)}(t) = \int_{-\infty}^{+\infty} p(a) \cos((2m+1)at) \, da \quad \text{with} \quad Q^{(m)}(0) = 1.
\]


\(12\) \text{G. Bonera} and \text{M. Galimberti}, Istituto Lombardo (Rend. Sci.) \textbf{A 100}, 617 [1966].
As calculated in the above mentioned papers $^5, ^{11}, ^{12}$ the amplitudes $A^M(\beta)$ and $A^Q(\beta)$ of the dipolar function $D(t)$ and the quadrupolar function $Q^{(m)}(t)$ strongly depend on the rotation angle $\beta$ of the second rf-pulse. Especially for $\beta = \pi$ the coefficients $A^Q(\beta)$ vanish and the spin echo shape $E_n(t)$ is determined only by the magnetic dipole interaction. The Table 1 shows the values of the amplitudes $A^M$, $A_Q$ for spin $I = 3/2$ which is the spin of the nucleus under investigation in this paper, and the angle $\beta_{opt}$ which leads to the maximum echo height $E_n(0)_{max}$.

<table>
<thead>
<tr>
<th>$\beta_{opt}$</th>
<th>$A^M(\beta_{opt})$</th>
<th>$A_Q(\beta_{opt})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>64°</td>
<td>0.366</td>
<td>0.634</td>
</tr>
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</table>

Table 1.

To obtain the wanted distribution function $p(a)$ from the spin echo signal $E_n(t)$, one has to measure the dipolar echo shape $D(t)$. As the dipolar distri-
The line shape of NMR spin echo signals in solids is a Gaussian function in a good approximation, the echo shape $D(t)$ is Gaussian too. Since the coefficients $A_M$, $A_Q$ are known, Eq. (11) yields the sum \( \sum_{m=-\frac{1}{2}}^{\frac{1}{2}} A_Q^{(m)} Q^{(m)}(t) \), from which the quadrupolar function $p(a)$ can be calculated by an inverse Fourier-transform [see Eq. (12 b)].

V. Experimental Details

The measurements discussed in the next section, are carried out with a coherent nuclear pulse spectrometer with a digital signal averaging computer discussed elsewhere. The resonance frequency was 10 Mc/s, the pulse rise and fall time <0.5 \( \mu \)s, the recovery time of the amplifying unit <20 \( \mu \)s after a rf-pulse of about 1 kW, the time resolution of the averager (Northern NS 544 with microsample) 1 \( \mu \)s and the $H_0$-field in the sample coil about 60 Gauss. Echo signals were measured on undeformed and deformed $\text{RbBr}_7$ single crystals having a size of about (8 x 8 x 20) mm$^3$. The crystals were supplied by Dr. Korth, Kiel, Germany. To determine the quadrupole functions $p(a)$ from the measured Echo $E_n(t)$ the needed calculations and Fourier-transformations were done by means of the IBM 360/50 computer. As an example for the sensitivity of the pulse spectrometer multiple spin echoes of $\text{J}^{127}$ in an undeformed and deformed (\( \varepsilon = 5\% \)) $\text{RbJ}$ single crystal are shown in Fig. 2 as given by the memory of the signal averager. Because of the $\text{J}^{127}$ spin $I=\frac{5}{2}$ there exist echoes at times $t \equiv 2\tau$, discussed by Solomon and Butterworth.

VI. Results

Fig. 3 shows the measured quadrupolar distribution function $p(a)$ (full lines) of an undeformed and plastically deformed (\( \varepsilon = 4\% \)) RbBr single crystal in comparison with the theoretical distribution function (dashed lines) given for dislocations [Eq. (10 a)] and point defects [Eq. (10 b)] respectively in a normalized representation for the crystal orientations $H_0$ parallel to (100). The hatched range in the figures gives the experimental error. As seen by Fig. 3 the quadrupole distribution function of the undeformed crystal is determined by the point defects in the sample, whereas in the deformed crystal the measured quadrupole distribution function drops proportional to $z^{-3}$, i.e. the dislocation model is valid approximately.

According to Kanert the width $\Delta a$ of the distribution function [Eq. (7)] is proportional to the square root of the mean dislocation density $c$:

\[ \Delta a = A \sqrt{c \int f_{ds}(\theta) d\theta + a_e \int f_{de}(\theta) d\theta} \]  

where $a_s$ and $a_e$ are the relative abundances and $f_{ds}$ and $f_{de}$ the orientation functions of screw and edge dislocations respectively. On the other hand the width $\Delta a$ is correlated by the Fourier-transform (12 b) with the half width $\Delta Q$ of the quadrupolar echo part $Q(t)$, which is equal to $Q^{(m)}(t) = Q^{(1/2)}(t)$.

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in the case of spin $I = 3/2$ discussed here. As calculated by MEHRING in many cases of screw and edge dislocations lying in 2, 4, or 6 slip planes of the crystal one obtains the following simple relation:

$$\Delta t_Q = 1.17 \frac{1}{\Delta \alpha}.$$  \hfill (14)

In Fig. 4 the inverse widths $\Delta t_Q^{-1}$ of the Rb87, Br79,81 echo signals of deformed RbBr single crystals are plotted as a function of the shear stress $\tau$.

Fig. 4. Dependence of the inverse half width $\Delta t_Q^{-1}$ of the quadrupolar part of Rb87 Br79,81 spin echoes on shear stress $\tau$ in a deformed RbBr single crystal.

acting during the deformation, for the two different crystal orientations $H_0$ parallel to $\langle 100 \rangle$ and $H_0$ parallel to $\langle 110 \rangle$ respectively. Since $\Delta t_Q^{-1}$ is proportional to the square root of the dislocation density $c$, Fig. 5 confirms the well-known relation (see for example SEEGER):

$$\tau = \alpha G b \sqrt{c}$$  \hfill (15)

($\alpha$: dimensionless parameter, $G$: shear modulus). For calculating the absolute values of the dislocation density $c$ by Eq. (13), one must take into account the numerical values of the several coefficients, given in Eqs. (3), (13), and (14). $[I = 3/2, \ b = 4.85 \text{Å}, \ a_c = a_e = 0.5; \ f = \int f_{\text{det}}(\theta) d\theta + \int f_{\text{det}}(\theta) d\varphi = 0.85; \ Q(\text{Br79}) = 0.33 \text{ barn}, \ Q(\text{Br81}) = 0.28 \text{ barn}; \ S_{44}(\text{Br79}) = S_{44}(\text{Br81}) = 1.3 \cdot 10^{16} \text{ dyn}^2/\text{cm}^2; \ Q(\text{Rb87}) = 0.14 \text{ barn}; \ S_{44}(\text{Rb87}) = 1.77 \cdot 10^{16} \text{ dyn}^2/\text{cm}^2; \text{ see KOTZUR}].$ The result of such a calculation is given in Fig. 5. All measurements lead to a single straight line with a coefficient $\alpha = 2.7$.

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16 D. KOTZUR, diploma work, Münster 1968.