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The temperature dependence of ^7Li nuclear magnetic resonance in a LiRbSO_4 single crystal

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Abstract. The temperature dependence of the ^7Li nuclear magnetic resonance in a LiRbSO_4 single crystal grown by the slow-evaporation method has been investigated by employing a Bruker FT NMR spectrometer. The three-line structure due to the quadrupole interaction was measured in three mutually perpendicular crystal planes. From the experimental data, the quadrupole coupling constant, $e^2qQ/h = 20.4 \pm 0.2$ kHz, and asymmetry parameter, $\eta = 0$, are determined at room temperature. The principal axes of the EFG tensor are parallel to the crystallographic a -, b -, and c -axes. The largest principal axis Z is parallel to the crystallographic c -axis. In the temperature range 140–400 K, the nuclear quadrupole coupling constant of Li in LiRbSO_4 decreases as the temperature increases. The temperature dependence of the quadrupole parameters is satisfactorily explained with a single torsional frequency of the Li–O ion by means of the simple Bayer theory.

1. Introduction

Studies on the successive phase transitions in LiRbSO_4 single crystal have been reported by several groups [1–5]. It has been discovered that LiRbSO_4 undergoes successive transitions at 439, 458, 475, and 477 K [1, 2]. These phases have been called I–IV and V in the order of descending temperature. Phases I and V are paraelectric [2]. Phases II and III are ferroelectric and antiferroelectric, respectively [6]. The microscopic observations indicate 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].

In this paper, we present the ^7Li nuclear magnetic resonance (NMR) of a LiRbSO_4 single crystal 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 ^7Li ($I = 3/2$) are determined at room temperature. Also, the temperature dependence of the quadrupole coupling constant of ^7Li in a LiRbSO_4 single crystal was analysed by means of experimental data obtained with a pulse NMR spectrometer. The ^7Li NMR in a LiRbSO_4 single crystal is a new result.

2. Crystal structure

Lithium rubidium sulphate, LiRbSO_4 , is a monoclinic structure with four molecular formula units per unit cell. The space group is $P2_1/n$, and the lattice parameters of the monoclinic cell are $a = 5.288$ Å, $b = 9.105$ Å, $c = 8.731$ Å, and $\gamma = 90.09^\circ$ at room temperature

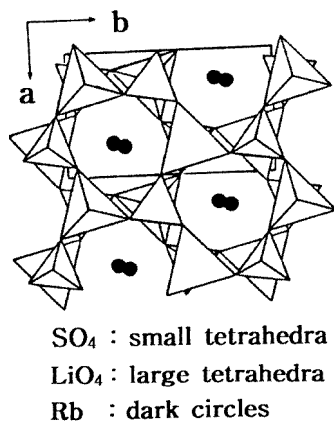


Figure 1. The projection of the structure of LiRbSO₄ along the [001] plane.

Table 1. The bond lengths and bond angles for LiO₄ tetrahedra in the LiRbSO₄ single crystal.

Bond lengths (Å)		Bond angles (deg)	
Li–O(1)	1.891	O(1)–Li–O(2)	102.4
Li–O(2)	1.913	O(1)–Li–O(3)	114.5
Li–O(3)	1.950	O(1)–Li–O(4)	109.1
Li–O(4)	1.928	O(2)–Li–O(3)	110.1
		O(2)–Li–O(4)	111.3
		O(3)–Li–O(4)	109.4

[8]. The projection of the structure of LiRbSO₄ along [001] is shown in figure 1. The Rb⁺ ions are shown as dark circles. As shown in figure 1, LiRbSO₄ has a pseudo-hexagonal network of six-membered rings of SO₄ (small tetrahedra) and LiO₄ (large tetrahedra). Also, the structure of LiRbSO₄ is characterized by the alternate rotation in opposite directions of each tetrahedron, layer by layer. The SO₄²⁻ anion is an almost regular tetrahedron, and each SO₄ tetrahedron shares all of its corners with distorted LiO₄ tetrahedra [8]. The bond lengths and bond angles for LiO₄ tetrahedra are given in table 1.

