

Exploring Crystal Symmetry for the Determination of EFG-Tensors from NMR-NQR Rotation Patterns*

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In contrast to the properties of the symmetry of the nucleus under consideration the information contained in the crystal symmetry is rarely used for the determination of EFG-tensors from NMR-NQR rotation patterns. This information is, however, extremely useful since already the presence of a single symmetry different from $\bar{1}$ provides all necessary information in a single rotation pattern. This is the case for all Bravais lattices except the triclinic one. It is shown how the crystal symmetry can be explored even in the case of an arbitrary direction of the rotation axis with respect to the crystal axes.

1. Introduction

The information contained in the electrical field gradient (EFG) tensor at the site of a given nucleus can be separated in two parts: properties which can be obtained from pure NQR, such as the magnitude, *eq*, and the asymmetry parameter, η , and properties which can be observed only when the degeneracy of the energy levels is removed by an external magnetic field, B_0 .

The magnitude *eq* yields information on the nature of chemical bonds and on the number of chemically inequivalent atoms of a certain kind in the system under consideration. From the asymmetry parameter, η , very restricted information about the site symmetry can be obtained, depending on whether η differs from zero or not. Unfortunately many good quadrupole nuclei have $I = \frac{3}{2}$ and thus a single NQR transition frequency which is proportional to $eq(1 + \eta^2/3)^{1/2}$, so that η and *eq* cannot be separated.

With the use of an external magnetic field, B_0 , one can obtain the five irreducible elements of the EFG-tensor, i.e. *eq*, η and the orientation of its principal axes in space. The orientation of the EFG *z*-axis is of particular interest, since it coincides very often with the direction of a strong covalent bond. The magnetic field, however, not only splits the degenerate energy levels but also breaks the sym-

metry of the system, i.e. chemically equivalent atoms become physically inequivalent and give rise to different rotation patterns. These rotation patterns are related by the crystal symmetry but this is a hidden property which can be directly observed only for special rotation axes. In this contribution it is shown, how the crystal symmetry can be used to determine completely the EFG tensors of chemically equivalent atoms by using the information contained in a single rotation pattern.

2. The Symmetry of the NMR-NQR-Hamiltonian

In the coordinate system of the principle EFG-tensor axes the Hamilton operator \mathcal{H} is given by

$$\mathcal{H} = \mathcal{H}_Q + \mathcal{H}_Z = \frac{e^2 q Q}{4I(2I-1)} [3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)] - \gamma \hbar (I_x B_x + I_y B_y + I_z B_z), \quad (1)$$

where the B_i are the projections of B_0 on the principal EFG-tensor axes *x*, *y*, *z* (see e.g. [1]). One can show that the secular equation of this Hamiltonian contains only terms with even functions of B_i (e.g. $B_i^2, B_i^4, B_i^2 B_j^2$) i.e. the eigenvalues do not depend on the sign of the projections B_i . From this it is evident that the NMR-NQR spectra are invariant under the operation $\bar{1}$ (inversion) on the EFG tensor, i.e. NMR-NQR spectroscopy cannot distinguish between two EFG-tensors related by a centre of inversion. Another consequence is that the Hamiltonians of two EFG-tensors related by a mirror plane, m_i , have the same eigenvalues, if the

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magnetic field, \mathbf{B}_0 , is parallel to the mirror plane, but different eigenvalues for any other direction of \mathbf{B}_0 . The same is true for a plane perpendicular to a two fold axis, 2_i , since $2_i = (\bar{1}) (m_i)$.

3. Experimental Features

The usual set-up to obtain a rotation pattern is a mechanism which allows either the rotation of the crystal around an axis perpendicular to the external magnetic field, \mathbf{B}_0 , or the rotation of \mathbf{B}_0 around an axis perpendicular to \mathbf{B}_0 . The transition frequencies are then plotted versus the rotation angle in the laboratory frame. For an observer in the coordinate system (E) of the principal EFG-tensor axes the magnetic field, \mathbf{B}_0 , moves within a plane for both cases. The essential point is that the resulting rotation pattern depends only on the orientation of this plane with respect to the E -system and on the sign of the rotation [2]. A rotation pattern can, therefore, provide information only concerning the orientation of the EFG-tensor with respect to the magnetic coordinate system (M) but not with respect to the crystal coordinate system (K) [3, 4]. The latter is, however, the information one would like to have. One needs, thus information about the relative orientation of the M - and K -systems, i.e. one must know the rotation axis in terms of crystal coordinates.

