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# $^7\text{Li}$ and $^{87}\text{Rb}$ nuclear magnetic resonance in a $\text{LiRbSO}_4$ single crystal with the growth twin domain

Ae Ran Lim<sup>1,4</sup>, Dong Young Jeong<sup>2</sup>, Jin Ho Kim<sup>3</sup> and Jong Hoon Hahn<sup>3</sup>

<sup>1</sup> Department of Physics, Jeonju University, Jeonju 560-759, Korea

<sup>2</sup> Institute of Quantum Information Processing and Systems, The University of Seoul, Seoul 130-742, Korea

<sup>3</sup> Department of Chemistry, Division of Molecular and Life Science, Pohang University of Science and Technology, Pohang 790-784, Korea

E-mail: aeranlim@hanmail.net

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## Abstract

The  $^7\text{Li}$  and  $^{87}\text{Rb}$  NMR in a  $\text{LiRbSO}_4$  single crystal with the growth twin domain grown by the slow evaporation method were investigated by employing a Bruker FT NMR spectrometer. Instead of the simple one set of signals caused by quadrupole interaction, three sets of NMR signals were obtained. From these results, all parameters were determined, and all lead to the same values for the quadrupole coupling constant and asymmetry parameter. The  $^7\text{Li}$  NMR parameter in the  $\text{LiRbSO}_4$  crystal was axially symmetric, whereas the  $^{87}\text{Rb}$  NMR parameter was non-axially symmetric; the lithium ion is surrounded by oxygen atoms located on a regular tetrahedron, and the resultant coordinating rubidium ion is surrounded by slightly distorted oxygen atoms located at nine regular tetrahedra. The obtained results can be explained by the existence of three kinds of growth twin domain, rotated with respect to each other by  $120^\circ$  around the  $c$ -axis.

## 1. Introduction

The phase transitions occurring in the sulphates of the  $\text{LiXSO}_4$  family ( $X = \text{K}, \text{Rb}, \text{Cs}$  and  $\text{NH}_4$ ) are approximately described as arising from changes in orientation of the  $\text{SO}_4$  tetrahedra, and show interesting phase transitions. Studies on successive phase transitions in  $\text{LiRbSO}_4$  single crystals have been reported by several groups [1–5]. It has been discovered that  $\text{LiRbSO}_4$  undergoes successive transitions at 439, 458, 475 and 477 K [1, 2]. These phases are referred to as I–IV and V with the temperature descending. Phases I and V are paraelectric [2]. Phases II and III are ferroelectric and antiferroelectric, respectively [6]. Microscopic observation indicates that phases IV and V are monoclinic and that the crystal system is orthorhombic above 458 K [5]. Ferrielectricity has been found in phase IV between 439 and 458 K [2, 7]. Nevertheless, it should be noted that even in the monoclinic phases, the distortion of the

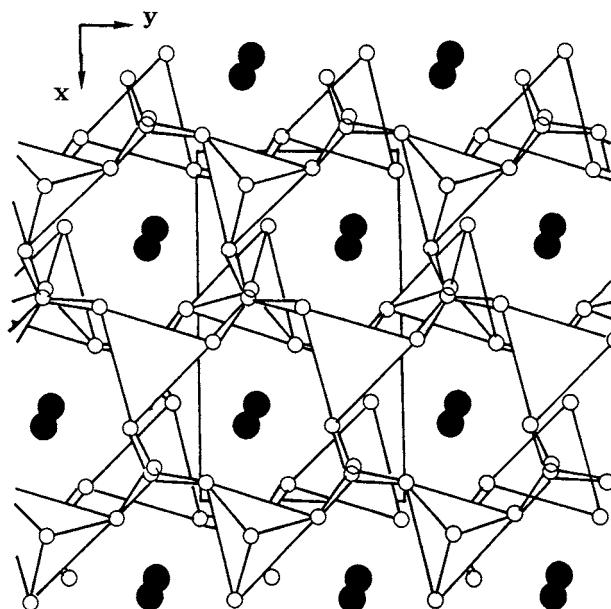
<sup>4</sup> To whom all correspondence should be addressed.

lattice from the orthorhombic structure is small since the monoclinic angles are very close to  $90^\circ$  [8]. Moreover, the  $b/a$  ratio of the lattice parameters is about 1.73 in all phases; i.e., the Bravais lattice is almost hexagonal.  $\text{LiRbSO}_4$  has been described by some authors as a pseudo-hexagonal network of six-membered rings of  $\text{SO}_4$  and  $\text{LiO}_4$  tetrahedra [9].