3. Experimental procedure

LiRbSO₄ single crystals were grown by slow evaporation from an aqueous solution containing equimolar amounts of Li₂SO₄·4H₂O and Rb₂SO₄. The colourless single crystals prepared were about 5 × 5 × 10 mm³. The orientations of the crystal were determined by the x-ray Laue method. The angular dependence of the NMR spectra was measured on the crystallographic *ab*-, *bc*-, and *ca*-planes.

The nuclear magnetic resonance signals of ⁷Li in the LiRbSO₄ single crystal were measured using a Bruker MSL 200 FT NMR spectrometer at Korea Basic Science Institute in Seoul. The static magnetic field was 4.7 T, and the central rf frequency was set at $\omega_0/2\pi = 77.768$ MHz. The NMR spectra of ⁷Li were recorded with a sequence of one 90° pulse, 20 scans, and a repetition time of 3 s. The ring-down delay time of 7 s was used to remove the effect of the pulse. Also, the temperature-dependent NMR measurements were made in the same way as was previously reported [9].

4. Experimental results and analysis

The Hamiltonian for NMR used to analyse the experimental results has the usual form:

$$H = H_Z + H_Q \tag{1}$$

where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction of the ⁷Li nucleus, which has the nuclear spin $I = 3/2$ with 92.58% natural abundance. The quadrupole Hamiltonian in the principal-axes system of the EFG tensor is given by [10, 11]

$$H_Q = e^2qQ[3I_z^2 - I(I + 1) + \eta(I_+^2 + I_-^2)/2]/4I(2I - 1) \tag{2}$$

where e^2qQ/h is the quadrupole coupling constant and η is the asymmetry parameter. Conventionally the X-, Y- and Z-axes are such that $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}| = eq$; then $0 \leq \eta \leq 1$. The matrix form of the spin Hamiltonian of equation (1) is employed to calculate the resonance points, with the magnetic field applied along a general direction. All of the resonance spectra and the parameters are calculated by numerically diagonalizing the matrix using computer data.

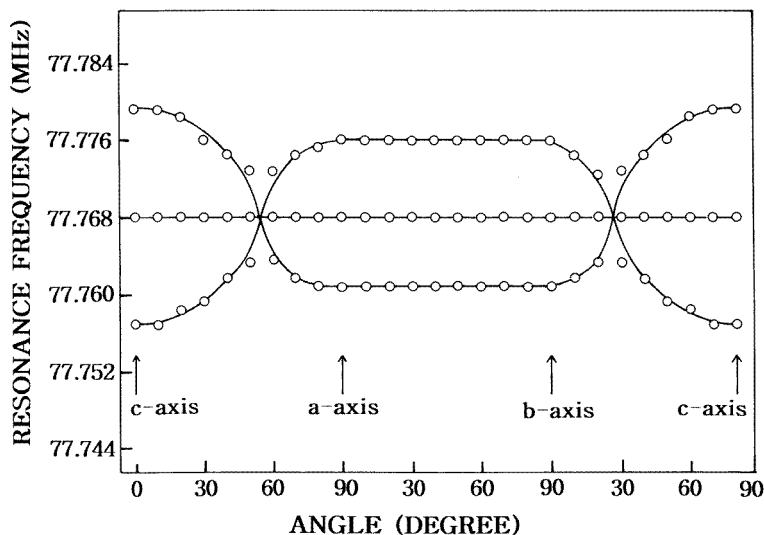


Figure 2. The rotation pattern of ⁷Li NMR measured in the *ca*-, *ab*-, and *bc*-planes at room temperature. The circles are experimental data and the lines are calculations based on the best-fit parameters.

