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

M. MEHRING and O. KANERT

Physikalisches Institut der Universität Münster

(Z. Naturforsch. 24 a, 332—336 [1969]; received 23 November 1968)

The spin echo line shapes of Rb87 and Br79,81 have been measured in undeformed and plastically deformed RbBr single crystals. Analysis of the line shape of the measured echoes shows that the quadrupolar part of the echoes is given by point defects in the case of undeformed crystals, whereas in deformed crystals this term is determined by dislocations. A quantitative evaluation of the width of the quadrupolar shape yields the mean dislocation density in the samples as a function of the shear stress acting during the deformation. It was found that the square root of the dislocation density is proportional to the shear stress.

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]

$$\mathcal{H}_Q = a\,\hbar \left(\mathbf{I}_z^2 - \frac{I(I+1)}{3} \right) \qquad (1)$$

where the quadrupole frequency a is given by

$$a = \frac{3\,e\,Q}{4\,I(2\,I-1)\,\hbar} V_{zz}\,. \qquad (1\,\mathrm{a})$$

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 ω_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, ϑ) relative to the dislocation line (given in an isotropic cubic lattice) may be written as

$$V_{zz} = \frac{b}{2\,\pi} S_{44}\, f_{\mathrm{d}}(\vartheta, h_i)\, \frac{1}{r}\,. \qquad (2)$$

Here b is the module 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 $\boldsymbol{\epsilon}$, and $f_{\mathrm{d}}(\vartheta, h_i)$ 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 $(i=1, 2, 3)$ 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

$$a(r, \vartheta, h_i) = A\, f_{\mathrm{d}}(\vartheta, h_i)\, \frac{1}{r} \qquad (3)$$

where $$A = \frac{3\,e\,Q}{4\,I(2\,I-1)\,h}\, b\, S_{44}\,.$$

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

$$V_{zz} = \frac{3\,S_{11}\,C}{2\,r^3} \cdot f_{\mathrm{p}}(\alpha_i, h_i^+)\,. \qquad (4)$$

Here C is the "strength" of the point defect which describes the degree of latice distortion, and S_{11} is

[1] E. OTSUKA, J. Phys. Soc. Jap. **13**, 1155 [1959].
[2] Y. FUKAI, J. Phys. Soc. Jap. **18**, 1580 [1963].
[3] O. KANERT, Z. Phys. **184**, 92 [1965].
[4] T. EBERT u. G. SEIFERT, Kernresonanz im Festkörper, Akad. Verlagsges., Leipzig 1966.
[5] M. MEHRING, to be published in Z. Naturforsch.
[6] A. ABRAGAM, Princ. Nucl. Magn., Oxford 1962.
[7] O. KANERT, Phys. Stat. Sol. **30**, 127 [1968].
[8] H. MÜLLER, diploma work, Münster 1965.
[9] R. G. SHULMAN et al., Phys. Rev. **107**, 953 [1957].

the corresponding element in the gradient-elastic matrix. The arguments α_i and h_i^+ ($i=1,2,3$) in the orientation function $f_p(\alpha_i, h_i^+)$ are the direction cosines of the distance vector $\boldsymbol{r}$ and the field $\boldsymbol{H}_0$ respectively, referred to the cube axes of the lattice. Therefore, the frequency a for a nucleus in the neighborhood of a point defect is

$$a(r, \alpha_i, h_i^+) = B\, f_p(\alpha_i, h_i^+)\, \frac{1}{r^3} \tag{5}$$

where $$B = \frac{3\, e\, Q}{4\, I(2\, I-1)\, \hbar}\, S_{11}\, C\,.$$

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 KANERT [7] the distribution function $p_d(a)$ has the form

$$p_d(a)\, da = \frac{c\, A^2}{2\,|a|^3} \int_0^{2\pi} f_d^2 \exp\left\{-\pi\, c\, \frac{A^2\, f_d^2}{|a|^2}\right\} d\vartheta\, da \tag{6}$$

or with the normalized frequency $s = a/A\sqrt{\pi\, c}$ in a normalized representation:

$$p_d(s)\, ds = \frac{1}{2\,\pi\,|s|^3} \int_0^{2\pi} f_d^2 \exp\{-f_d^2/|s|^2\}\, d\vartheta\, ds\,. \tag{7}$$

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 ϑ can be done, if the functions $f(\vartheta)$ are known. Fig. 1 a and Fig. 1 b 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 MEHRING [10], one obtains for the distribution function $p_p(a)$ in the case of point defects:

$$p_p(a)\, da = \frac{n\, B}{6\,|a|^2} \int_\Omega f_p \exp\left\{-\frac{4\,\pi}{3}\, n\, \frac{B}{|a|}\, f_p\right\} d\Omega(\alpha_i)\, da \tag{8}$$