In this paper, we discuss the  $^7\text{Li}$  and  $^{87}\text{Rb}$  nuclear magnetic resonance (NMR) in a  $\text{LiRbSO}_4$  single crystal with the growth twin domain grown by the slow evaporation method. The quadrupole coupling constant, the asymmetry parameter, and the direction of the principal axes of the electric field gradient (EFG) tensor of  $^7\text{Li}$  ( $I = 3/2$ ) and  $^{87}\text{Rb}$  ( $I = 3/2$ ) were determined at room temperature. The  $^7\text{Li}$  and  $^{87}\text{Rb}$  NMR in this single crystal is a new finding.

## 2. Crystal structure

Lithium rubidium sulphate,  $\text{LiRbSO}_4$ , has a monoclinic structure with four molecular formula units per unit cell. The space group is  $P2_1/n$  ( $C_{2h}^5$ ) and the lattice parameters of the monoclinic cell are  $a = 5.288 \text{ \AA}$ ,  $b = 9.105 \text{ \AA}$ ,  $c = 8.731 \text{ \AA}$  and  $\gamma = 90.09^\circ$  at room temperature [10]. The projection of the structure of  $\text{LiRbSO}_4$  along  $[001]$  is shown in figure 1. The  $\text{Rb}^+$  ions are shown as dark circles. As shown in figure 1,  $\text{LiRbSO}_4$  has a pseudo-hexagonal network of six-membered rings of  $\text{SO}_4$  and  $\text{LiO}_4$ , and the structure of  $\text{LiRbSO}_4$  is characterized by the alternate rotation in opposite directions of each tetrahedron, layer by layer. The  $\text{SO}_4^{2-}$  anion is an almost regular tetrahedron, and each  $\text{SO}_4$  tetrahedron shares all of its corners with distorted  $\text{LiO}_4$  tetrahedra [10].



**Figure 1.** Projection of the structure of  $\text{LiRbSO}_4$  along the  $[001]$  plane. The  $\text{SO}_4$  and  $\text{LiO}_4$  tetrahedra are shown. The  $\text{Rb}^+$  ions are shown as dark circles.

From  $\text{LiRbSO}_4$ , pseudo-hexagonal multidomain platelets perpendicular to the  $c$ -axis were generally obtained. In most cases, each platelet contained three distinct domain orientations, which corresponded to the three equivalently available pseudo-orthorhombic directions of the  $a$ -axis at  $120^\circ$  from each other, derived from the virtual high-symmetry hexagonal structure.

The crystals were shaped in the form of hexagonal plates, and the specimen consisted of three-domain sectors [11]. LiRbSO<sub>4</sub> has a pseudo-hexagonal crystal structure which is similar to LiNH<sub>4</sub>SO<sub>4</sub> [12]. The characteristic feature of the LiRbSO<sub>4</sub> structure can be described by a framework consisting of six-membered rings of alternating LiO<sub>4</sub> and SO<sub>4</sub> tetrahedra normal to the *c*-axis [12–14]. The basal plane of the tetrahedra is nearly parallel (001). The Rb ions occupy cavities within this framework.

### 3. Experimental procedure

Single crystals of LiRbSO<sub>4</sub> were grown at about 75 °C by slow evaporation from an aqueous solution. The solution was prepared from equimolar amounts of Li<sub>2</sub>SO<sub>4</sub>·H<sub>2</sub>O and Rb<sub>2</sub>SO<sub>4</sub>. The colourless single crystals prepared were about 7 × 7 mm<sup>2</sup> in area, and 3 mm in thickness, and were prepared from twinned parts of single crystals. The orientations of the crystal were determined by the x-ray Laue method. The angular dependence of the NMR spectra was measured for rotation on the crystallographic *a*-, *b*- and *c*-axes, respectively.