4. The Three Coordinate Systems and Their Relationships

For the sake of simplicity the E , M , and K systems have to be orthonormalized, i.e. the transformations (U) leading from one system to another are composed of simple rotation matrices of the Euclidian space. Hereafter we will use the following transformation matrices U :

- (ME) \rightarrow M -system in E -coordinates,
- (MK) \rightarrow M -system in K -coordinates,
- (EK) \rightarrow E -system in K -coordinates.

These matrices act as passive operators, i.e. they transform a vector in the system of the first letter into the system of the second letter. Thus the columns are the basis vectors of the first system in coordinates of the second. The corresponding active operators are the inverse operators U^{-1} , which in

our case correspond to the transposed matrices $U^{-1} = U^T$.

4.1 The E -system

The coordinate system of the principle EFG-tensor axes is defined by using the usual convention

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|. \quad (2)$$

4.2 The K -system

The coordinate system of the crystal is essentially given by the basic translations defining the unit cell. One can, however, always find a suitable orthogonal system. In monoclinic systems for example one can define the monoclinic axes to be the c -axis $[0, 0, 1]_K$ and any direction in the $(0, 0, 1)_K$ plane can be chosen as $[1, 0, 0]_K$ axis. (Note: Directions defined by linear combinations of lattice unit vectors are different from those obtained by the same linear combination of the normalized unit vectors.)

4.3 The M -system and the M - K -relationship

The magnetic coordinate system (M) is special in that the actual orientation of the magnetic field \mathbf{B}_0 is not an axis of the system. The reason for this choice is in order to fix the magnetic system completely in terms of crystal coordinates, i.e. to fix the rotation axis $[0, 0, 1]_K$ and the zero position $[1, 0, 0]_M$. The zero position is defined as intersection between the magnetic $(0, 0, 1)_M$ plane and the crystal $(0, 0, 1)_K$ plane. (If the two planes coincide we define $[1, 0, 0]_M = [1, 0, 0]_K$.) In this way the matrix MK is defined for any rotation axis $[0, 0, 1]_M = [x, y, z]_K$. With $x^2 + y^2 + z^2 = 1$ we have

$$MK = \begin{pmatrix} y/r, & xz/r, & x \\ -x/r, & yz/r, & y \\ 0, & -r & z \end{pmatrix}, \quad r = (x^2 + y^2)^{1/2} \quad (3)$$

with the conditions: $\text{sign } r = \text{sign } y$ and $MK = \mathbf{1}$ for $r = 0$ ($\mathbf{1}$ is the unit matrix).

4.4 The M - E relation

Similarly to the M - K relationship we can define a M' coordinate system in terms of E coordinates. The $[0, 0, 1]_{M'}$ -axis is again the rotation axis but for historical reasons the $[0, 1, 0]_{M'}$ direction is now defined as the intersection between the $(0, 0, 1)_E$

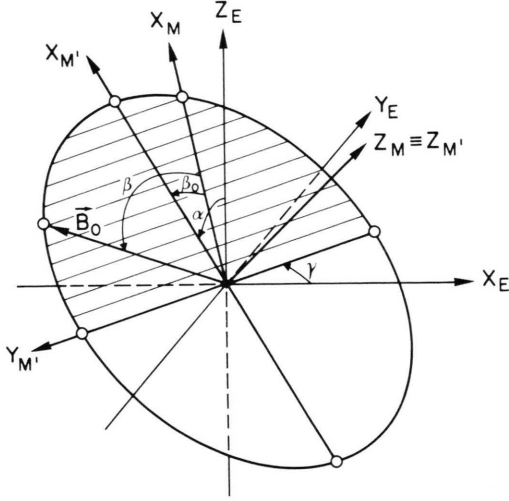


Fig. 1. Motion of the \mathbf{B}_0 -vector during the measurement of an NMR-NQR-rotation pattern with respect to the principal axes system (x_E, y_E, z_E) of an arbitrarily oriented EFG tensor. The definitions of the various angles are given in the text.

plane and the $(0, 0, 1)_{M'} \equiv (0, 0, 1)_M$ plane [2, 3, 4]. The $[1, 0, 0]_{M'}$ direction corresponds thus the projection of the $[0, 0, 1]_E$ axis along the $[0, 0, 1]_M$ axis on the $(0, 0, 1)_{M'}$ plane.

