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Nuclear magnetic resonance of ^{93}Nb in $LiNbO_3$: effect of structural distortions on lineshapes

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Abstract

The expression for the angular dependence of the first moment of the nuclear magnetic resonance central transition ($\pm 1/2 \leftrightarrow \mp 1/2$) lineshapes of a quadrupolar nuclei with half integer spins in a disordered solid is derived and used for investigation of the structural distortions in $LiNbO_3$.

Keywords: ^{93}Nb nuclear magnetic resonance; Lineshape; Quadrupolar nuclei; Structural distortions; $LiNbO_3$

1. Introduction

The structural distortions of $LiNbO_3$ arising from the non-stoichiometry as well as the paramagnetic defects play a leading role in the variability of the physical properties of this crystal (ferroelectric, piezoelectric, pyroelectric) [1]. The effect of the structural distortions of $LiNbO_3$ on the lineshape of ^{93}Nb nuclear magnetic resonance (NMR) signals is observed in the asymmetry of the lineshape of the central transition ($\pm 1/2 \leftrightarrow \mp 1/2$) [2–6]. For the interpretation of the observed lineshape asymmetry in this and other crystals [3,7], a familiar approach as analysis of image reconstruction from projections was proposed [8]. In spite of the limitations of this approach [7], some qualitative information about the probability distribution functions of the components of the electric field gradient (EFG) tensor may be obtained [3,7]. In Refs. [9–11] different methods have been developed for determining the orientational distribution functions of partially ordered ensembles of spin systems from the analysis of magnetic resonance lineshapes. These methods may also be applied to the analysis of the NMR lineshape asymmetry of quadrupolar nuclei, but only in those cases where other anisotropic interactions of quadrupolar nuclei (dipolar, chemical shift) are small and the principal components of the EFG tensor are not altered.

The purpose of this paper is to describe a simple method for the investigation of structural distortions in solids by NMR of quadrupolar nuclei. The method is based on the analysis of the angular dependence of the first moment of the NMR central-transition lineshapes of quadrupolar nuclei with half-integer spins.

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2. First moment of central-transition lineshape

As has been shown in earlier works [3,12], the second-order quadrupolar shift of the $\pm 1/2 \leftrightarrow \mp 1/2$ transition of nuclei with half-integer spins [13] may be written as

$$\Delta\nu^{(2)}_{1/2} = \nu - \nu_0 = W \sum_{k,l=1}^{5} Q_{kl} b_{lk} \tag{1}$$

where $W = -3(eQ)^2/[h\nu_0 2I^2(2I-1)^2]$; $\nu_0 = \gamma B_0/2\pi$ [13].

The functions b_{kl} are defined by the spherical angles ϑ and φ of the magnetic field direction $\mathbf{B}_0$ in a crystal-fixed coordinate frame. These functions are given in the Appendix.

The functions Q_{kl} are defined by the components of the EFG tensor and have the form

$$Q_{kl} = q_k q_l \tag{2}$$

where

$$q_1 = V_{ZZ}; \quad q_2 = (V_{XX} - V_{YY}); \quad q_3 = V_{XZ}; \quad q_4 = V_{XY}; \quad q_5 = V_{YZ} \tag{3}$$

and V_{ij} $(i,j = X,Y,Z)$ are the components of the electric field gradient tensor [13] in a crystal-fixed coordinate frame.

The presence of structural distortions in a crystal leads to alteration of the EFG tensor in both magnitude and orientation. These alterations of the EFG tensor components lead to the inhomogeneous broadening of the central transition lineshape and this NMR line broadening may be described by the method of moments [13]. In particular, the first moment can then be written as

$$M_{1Q} = \overline{\Delta\nu^{(2)}_{1/2}} = W \sum_{k,l=1}^{5} \overline{Q}_{kl} b_{lk} \tag{4}$$

where $\overline{Q}_{kl} = \int P(\mathbf{q}) Q_{kl}(\mathbf{q}) d\mathbf{q}$ and $P(\mathbf{q})$ is the joint probability density distortion in the five-dimensional parameter space that describes the spectral broadening.