**Table 1.** Direction cosines of <sup>7</sup>Li EFG tensor in LiRbSO<sub>4</sub>.

	$\mu_a$	$\mu_b$	$\mu_c$
(a) 0° domain	0.4470	0.8654	0.2265
	0.7712	-0.5011	0.3927
	0.4533	-0.0009	-0.8914
(b) 120° domain	-0.1485	-0.9861	-0.0749
	0.9820	-0.1381	-0.1286
	0.1165	-0.0926	0.9888
(c) 240° domain	0.4582	0.8673	-0.1944
	0.7995	-0.4977	-0.3362
	-0.3884	-0.0014	-0.9215

Nuclear magnetic resonance signals of <sup>7</sup>Li and <sup>87</sup>Rb in the LiRbSO<sub>4</sub> single crystal were measured using a Bruker MSL 200 FT NMR spectrometer at the Korea Basic Science Institute in Seoul. The static magnetic field was 4.7 T and the central radio frequency was set at  $\omega_0/2 = 77.777$  MHz for the <sup>7</sup>Li nucleus and  $\omega_0/2 = 65.442$  MHz for the <sup>87</sup>Rb nucleus, respectively.

### 4. Experimental results and analysis

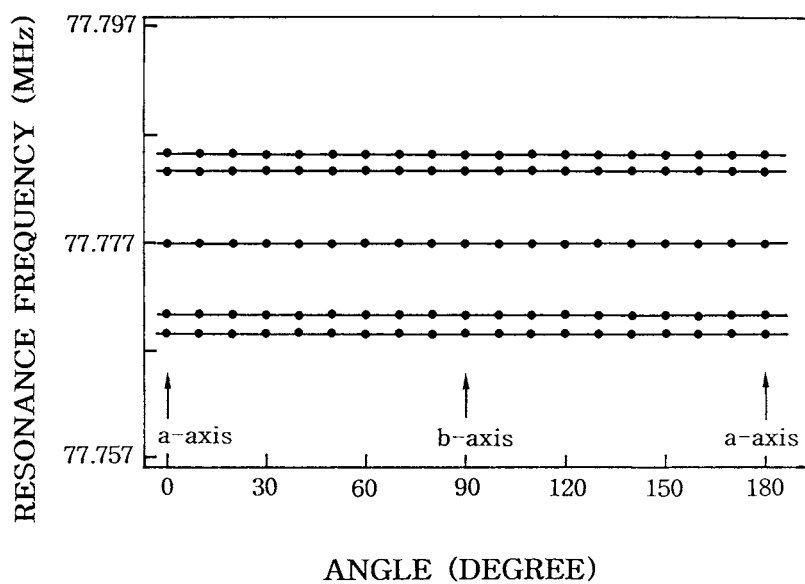
The Hamiltonian for the NMR to analyse the experimental results is the usual [15, 16]

$$H = H_Z + H_Q$$

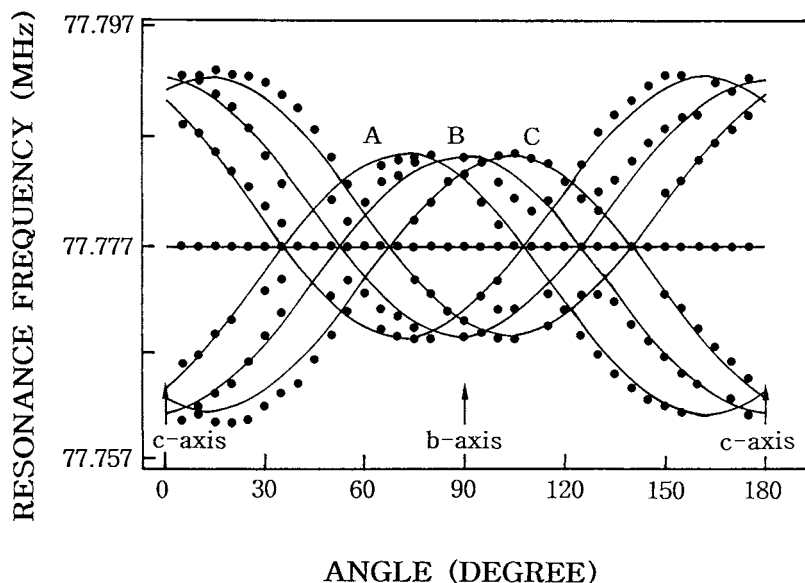
where  $H_Z$  is the Zeeman term and  $H_Q$  describes the nuclear electric quadrupole interaction. The Hamiltonian in a principal axes system of the EFG tensor is given by