The M' - E relationship is defined by two angles α and γ . α is the angle between the $[0, 0, 1]_E$ axis and the $[1, 0, 0]_{M'}$ axis and γ is the angle between the $[1, 0, 0]_{M'}$ axis and the $[0, -1, 0]_{M'}$ axis. The M' system can be transformed into the M system by a rotation around the common $[0, 0, 1]_{M'} \equiv [0, 0, 1]_M$ axis (rotation angle β_0) (Figure 1). The matrix (ME) is thus defined by the three angles α , β_0 and γ :

$$ME = \begin{pmatrix} -\sin \gamma \sin \alpha \cos \beta_0 + \cos \gamma \sin \beta_0, & -\sin \gamma \sin \alpha \sin \beta_0 - \cos \gamma \cos \beta_0, & +\sin \gamma \cos \alpha \\ +\cos \gamma \sin \alpha \cos \beta_0 + \sin \gamma \sin \beta_0, & +\cos \gamma \sin \alpha \sin \beta_0 - \sin \gamma \cos \beta_0, & -\cos \gamma \cos \alpha \\ \cos \alpha \cos \beta_0, & \cos \alpha \sin \beta_0, & \sin \alpha \end{pmatrix}. \quad (4)$$

4.5 The E - K relationship

Knowing (ME) and (MK) , both the principal EFG-tensor axes and the EFG tensor V_E can be expressed in terms of crystal coordinates:

$$(EK) = (MK)(ME)^T, \quad (5)$$

$$V_K = (EK) V_E (EK)^T,$$

$$V_E = \frac{eq}{2} \begin{pmatrix} -1 + \eta, & 0 & 0 \\ 0 & -1 - \eta, & 0 \\ 0 & 0 & 2 \end{pmatrix}. \quad (6)$$

From the experiment we can obtain, as we shall see later on, the angles α , β_0 and γ , so that (ME) is defined. The MK matrix is, however, only defined if we know the rotation axis in crystal coordinates which is not the case for an arbitrary rotation axis. In this latter case, however, the crystal symmetry can help to find MK .

5. The Calculation of Rotation Patterns

For the sake of simplicity let us assume that the M' and M systems coincide (i.e. $\beta_0 = 0$). Now the magnetic field \mathbf{B}_0 is rotated from the zero direction $[1, 0, 0]_M$ through the angle $\beta = 90^\circ$ into $[0, 1, 0]_M$. Since $[0, 1, 0]_M = [0, 1, 0]_{M'}$ \mathbf{B}_0 is now in the x - y plane of the EFG-system, i.e. $B_z = 0$, whereas for $\beta = 0$ we have $B_z = \mathbf{B}_0 \cos \alpha$, which is the maximum value of B_z . B_x , B_y and B_z are thus defined by α , β and γ [2, 3, 4]:

$$\begin{aligned} B_x/B_0 &= -\sin \gamma \sin \alpha \cos \beta - \cos \gamma \sin \beta, \\ B_y/B_0 &= \cos \gamma \sin \alpha \cos \beta - \sin \gamma \sin \beta, \\ B_z/B_0 &= \cos \alpha \cos \beta \end{aligned} \quad (7)$$

in contrast to the usual definition in polar coordinates (θ, φ) . If the M' and M systems do not coincide, but are related by the angle β_0 , one has to rotate \mathbf{B}_0 from the zero direction $[1, 0, 0]_M$ through angle $+\beta_0$ in order to reach the $[1, 0, 0]_{M'}$ direction where B_z is maximum (Figure 1). To take this into account one has to replace β in (7) by $(\beta - \beta_0)$. For $\beta = 0$ we have $\mathbf{B}_0 \parallel [1, 0, 0]_M$, i.e. according to our

definition in Sect. 4.3 \mathbf{B}_0 is parallel to the crystal $(0, 0, 1)_K$ -plane. The scale of β is related to the laboratory scale by an offset which is of no importance as soon as the $\beta = 0$ direction is identified in the measured rotation pattern.