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

$$z = \frac{3}{4\,\pi}\, \frac{a}{n\, B}$$

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

$$p_p(z)\, dz = \frac{1}{8\,\pi\,|z|^2} \int_\Omega f_p \exp\{-f_p/|z|\}\, d\Omega(\alpha_i)\, dz\,. \tag{9}$$

Since the function f_p is known (FUKAI [2]), the integration over the angle $\Omega(\alpha_i)$ can be done. Eqs. (7) and (9) may be rewritten as

$$p_d(s)\, ds = F_d(s)\, |s|^{-3}\, ds\,, \tag{10 a}$$

$$p_p(z)\, dz = F_p(z)\, |z|^{-2}\, dz\,. \tag{10 b}$$

Since the orientation functions f_p, f_d are limited, the integral functions $F_d(s)$ and $F_p(z)$ obey the following condition:

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

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

As calculated by MEHRING [5], BUTTERWORTH [11], 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

$$E_n(t) = D(t)\, A_M(\beta) + \sum_{m=\frac{1}{2}}^{I-1} A_Q^{(m)}(\beta)\, Q^{(m)}(t)\,. \tag{11}$$

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:

$$D(t) = \int_{-\infty}^{+\infty} p(b) \cos(b\, t)\, db \quad \text{with} \quad D(0) = 1\,, \tag{12 a}$$

$$Q^{(m)}(t) = \int_{-\infty}^{+\infty} p(a) \cos[(2\, m+1)\, a\, t]\, da \quad \text{with} \quad Q^{(m)}(0) = 1. \tag{12 b}$$

[10] M. MEHRING, Thesis, Münster 1968.

[11] J. BUTTERWORTH, Proc. Phys. Soc. London **86**, 297 [1965].

[12] G. BONERA and M. GALIMBERTI, Istituto Lombardo (Rend. Sci.) A **100**, 617 [1966].