$$\begin{aligned}
 H = & -\gamma\hbar\mathbf{B}_0 \cdot \mathbf{I} + e^2qQ/4I(2I - 1)[1/2\{3I_z^2 - I(I + 1)\}(3\cos^2\theta - 1) + \eta\sin^2\theta\cos 2\varphi] \\
 & + 1/4(I_+^2 + I_-^2)\{3\sin^2\theta + \eta\cos 2\varphi(1 + \cos^2\theta)\} \\
 & + 1/4\{(I_+ + I_-)I_z + I_z(I_+ + I_-)\}(6\sin\theta\cos\theta - \eta\sin 2\theta\cos 2\varphi) \\
 & - \eta/2i(I_+^2 - I_-^2)\cos\theta\sin 2\varphi + \eta/2i\{(I_+ - I_-)I_z + I_z(I_+ - I_-)\}\sin\theta\sin 2\varphi]
 \end{aligned}
 \tag{1}$$

where  $e^2qQ/h$  is the quadrupole coupling constant and  $\eta$  is the asymmetry parameter. Conventionally, the *X*, *Y* and *Z* axes are such that  $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}| = eq$ ; then



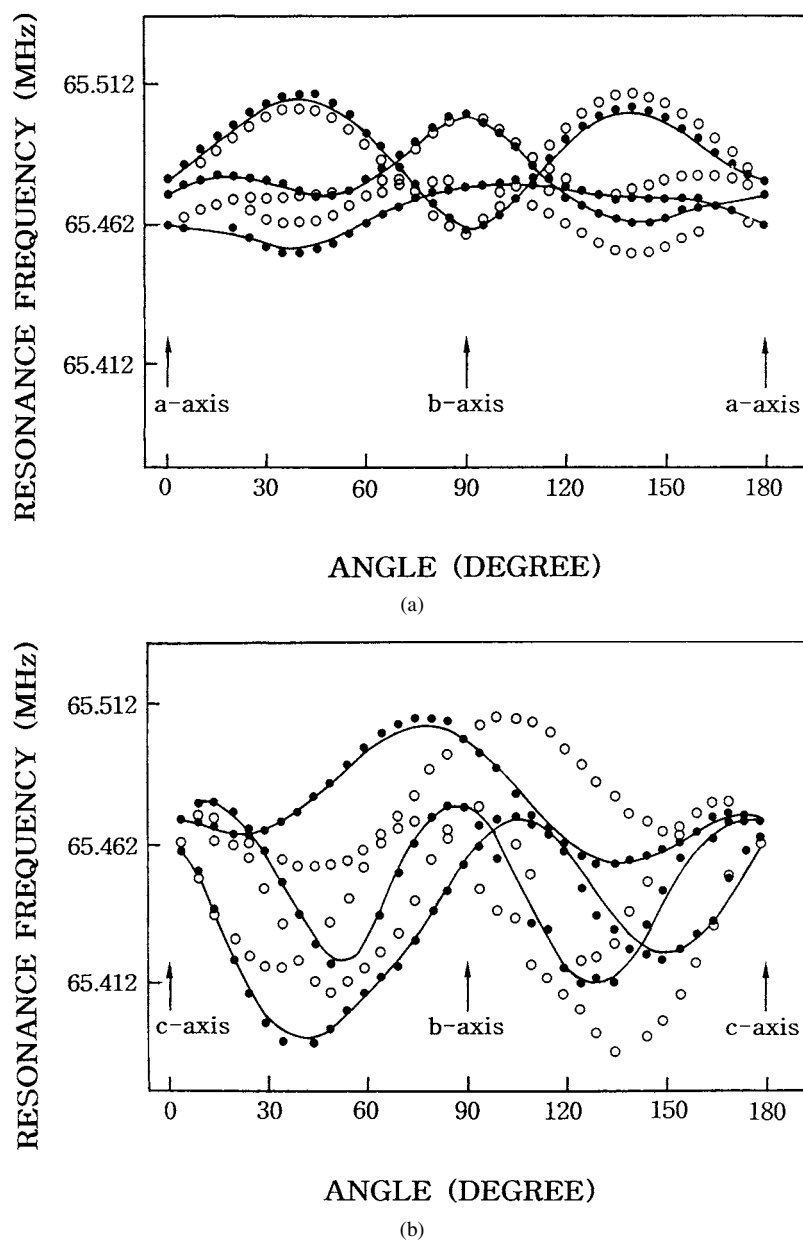
(a)