Table 2. Quadrupole parameters of ⁷Li in LiRbSO₄ and LiKSO₄ at room temperature.

e^2qQ/h (kHz)	η	Principal axes	References
20.4 ± 0.2	0	$X = a, Y = b, Z = c$	Present work
25 ± 1	0.15 ± 0.01	$X = a, Y = b, Z = c$	Lim <i>et al</i> [12]

In general, the rotation patterns in three mutually perpendicular planes are required to determine the quadrupole interaction completely [10]. The rotation pattern of Li, measured in the three crystallographic planes at room temperature, is shown in figure 2, where the

angle γ ($=90.09^\circ$) is only slightly different from 90° . From the fact that the resonance frequency 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 may be sufficient for the analysis. The maximum separation resulting from the quadrupole interaction was observed when the magnetic field was applied along the c -axis of the crystal. This direction is found by analysis to be the Z -axis of the EFG tensor. The satellite resonance lines show the angular dependence of $3\cos^2\theta - 1$, where the polar angle θ is the direction of the magnetic field with respect to the c -axis, whereas the central line is angle independent. The parameters were determined by a least-squares fit using the experimental data of figure 2; the quadrupole coupling constant $e^2qQ/h = 20.4 \pm 0.2$ kHz and the asymmetry parameter $\eta = 0$ are determined at room temperature. The parameters for the ^7Li nucleus in a LiRbSO_4 crystal found by analysis were similar to those for the ^7Li nucleus in a LiKSO_4 crystal [12, 13]. This similarity is consistent with the fact that LiRbSO_4 and LiKSO_4 single crystals have isomorphous structures. These results are summarized in table 2, together with the previous report.

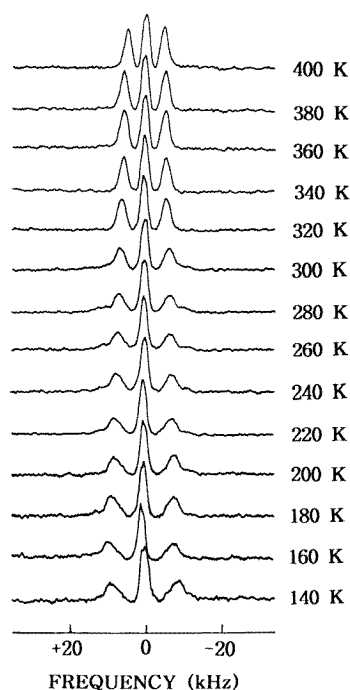


Figure 3. The temperature dependence of the ^7Li NMR spectra for the temperature range 140–400 K. The static magnetic field B_0 is parallel to the a -axis. The zero point corresponds to the resonance frequency 77.768 MHz of the ^7Li nucleus.

In order to examine the temperature dependence of e^2qQ/h for ^7Li in the LiRbSO_4 single crystal, the resonance spectra were measured at fourteen different temperatures in the range 140–400 K as shown in figure 3. While the central transition stays constant, the splitting between the central and satellite lines is found to decrease as the temperature increases. The temperature dependences of e^2qQ/h for ^7Li are shown in figure 4. The value of e^2qQ/h was found to decrease almost linearly as a function of increasing temperature.

A simple model given by Bayer [14] and Wang [15], which ascribes the temperature

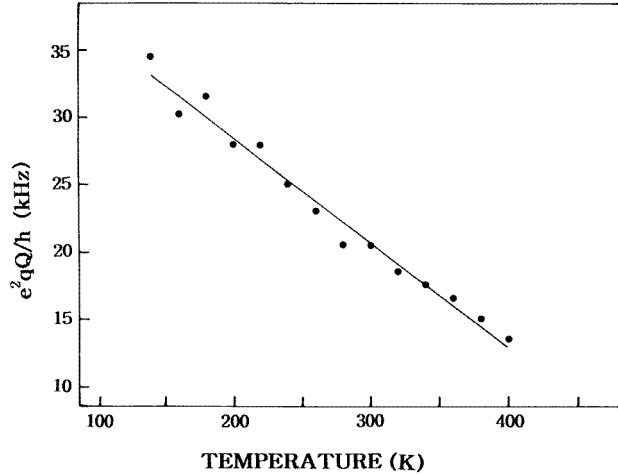


Figure 4. The temperature dependence of the nuclear quadrupole coupling constant for ⁷Li in a LiRbSO₄ single crystal. Measured values are indicated by points. The solid lines are the predictions based on the theory of Bayer and of Wang.