From (7) one can see that the B_i^2 have π -periodicity in $(\beta - \beta_0)$ which leads to the π -periodicity of the rotation patterns. The same periodicity exists for $B_i^2(\gamma)$. One can also see that there is no change in the rotation pattern if the signs of the angles α and γ are changed simultaneously. However, this change of signs results in a change of

$(ME)^+$ to $(ME)^-$ and thus from $(EK)^+$ to $(EK)^-$ which is the mirror image of $(EK)^+$ with respect to the magnetic $(0, 0, 1)_M$ plane. From one single-site rotation pattern one can therefore not tell whether $(EK)^+$ or $(EK)^-$ is the correct solution.

Knowing B_x , B_y and B_z as well as e^2qQ and η , one can now calculate the rotation pattern by diagonalizing the Hamiltonian equation (1). For the low field case ($\mathcal{H}_Q \gg \mathcal{H}_z$) one can apply first order perturbation theory and thus obtain for $I = \frac{3}{2}$ for example the following splitting of the degenerate NQ-eigenvalues:

$$\lambda_{2,3}^2 = \frac{\nu_L^2}{B_0^2} \left[\left(\frac{1}{2} a^2 - \frac{3}{2} b^2 \right)^2 B_z^2 + a^2 (a^2 + 3b^2 + 2\sqrt{3}ab) B_y^2 + a^2 (a^2 + 3b^2 - 2\sqrt{3}ab) B_x^2 \right], \quad (8)$$

$$\lambda_{1,4}^2 = \frac{\nu_L^2}{B_0^2} \left[\left(\frac{3}{2} a^2 - \frac{1}{2} b^2 \right)^2 B_z^2 + b^2 (b^2 + 3a^2 + 2\sqrt{3}ab) B_x^2 + b^2 (b^2 + 3a^2 - 2\sqrt{3}ab) B_y^2 \right],$$

where ν_L is the Larmor frequency, $a = \cos \delta/2$, $b = \sin \delta/2$ with $\tan \delta = \eta/\sqrt{3}$. (Note that the splitting does not depend on e^2qQ in this limit.) The rotation patterns in Fig. 2 were calculated using (8). By comparing measured and calculated rotation patterns one can obtain η , α , β_0 and γ of the EFG-tensor, i.e. $(EK)_+$ and $(EK)_-$.

For the high field case ($\mathcal{H}_z \gg \mathcal{H}_Q$) first order perturbation theory provides a much simpler equation but one has to pay for this with a loss of information:

$$\Delta\nu = \pm \frac{\nu_Q}{2} \{ [3 \cos^2(\alpha) \cos^2(\beta - \beta_0) - 1] + \eta [\sin(2\gamma) \sin(2\beta - 2\beta_0) \sin(\alpha) + \cos(2\gamma) (\sin^2(\beta - \beta_0) - \sin^2(\alpha) \cos^2(\beta - \beta_0))] \}, \quad (9)$$

where

$$\nu_Q = \frac{e^2qQ}{h} \frac{3}{2I(2I-1)} \quad \text{for half integer spins}$$

and

$$\nu_Q = \frac{3e^2qQ}{4h} \quad \text{for } I = 1.$$

Equation (9) yields pure cosine curves with the periodicity π in $(\beta - \beta_0)$ which can be described by an offset, an amplitude and a phase, i.e. one obtains only 3 values from a rotation pattern but is faced

with the problem of determining five parameters: e^2qQ , η , α , β_0 and γ . One needs thus two rotation patterns. This can be achieved either by taking the spectra from a rotation around a second axis or by analyzing the symmetry related rotation pattern, if present. (EK) can now be determined unambiguously.

6. Exploring the Crystal Symmetry

Using the ideas introduced in the previous sections it is now easy to take advantage of the crystal symmetry. This will be demonstrated in two examples:

6.1 A Single Crystal with Unknown Symmetry and Orientation

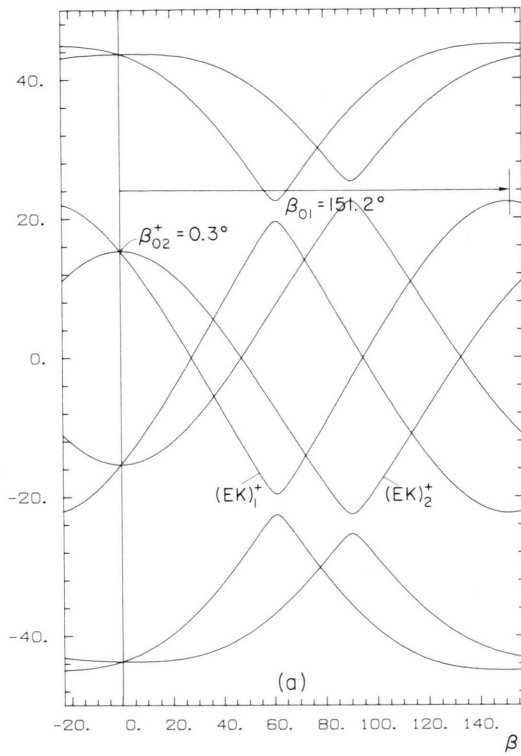
Figure 2a shows the fitted rotation pattern for one out of the four ^{35}Cl NQR-lines of $(\text{CH}_3)_3\text{CCOOSbCl}_4$. The rotation axis is unknown since the crystal was grown in a sealed glass tube. The plot reveals the existence of two physically inequivalent Cl-sites. There are now two possibilities: either we have two differently oriented crystallites in the sample, or the two sites are related by a mirror plane or a twofold axis respectively. In the latter case the crystal is monoclinic with point symmetry 2, m or $2/m$. Since NMR cannot distinguish between the three cases let us assume that we have a mirror plane, m , which according to Sect. 4.2 is the $(001)_K$ -plane. If this is the case, all corresponding lines of the two sites must coincide for one orientation of B_0 which corresponds to $\beta = 0$. This was in fact observed in the spectrum Figure 2a. For the two sites one can now determine α_i , β_{0i} and γ_i by using the same η for the fit.

Starting with α_1 , β_{01} and γ_1 we can calculate $(ME)_1^+$ and $(ME)_1^-$ from (4). Since only the monoclinic axis is of importance for the symmetry we can define (MK) by the unknown tilt angle δ between the rotation axis and $[001]_K$: $x = \sin \delta$, $y = 0$, $z = \cos \delta$,

$$(MK) = \begin{pmatrix} 0, & \cos \delta, & \sin \delta, \\ -1, & 0, & 0 \\ 0, & -\sin \delta, & \cos \delta \end{pmatrix}. \quad (10)$$

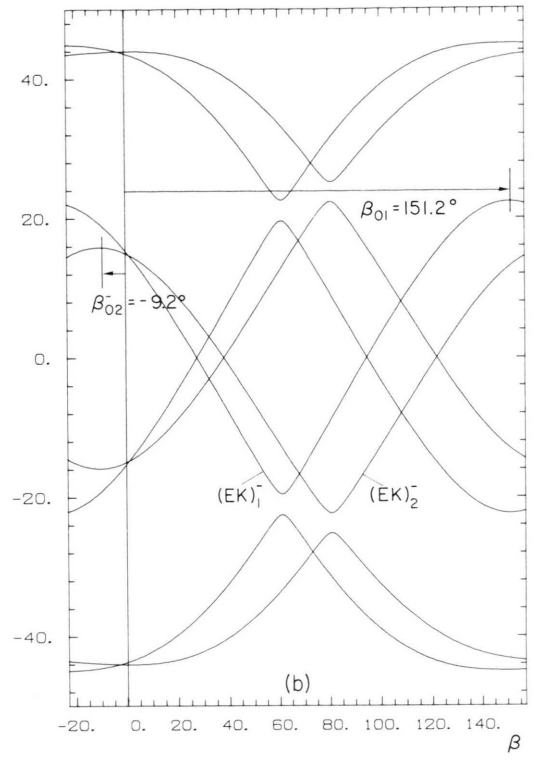
By using (5) we can calculate $(EK)_1^+$ and $(EK)_1^-$, and applying the symmetry operation (m_z) on $(EK)_1$ we

ZEEMAN SPLITTING (KHZ)



CRYSTAL ROTATION (DEGREE)

ZEEMAN SPLITTING (KHZ)



CRYSTAL ROTATION (DEGREE)

Fig. 2. ^{35}Cl -NQR rotation pattern for two symmetry related sites calculated for the angles α_i^\pm , β_{0i}^\pm , γ_i^\pm with $\eta = 0.13$ for a rotation axis tilted by the angle $\delta = 40.8^\circ$ from the monoclinic axis of the crystal.

a) $(EK)_i^+$: $\alpha_1 = 4.2$, $\beta_{01} = 151.2^\circ$, $\gamma_1 = -4^\circ$; $\alpha_2 = -29.1^\circ$, $\beta_{02} = 0.3^\circ$, $\gamma_2 = -87.0$.