(b)

**Figure 2.** Rotation pattern of  ${}^7\text{Li}$  NMR measured (a) in the  $ab$ -plane and (b) in the  $bc$ -plane at room temperature.

$0 \leq \eta \leq 1$ . The matrix form of the spin Hamiltonian of equation (1) is employed to calculate the resonance fields with the magnetic field applied along a general direction. All resonance spectra and parameters were calculated by numerically diagonalizing the matrix using a computer program. The program used also included the Eulerian transformation of the magnetic field vector with respect to the coordinate system made of principal axes of the electric field gradient (EFG) tensor.



**Figure 3.** Rotation pattern of  $^{87}\text{Rb}$  NMR measured (a) in the  $ab$ -plane and (b) in the  $bc$ -plane at room temperature.

#### 4.1. $^7\text{Li}$ NMR

The rotation pattern of  $^7\text{Li}$  measured in the three crystallographic planes at room temperature is shown in figures 2(a) and (b). Dots correspond to the experimental values and the full curves were obtained by fitting these data. The  $^7\text{Li}$  resonance lines in the  $ab$ -plane were observed to be two sets, whereas the those in the  $bc$ -plane were three sets. The explanation for this lies in the existence of three kinds of growth twin domain. The rotation patterns of the two

**Table 2.** Direction cosines of  $^{87}\text{Rb}$  EFG tensor in  $\text{LiRbSO}_4$ .

	$\mu_a$	$\mu_b$	$\mu_c$
(a) $0^\circ$ domain	1	0	0
	0	1	0
	0	0	1
(b) $120^\circ$ domain	-0.5000	0.8660	0.0000
	-0.8660	-0.5000	0.0000
	0.0000	0.0000	1.0000
(c) $240^\circ$ domain	-0.5000	-0.8660	0.0000
	0.8660	-0.5000	0.0000
	0.0000	0.0000	1.0000

sets in the  $ab$ -plane were a superposition of resonance lines obtained by rotation A and C for three domain in the  $bc$ -plane of  $^7\text{Li}$  NMR. Because the resonance field of the central line is almost constant and the spacings between adjacent lines are equal, the first-order perturbation of  $H_Q$  with respect to  $H_Z$  should be sufficient for analysis. Three resonance lines of  $^7\text{Li}$  had the same magnitude of quadrupole coupling constants and asymmetry parameters, but had different orientations. In figure 2, the satellite resonance lines did not show maximum or minimum separation in the crystallographic axis. Based on these experimental results, we can conclude that the principal axes of the Li ion are not consistent with the crystallographic axes. The parameters were determined by a least-squares fit to the experimental data. The nuclear quadrupole coupling constant and asymmetry parameter of  $^7\text{Li}$  in a  $\text{LiRbSO}_4$  crystal were determined as  $39.6 \pm 0.05$  kHz and 0 at room temperature. The EFG tensor of  $^7\text{Li}$  was found to be axially symmetric. The direction of the principal EFG tensor for the Li ion is shown in table 1. Here,  $\mu_a$ ,  $\mu_b$  and  $\mu_c$  are the direction cosines relative to the crystallographic  $a$ ,  $b$  and  $c$ -axes of  $\text{LiRbSO}_4$ , respectively.