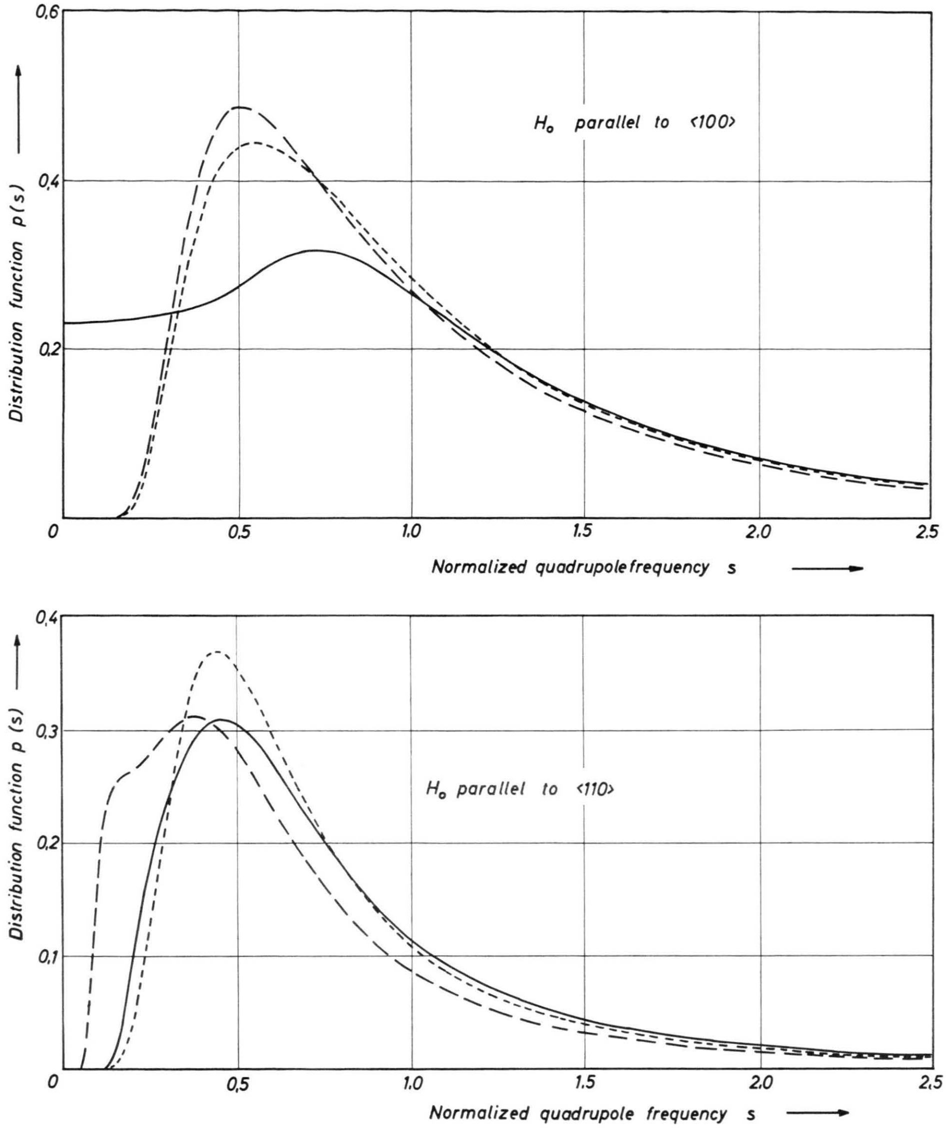

Fig. 1. Computer calculated distribution function $p(s)$ [Eq. (8)] for screw (———), edge (— — —) and 5% screw + 50% edge (- - - - - -) dislocations in a NaCl type lattice distributed in the six possible slip planes. a) Magnetic field H_0 parallel to ⟨100⟩; b) Magnetic field H_0 parallel to ⟨110⟩.

As calculated in the above mentioned papers [5, 11, 12] the amplitudes $A_{\mathrm{M}}(\beta)$ and $A_Q^{(m)}(\beta)$ of the dipolar function $D(t)$ and the quadrupolar function $Q^{(m)}(t)$ strongly depend on the rotation angle β of the second rf-pulse. Especially for $\beta=\pi$ the coefficients $A_Q^{(m)}(\beta)$ 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 β_{opt} which leads to the maximum echo height $E_n(0)_{\max}$.

β_{opt}	$A_{\mathrm{M}}(\beta_{\mathrm{opt}})$	$A_Q(\beta_{\mathrm{opt}})$
64°	0,366	0,634

Table 1.

To obtaine 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 distribution function $p(b)$ 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 $\sum_{m=\frac{1}{2}}^{I-1} A_Q^{(m)} Q^{(m)}(t)$, 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 [13]. The resonance frequency was 10 Mc/s, the pulse rise and fall time $< 0.5\ \mu$s, the recovery time of the amplifying unit 2 μs after a rf-pulse of about 1 kW, the time resolution of the averager (Northern NS 544 with microsampler) 1 μs and the H_1-field in the sample coil about 60 Gauss. Echo signals were measured on undeformed and deformed $Rb^{87}Br^{79,81}$ single crystals having a size of about $(8 \times 8 \times 20)$ 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 J^{127} in an undeformed and deformed $(\varepsilon = 5\%)$ RbJ single crystal are shown in Fig. 2 as given by the memory of the signal averager. Because of the J^{127} spin $I = 5/2$ there exist echoes at times $t \mp 2\tau$, discussed by SOLOMON [14] and BUTTERWORTH [11].

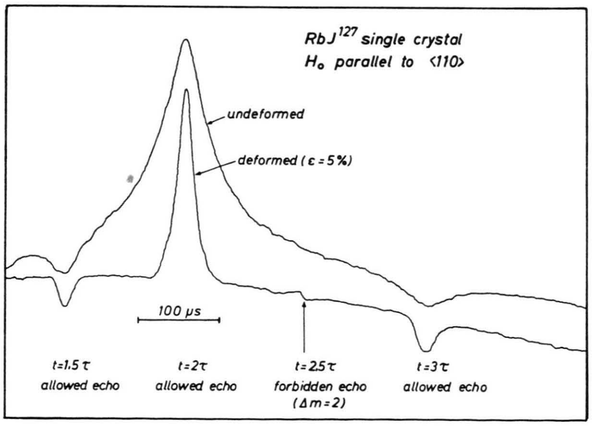

Fig. 2. Recorder trace of multiple spin echoes of J^{127} in an undeformed and deformed $(\varepsilon = 5\%)$ RbJ single crystal.

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.

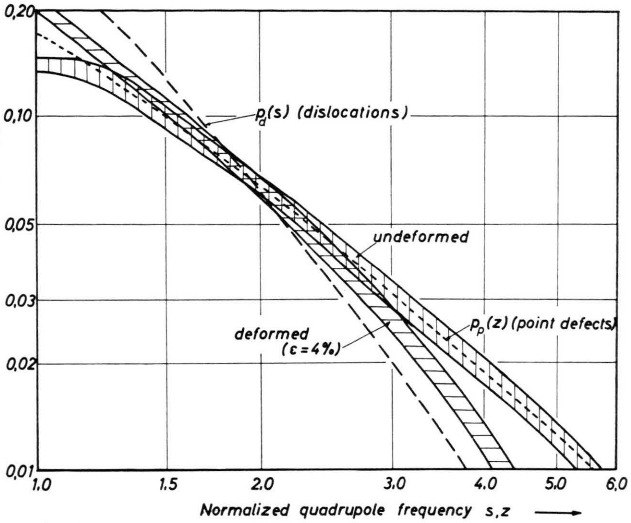

Fig. 3. Logarithmic plot of calculated (dashed lines) distribution functions $p_d(s)$ for dislocations [Eq. (7)] and $p_p(z)$ for point defects [Eq. (9)] respectively versus normalized quadrupole frequency in comparison with experimental distribution functions (full lines) measured on an undeformed and deformed $(\varepsilon = 4\%)$ RbBr79,81 single crystal. The hatched range gives the experimental error.