b) $(EK)_i^-$: $\alpha_1 = -4.2$, $\beta_{01} = 151.2^\circ$, $\gamma_2 = 4^\circ$; $\alpha_2 = -27.7^\circ$, $\beta_{02} = -9.2^\circ$, $\gamma_2 = -74.46$.

obtain the symmetry related EFG-tensor

$$(EK)_2^\pm = (m_z)(EK)_1^\pm = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} (EK)_1^\pm. \quad (11)$$

From this we can calculate $(ME)_2^\pm$

$$(ME)_2^\pm = [(MK)^T(EK)_2^\pm]^T = ((EK)_2^\pm)^T(MK). \quad (12)$$

Knowing $(ME)_2^\pm$ one can calculate α_2^\pm , β_{02}^\pm and γ_2^\pm and compare them with α_2 , β_{02} and γ_2 obtained from the experiment. By varying the angle δ it was possible to obtain a fit and to determine $(EK)_1$ and $(EK)_2$ unambiguously. In Fig. 2a and 2b rotation patterns are calculated from α_1 , β_{01} and γ_1 for $(EK)_1^+$ and $(EK)_2^+$, and $(EK)_1^-$ and $(EK)_2^-$ respectively. Superposition of the curves shows that those for $(EK)_1^+$ and $(EK)_1^-$ are identical, whereas those for $(EK)_2^+$ and $(EK)_2^-$ differ considerably and thus allow unambiguous assignment to be made.

Moreover the precision of the individually fitted α_i , β_{0i} and γ_i could be improved considerably using the relationship between α_1 and β_{02} , and α_2 and β_{01} respectively. β_0 corresponds to a horizontal shift of the rotation pattern and thus all data points contribute with equal weight to the fit. β_0 can therefore be determined very precisely. α on the other hand mainly changes the magnitude of the splitting at $\beta = \beta_0$ and thus these data points are heavily weighted in the fit. Moreover α is essentially determined from a $\cos \alpha$ term and for small α this factor is very insensitive. Since changes in α are transformed into changes in β_0 in the symmetry related spectrum the latter can be used to determine α more precisely. Using this technique for the analysis of the four chemically inequivalent Cl sites it was possible to obtain all Cl-Sb-Cl bond angles, as well as the relative orientation of the two symmetry related molecules in the crystal [5].