From the symmetry of the $LiNbO_3$ crystal it follows that when the crystallographic symmetry axis c is parallel to the Z axis of a crystal-fixed coordinate frame, the expression for M_{1Q} is simplified to

$$M_{1Q} = A_1 + A_2 \cos 2\vartheta + A_3 \cos 4\vartheta \tag{5}$$

where

$$A_1 = W\left(\frac{45}{16}\overline{Q}_{11} + \frac{5}{32}\overline{Q}_{22} + \frac{11}{2}\overline{Q}_{33} + \frac{5}{8}\overline{Q}_{44} + \frac{11}{2}\overline{Q}_{55}\right)$$

$$A_2 = W\left(\frac{9}{4}\overline{Q}_{11} - \frac{15}{8}\overline{Q}_{22} + 6\overline{Q}_{33} - \frac{15}{2}\overline{Q}_{44} + 6\overline{Q}_{55}\right)$$

$$A_3 = W\left(-\frac{81}{16}\overline{Q}_{11} - \frac{9}{32}\overline{Q}_{22} + \frac{9}{2}\overline{Q}_{33} - \frac{9}{8}\overline{Q}_{44} + \frac{9}{2}\overline{Q}_{55}\right) \tag{6}$$

In the perfect crystal $LiNbO_3$ the niobium lattice position has a three-fold symmetry and therefore, the major EFG principal axis is parallel to the crystallographic c axis and the asymmetry parameter of the EFG tensor is zero. Reexpressing the EFG components V_{ij}, referring to the crystallographic axes, in terms of the EFG tensor principal parameters (asymmetry parameter η and coupling constant eq_0 [13]) and the Euler angles (α, β, γ) that take the crystal frame into the principal axes frame, and assuming that the asymmetry parameter η and the deviation of the major axis from the crystallographic c axis (angle β) are small, we obtained

$$A_1 = -\frac{15}{4}\overline{(\nu_Q^2/\nu_0)\left\{1 + \frac{7}{5}\beta^2 + \frac{5}{144}\eta^2\left[1 - \frac{3}{5}\cos[4(\alpha+\gamma)]\right]\right\}}$$

$$A_2 = -3\overline{(\nu_Q^2/\nu_0)\left\{1 + 3\beta^2 - \frac{25}{48}\eta^2\left[1 - \frac{3}{5}\cos[4(\alpha+\gamma)]\right]\right\}}$$

$$A_3 = -\frac{27}{4}\overline{(\nu_Q^2/\nu_0)\left\{-1 + 5\beta^2 - \frac{5}{144}\eta^2\left[1 - \frac{3}{5}\cos[4(\alpha+\gamma)]\right]\right\}}$$

where

$$\nu_Q = \frac{3e^2 q_0 Q}{2hI(2I-1)}$$

In the crystal $LiNbO_3$ there are other anisotropic interactions of quadrupolar nuclei ^{93}Nb –dipolar and electron–nuclear interactions [13,14]. These interactions give also rise to the NMR line broadening. The contribution to the first moment of

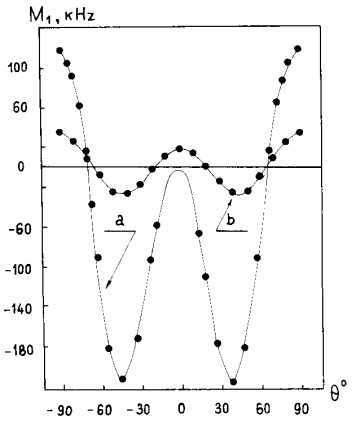

Fig. 1. The angular dependencies of M_1 in the undoped crystal $LiNbO_3$. (a) $B_0 = 1$ T; (b) $B_0 = 5$ T. ν_0 is the resonance frequency of ^{93}Nb in NbF_5 dissolved in HF.

the NMR lineshape arisen by the dipole–dipole interactions between nuclei is zero [13]. The electron–nuclear interactions (chemical shift) lead to the following contribution to M_1 [14]:

$$M_{1e-n} = \nu_0\left[\sigma_\perp - (\sigma_\parallel - \sigma_\perp)\cos^2\vartheta\right] \tag{7}$$

where $\sigma_\parallel$ and $\sigma_\perp$ are the principal components of the chemical shift tensor [14].

The total moment M_1 of the central transition lineshape is

$$M_1 = M_{1Q} + M_{1e-n} \tag{8}$$

We used Eqs. 5–8 for the analysis of the experimental results of ^{93}Nb NMR in the undoped crystal $LiNbO_3$ (Fig. 1)[1].