dependence to a torsional oscillation of the Li–O ion in LiRbSO₄, was adopted in this study to explain the temperature dependence of e^2qQ/h for ⁷Li. The temperature dependence of e^2qQ/h may be explained by a single torsional mode about the X-axis of the EFG tensor. If the terms of second order in the angular displacement are retained, then the following equation holds [16]:

$$q' = q[1 - (3 + \eta)\langle\theta_X^2\rangle/2] \quad (3)$$

where the unprimed and primed quantities are for the rigid and the motional molecules, respectively. As the torsional motion is quantized, $\langle\theta_i^2\rangle$ is related to the temperature by

$$I_i\omega_i^2\langle\theta_i^2\rangle = \hbar\omega_i[1/2 + 1/\{\exp(\hbar\omega_i/kT) - 1\}] \quad (4)$$

where ω_i ($i = X, Y, Z$) is the torsional angular frequency. I_i is the corresponding moment of inertia, and T is the temperature. In this torsional motion about the X-axis, e^2qQ/h decreases with the increasing temperature. The solid line in figure 4 is the prediction for e^2qQ/h for ⁷Li with $I_X = 2.48 \times 10^{-46}$ kg m² and $\omega_X = 8.3 \times 10^{12}$ rad s⁻¹. Therefore, Bayer's and Wang's theory can satisfactorily explain our data for the temperature range 140–400 K.

5. Discussion and conclusions

From the experimental results, the nuclear quadrupole coupling constant, $e^2qQ/h = 20.4 \pm 0.2$ kHz, and the asymmetry parameter, $\eta = 0$, for ⁷Li in a LiRbSO₄ single crystal are determined at room temperature. The maximum separation of the resonance line due to the quadrupole interaction was observed when the magnetic field was applied along the *c*-axis of the crystal. This direction is determined to be the Z-axis of the EFG tensor. The principal axes of the EFG tensor are parallel to the crystallographic axes *a*, *b*, *c*. The largest principal axis, Z, is parallel to the crystallographic *c*-axis. Also, the quadrupole coupling constants of ⁷Li in LiRbSO₄ decrease as the temperature increases. The temperature dependence of

e^2qQ/h for the temperature range 140–400 K is explained by a single torsional frequency of the Li–O ion, by means of the simple Bayer and Wang theory.

Acknowledgments

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References

- [1] Shiroishi Y, Nakata A and Sawada S 1976 *J. Phys. Soc. Japan* **40** 911
- [2] Shiroishi Y and Sawada S 1979 *J. Phys. Soc. Japan* **46** 148
- [3] Mashiyama H and Unruh H G 1985 *J. Phys. Soc. Japan* **54** 822
- [4] Kurihama T, Izumi T and Sawada S 1986 *J. Phys. Soc. Japan* **55** 2469
- [5] Kunishige A and Mashiyama H 1987 *J. Phys. Soc. Japan* **56** 3189
- [6] Yamaguchi T and Sawada S 1980 *Proc. JSSF-2 (Kyoto); J. Phys. Soc. Japan* **49** 81
- [7] Mashiyama H, Hasebe K, Tanisaki S, Shiroishi Y and Sawada S 1979 *J. Phys. Soc. Japan* **46** 1959
- [8] Tanisaki S, Mashiyama H, Hasebe K, Shiroishi Y and Sawada S 1980 *Acta Crystallogr. B* **36** 3084
- [9] Lim A R, Yeom T H, Choh S H and Jeong S Y 1996 *J. Phys.: Condens. Matter* **7** 7265
- [10] Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Oxford University Press) ch VII
- [11] Slichter C P 1989 *Principles of Magnetic Resonance* (Berlin: Springer) ch X
- [12] Lim A R, Choh S H and Jeong S Y 1996 *J. Phys.: Condens. Matter* **8** 4597
- [13] Guo Q and Cao Q J 1981 *Wultral Wu Li* **10** 475
- [14] Bayer H 1951 *Z. Phys.* **130** 227
- [15] Wang T C 1955 *Phys. Rev.* **99** 566
- [16] Das T P and Hahn E L 1958 *Nuclear Quadrupole Resonance Spectroscopy* (New York: Academic) ch I