#### 4.2. $^{87}\text{Rb}$ NMR

The rotation pattern of  $^{87}\text{Rb}$  measured in the crystallographic  $ab$ -plane and  $bc$ -plane at room temperature is shown in figures 3(a) and (b). Figure 3 represents the central transition ( $\pm 1/2 \leftrightarrow \mp 1/2$ ) of  $^{87}\text{Rb}$  NMR lines. Two satellite lines for the  $^{87}\text{Rb}$  ( $I = 3/2$ ) nucleus, corresponding to transitions between the levels ( $+3/2 \leftrightarrow +1/2$ ) and ( $-1/2 \leftrightarrow -3/2$ ), are out of the range.  $^{87}\text{Rb}$  central lines have the angular dependences of second-order quadrupolar shifts. Instead of the one central resonance line, six different sets of resonance lines were obtained from the  $^{87}\text{Rb}$  nucleus. These rotation patterns indicate strongly anisotropic EFG tensors. Dots correspond to the experimental values and full curves were obtained by fitting these data to symmetric second rank EFG tensors. From the angular dependence of the second-order quadrupole shift in the central transition of  $^{87}\text{Rb}$  NMR, the quadrupole coupling constant and the asymmetry parameter were determined. Results all lead to the same values for the quadrupole coupling constant and asymmetry parameter:  $^{87}\text{Rb}$  quadrupole coupling constant,  $e^2qQ/h = 4.53 \pm 0.07$  MHz, and the asymmetry parameter,  $\eta = 0.35 \pm 0.03$ . The EFG tensor of  $^{87}\text{Rb}$  was found to be asymmetric; the rubidium ion is surrounded by slightly distorted oxygen atoms located at nine regular tetrahedrons. The direction of the principal EFG tensor for the Rb ion is shown in table 2. The principal axis corresponding to the largest principal value of  $^{87}\text{Rb}$  EFG tensor is parallel to the crystallographic  $c$ -axis. This direction was determined to be the  $Z$ -axis of the EFG tensor.

The three resonance lines of  $^{87}\text{Rb}$  displayed as dark circles are rotated with respect to each other by  $120^\circ$  around the  $c$ -axis. Three resonance lines of  $^{87}\text{Rb}$  represented as open circles are

related through the crystallographic mirror plane. These results are similar to the <sup>39</sup>K NMR result in LiKSO<sub>4</sub> single crystals at 180 K obtained by our recent experiment [17].

## 5. Discussion and conclusion

The <sup>7</sup>Li and <sup>87</sup>Rb NMRs in a LiRbSO<sub>4</sub> single crystal with the growth twin domain grown by the slow evaporation method were investigated by employing a Bruker FT NMR spectrometer. Instead of simple one set signals due to quadrupole interaction, three sets of NMR signals were obtained. From these results, all parameters were determined, and all lead to the same values for the quadrupole coupling constant and asymmetry parameter. The obtained results can be explained by the existence of three kinds of growth twin domain, rotated with respect to each other by 120° around the *c*-axis. The <sup>7</sup>Li NMR parameter in LiRbSO<sub>4</sub> crystal was axially symmetric, whereas the <sup>87</sup>Rb NMR parameter was non-axially symmetric. The nuclear electric quadrupole interaction of the <sup>7</sup>Li and <sup>87</sup>Rb nuclei having the nuclear spin  $I = 3/2$  provides information about the electric field gradient produced by ions surrounding the resonant nucleus. Thus, the quadrupole coupling constant and asymmetry parameter of <sup>7</sup>Li and <sup>87</sup>Rb reveal the configuration of ionic charges around the Li<sup>+</sup> and Rb<sup>+</sup>. The lithium ion is surrounded by oxygen atoms located on a regular tetrahedron, and the resultant coordinating rubidium ion is surrounded by slightly distorted oxygen atoms located at nine regular tetrahedra. Therefore, the environment of the Li and Rb atoms surrounded by oxygen atoms are clearly comprehended by <sup>7</sup>Li and <sup>87</sup>Rb NMR results.

LiRbSO<sub>4</sub> crystals have a strong tendency to be twinned. Under normal growth conditions, they take the form of pseudo-hexagonal plates composed of three 120° twin domains. Most of the seeds of this crystal are hexagonal in form with 120° twin domains. The twin domain structure of the LiRbSO<sub>4</sub> crystal is not a result of accidental nucleation, but the consequence of a growth habit dependent on the symmetry of the prototypic phase. Consequently, LiRbSO<sub>4</sub> single crystals may have different crystal structures according to the conditions of crystal growth.

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