According to KANERT [7] the width Δa of the distribution function [Eq. (7)] is proportional to the square root of the mean dislocation density c:

$$\Delta a = A \sqrt{c} [a_s \int f_{ds}(\vartheta)\ d\vartheta + a_e \int f_{de}(\vartheta)\ d\vartheta] \quad (13)$$

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 Δa is correlated by the Fourier-transform (12 b) with the half width Δt_Q of the quadrupolar echo part $Q(t)$, which is equal to $Q^{(m)}(t) = Q^{(1/2)}(t)$

[13] M. MEHRING and O. KANERT, Proc. of XIVth Colloque Ampère, Ljubljana 1966.

[14] I. SOLOMON, Phys. Rev. **110**, 61 [1958].

in the case of spin $I=3/2$ discussed here. As calculated by MEHRING[10] 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:

$$\Delta t_Q = 1.17 \frac{1}{\Delta a}. \tag{14}$$

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

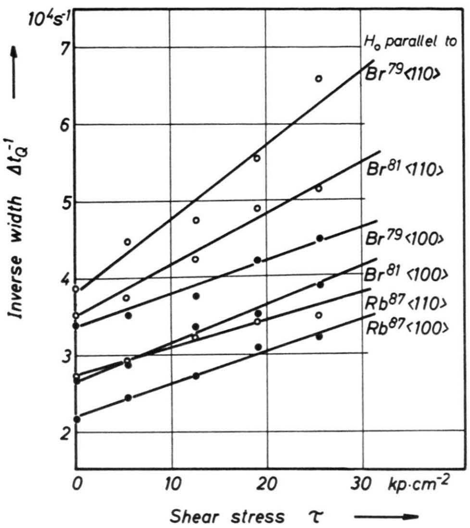

Fig. 4. Dependence of the inverse half width Δt_Q^{-1} of the quadrupolar part of Rb87 Br79,81 spin echoes on shear stress τ in a deformed RbBr single crystal.

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 Δt_Q^{-1} is proportional to the square root of the dislocation density c, Fig. 5 confirms the well-known relation (see for example SEEGER[15]):

$$\tau = \alpha\, G\, b \sqrt{c} \tag{15}$$

(α: 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). [$I=3/2$, $b=4.85$ Å, $a_s=a_e=0.5$; $f=(\int f_{ds}(\vartheta)\,d\vartheta + \int f_{de}(\vartheta)\,d\vartheta) = 0.85$; Q(Br79) $= 0.33$ barn, Q(Br81) $= 0.28$ barn; S_{44}(Br79) $= S_{44}$(Br81) $= 1.3 \cdot 10^{16}$ dyn$^{1/2}$/cm^2; Q(Rb87) $= 0.14$ barn; S_{44}(Rb87) $= 1.77 \cdot 10^{16}$ dyn$^{1/2}$/cm^2; see KOTZUR[16].] The result of such a calculation is given in Fig. 5. All measurements lead to a single straight line with a coefficient $\alpha = 2.7$.

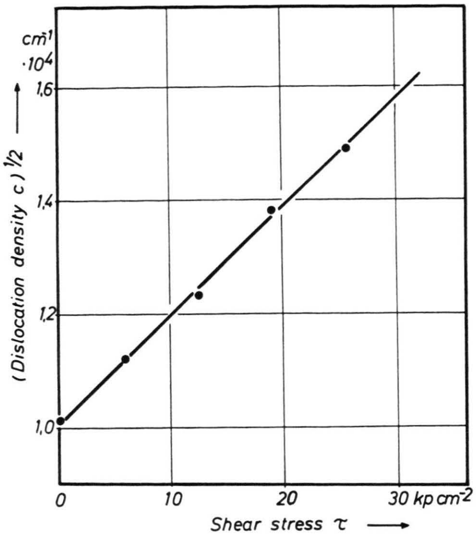

Fig. 5. Square root of dislocation density c in RbBr calculated by Eqs. (13), (14) from the measured values shown in Fig. 4 as a function of shear stress τ.

Acknowledgements

The authors like to express their thanks to Prof. Dr. E. KAPPLER for valuable suggestions in this investigations. The "Volkswagen-Stiftung" has given a significant financial support for the construction of the spin echo spectrometer.

[15] A. SEEGER, Moderne Probleme der Metallphysik, Springer-Verlag, Berlin 1965.

[16] D. KOTZUR, diploma work, Münster 1968.