Assuming that the five independent EFG components q_k ($k = 1, 2, \ldots, 5$) are also statistically independent and using the least-squares method we obtained

$$\sigma_\parallel = (140 \pm 15) \times 10^{-6},$$

$$\sigma_\perp = (-35 \pm 15) \times 10^{-6},$$

$$\left(\overline{\eta^2}\right)^{1/2} \approx 0,$$

$$\left(\overline{\nu_Q^2}\right)^{1/2} = (0.42 \pm 0.003)\ \text{MHz},$$

$$\left(\overline{\beta^2}\right)^{1/2} = 3°46' \pm 15'$$

The investigations of the angular dependencies of M_1 in doped crystals of $LiNbO_3$ containing various amounts of Fe ions demonstrate that the parameter $\overline{\nu_Q^2}$ is almost unaffected by paramagnetic ion effects. In contrast, the parameter $\overline{\beta^2}$ is sensitive to the paramagnetic ions content (Fig. 2).

It is interesting to note that, as follows from Fig. 1 and Fig. 2, the deviation of the major axis of the EFG tensor from the c axis is also not zero in undoped (perfect) crystals of $LiNbO_3$. Perhaps this disordering in the direction of the major axis of the EFG tensor is a result of a temperature disordering of the electric dipolar moments of the NbO_6 distorted octahedrals.

3. Conclusions

We have shown that the analysis of the lineshape asymmetry of NMR central transitions of quadrupolar nuclei with half-integer spins by the method of moments gives important information about the structural distortions of solids. In particular, it was shown that in $LiNbO_3$ there are deviations in the direction of the major axis of the

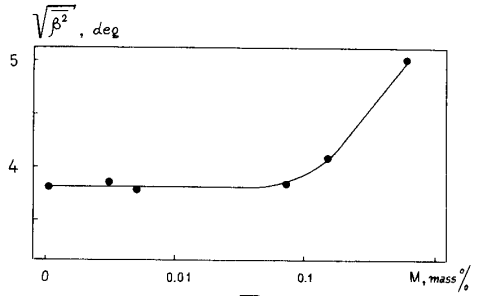

Fig. 2. The angle of deviation $(\overline{\beta^2})^{1/2}$ of the major axis of the EFG tensor from the crystallographic c axis in the doped $LiNbO_3$ crystal as a function of the content of Fe ions.

[1] The experimental spectra of ^{93}Nb were obtained on a home-built wide-line NMR spectrometers at $B_0 = 1.0$ T and $B_0 = 5.0$ T at room temperature. The small r.f. field was used to avoid saturation of the NMR spectra.

EFG tensor from the c axis and this disordering is sensitive to the content of paramagnetic ions.

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Appendix

The functions b_{kl} in Eq. 1 are [2]:

$$b_{11} = \frac{45}{32} + \frac{9}{8}\cos 2\vartheta - \frac{81}{32}\cos 4\vartheta$$

$$b_{12} = \left(-\frac{39}{32} + \frac{3}{8}\cos 2\vartheta + \frac{27}{32}\cos 4\vartheta\right)\cos 2\varphi$$

$$b_{13} = \left(-\frac{27}{8}\sin 4\vartheta + \frac{3}{4}\sin 2\vartheta\right)\cos\varphi$$

$$b_{14} = \left(-\frac{39}{16} + \frac{3}{4}\cos 2\vartheta + \frac{27}{16}\cos 4\vartheta\right)\sin 2\varphi$$

$$b_{15} = \left(\frac{3}{4}\sin 2\vartheta - \frac{27}{8}\sin 4\vartheta\right)\sin\varphi$$

$$b_{22} = \frac{5}{64} - \frac{15}{16}\cos 2\vartheta - \frac{9}{64}\cos 4\vartheta + \left(\frac{9}{16}\cos 2\vartheta - \frac{9}{64}\cos 4\vartheta - \frac{27}{64}\right)\cos 4\varphi$$

$$b_{23} = \left(\frac{9}{16}\sin 4\vartheta + \frac{15}{8}\sin 2\vartheta\right)\cos\varphi + \left(\frac{9}{16}\sin 4\vartheta - \frac{9}{8}\sin 2\vartheta\right)\cos 3\varphi$$