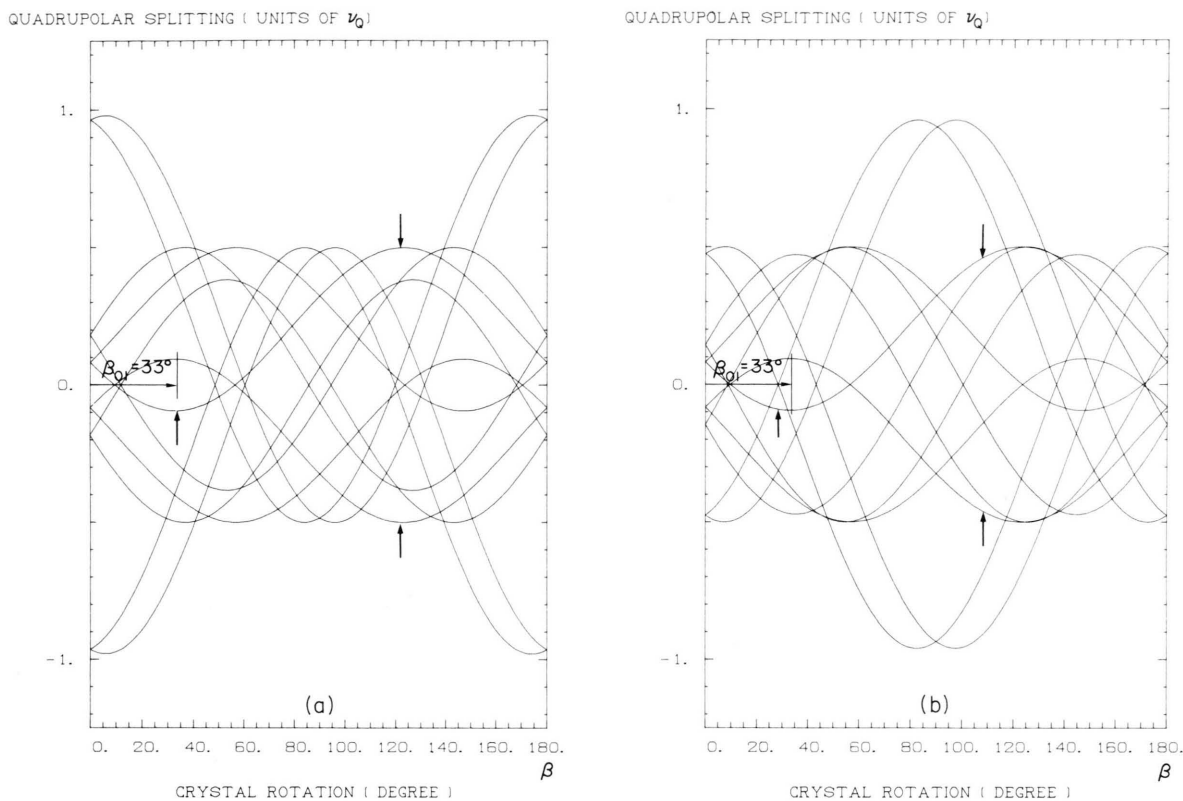


Fig. 3. ^2H -NMR rotation pattern for six sites related by the symmetry 32 calculated for the angles α_1^\pm, β_{01} with $\eta = 0$ and a rotation about a pseudo cubic axis of the trigonal system.

a) $(EK)_1^+$: $\alpha_1 = +51^\circ$, $\beta_0 = 33^\circ$. - b) $(EK)_1^-$: $\beta_1 = -51^\circ$, $\beta_0 = 33^\circ$.

6.2 A Crystal with Known Symmetry and Rotation Axis

The compound $\text{CD}_3\text{NH}_3\text{HgCl}_3$ exhibits two structural phase transitions which are connected with the “freezing-in” of the methylammonium motion. At room temperature the structure is P3_2 with $Z = 3$, but the crystal is twinned in such a way that the apparent symmetry is P3_22 [6]. In order to investigate the CD_3NH_3 -group motion a DMR-rotation pattern was measured for a rotation about a pseudo cubic axis (perpendicular to a grown face) of the crystal. The EFG-tensor at the deuteron sites are the result of two time averaging processes. The first one is due to a rapid rotation of the CD_3 -groups around the molecular axis. The second one is due to the reorientational motion of the whole molecule. Therefore, the z -axes of the deuteron EFG-tensors become parallel to the 6 time averaged

N–C bond directions of the system. Accordingly the number of lines in the rotation pattern is 12. Due to the reduced NQ-splitting (from time average) and to the natural line with the individual lines could be traced only for parts of the rotation pattern and an unambiguous assignment to the deuteron sites was not possible without using the hidden information of the crystal symmetry.

Figure 3a shows the calculated rotation pattern which fitted best to the data points. It was calculated from one line (marked with arrows) which could be traced reasonably well through the pattern. For this line (1) α_1 and β_{01} were determined. Since the asymmetry parameter is essentially zero the angle γ is of no importance. There is, however, an ambiguity in the determination of β_0 which is due to a symmetry property of the high field case: All lines which coincide at $\beta = 0$ coincide also at $\beta = 90^\circ$. In order to find the correct $\beta = 0$ orientation

of B_0 one has to know the approximate orientation of the crystal in laboratory frame. From α_1 and β_{01} $(ME)_1^\pm$ and $(EK)_1^\pm$ were calculated. The $(EK)_n^\pm$ ($n = 2, 3, \dots, 6$) were then obtained by applying the symmetry operations of the point group 32. From this the $(EM)_n^\pm$ and afterwards the α_n^\pm and β_{0n}^\pm as well as the corresponding rotation patterns were calculated. Figure 3a shows the pattern for the $(EK)_n^+$ whereas the pattern for the $(EK)_n^-$ are plotted in Figure 3b. By adjusting the parameters α_1 and β_{01} a very good agreement with the data points was obtained for the $(EK)_n^+$. The 6 time averaged N-C bond directions obtained in this way are in very good agreement with those obtained from neutron scattering [7].

7. Conclusions

We have shown that the information contained in the crystal symmetry is very useful for the determination of EFG-tensors. The computer program which does all the calculations consists essentially of a sequence of matrix multiplications and is critical only for special angles, where one has to prevent divisions by zero. The program is small enough to run on a pocket calculator HP-41 CX.

Acknowledgements

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