$$b_{24} = \left(\frac{9}{8}\cos 2\vartheta - \frac{9}{32}\cos 4\vartheta - \frac{27}{32}\right)\sin 4\varphi$$

$$b_{25} = \left(-\frac{15}{8}\sin 2\vartheta - \frac{9}{16}\sin 4\vartheta\right)\sin\varphi + \left(-\frac{9}{8}\sin 2\vartheta + \frac{9}{16}\sin 4\vartheta\right)\sin 3\varphi$$

$$b_{33} = \frac{11}{4} + 3\cos 2\vartheta + \frac{9}{4}\cos 4\vartheta + \left(\frac{3}{4} - 3\cos 2\vartheta + \frac{9}{4}\cos 4\vartheta\right)\cos 2\varphi$$

$$b_{34} = \left(\frac{15}{4}\sin 2\vartheta + \frac{9}{8}\sin 4\vartheta\right)\sin\varphi + \left(-\frac{9}{4}\sin 2\vartheta + \frac{9}{8}\sin 4\vartheta\right)\sin 3\varphi$$

$$b_{35} = \left(\frac{9}{4}\cos 4\vartheta - 3\cos 2\vartheta + \frac{3}{4}\right)\sin 2\varphi$$

$$b_{44} = \left(\frac{5}{16} - \frac{15}{4}\cos 2\vartheta - \frac{9}{16}\cos 4\vartheta\right) + \left(\frac{27}{16} - \frac{9}{4}\cos 2\vartheta + \frac{9}{16}\cos 4\vartheta\right)\cos 4\varphi$$

$$b_{45} = \left(\frac{15}{4}\sin 2\vartheta + \frac{9}{8}\sin 4\vartheta\right)\cos\varphi + \left(\frac{9}{4}\sin 2\vartheta - \frac{9}{8}\sin 4\vartheta\right)\cos 3\varphi$$

$$b_{55} = \left(\frac{11}{4} + 3\cos 2\vartheta + \frac{9}{4}\cos 4\vartheta\right) + \left(-\frac{3}{4} + 3\cos 2\vartheta - \frac{9}{4}\cos 4\vartheta\right)\cos 2\varphi$$

[2] The functions b_{kl} in Appendix of Ref. [3] are obtained from the functions $2b_{kl}$ in this Appendix by replacing φ with $(180° - \gamma_0)$ and ϑ with β_0.

References

[1] A. Raüber in E. Kaldis (Ed.), Current Topics in Materials Science, Vol. 1, North-Holland, Amsterdam, 1978.
[2] G.E. Peterson and A. Carnavale, J. Chem. Phys., 56 (1972) 4848.
[3] D.C. Douglas, G.E. Peterson and V.J. McBrierty, Phys. Rev. B, 40 (1989) 10694.
[4] A.V. Yatsenko, V.N. Shcherbakov and S.P. Gabuda, Bull. Magn. Reson., 2 (1980) 197.
[5] A.V. Yatsenko and N.A. Sergeev, Sov. Phys. Solid State, 27 (1985) 1239.
[6] A.V. Yatsenko and N.A. Sergeev, Sov. Phys. Solid State, 28 (1986) 2567.
[7] D.C. Douglass, L.F. Schneemeyer and S.E. Spengler, Phys. Rev. B, 36 (1987) 1831.
[8] P.T. Callaghan, Principles of Nuclear Magnetic Resonance Microscopy, Clarendon Press, Oxford, 1991.
[9] V.J. McBrierty, J. Chem. Phys., 61 (1974) 872.

[10] R. Hentschel, J. Schlitter, H. Sillescu and H.S. Spiess, J. Chem. Phys., 68 (1978) 56.
[11] R. Friesner, J.A. Naira and K. Sauer, J. Chem. Phys., 71 (1979) 358.
[12] A.V. Yatsenko and N.A. Sergeev, Quadrupolar Effects and Angular Dependence of Line Shape NMR Moments, Ukr. NII NTI -62-Yk-85 Dep., Simferopol State University, 1984, (in Russian).
[13] A. Abragam, Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.
[14] R.R. Ernst, G. Bodenhausen and A. Wokaun, Principles of Nuclear Magnetic Resonance in One and Two Dimensions, Clarendon Press, Oxford, 1987.