^{7}Li nuclear magnetic resonance in a LiKSO$_4$ single crystal

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Abstract. The nuclear magnetic resonance of ^{7}Li ($I = 3/2$) in a LiKSO$_4$ single crystal grown by the slow evaporation method has been investigated by employing a Bruker FT NMR spectrometer. From the experimental data, the quadrupole coupling constant $e^2qQ/h = 25 \pm 1$ kHz and asymmetry parameter $\eta = 0.15 \pm 0.01$ are determined at room temperature; however, these values turn out to be non-axially symmetric, and slightly different from those in an earlier report. This non-axial symmetry is consistent with the fact that the coordination of a lithium ion surrounded by oxygen atoms is not a perfectly regular tetrahedron. The principal Z-axis of the EFG tensor of the ^{7}Li—the largest component—is parallel to the crystallographic c-axis.

1. Introduction

Lithium potassium sulphate is an object of great interest, due to the complexity and richness of its sequence of phase transitions in the temperature range from 10 K to 1000 K [1–3]. In recent years, an increasing number of studies have been reported on the physical properties of LiKSO$_4$ crystals because this material has excellent optical quality. The results of NMR [4–6], EPR [7, 8], Raman [9], thermal expansion [10], and DSC experiments [11] for the phase transitions are not totally consistent. Also, ferroelastic properties of LiKSO$_4$ crystals have been reported for the temperature range below 190 K [12]. The crystal structure of LiKSO$_4$ at room temperature is hexagonal with the space group C_6^6 ($P6_3$) [13].

In this paper, we present the results of a ^{7}Li nuclear magnetic resonance (NMR) study of a LiKSO$_4$ 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 ^{7}Li ($I = 3/2$) are determined at room temperature.

2. Crystal structure

LiKSO$_4$ is hexagonal, with two molecular formula units per unit cell. The lattice parameters of the hexagonal cell are $a = 5.147$ Å and $c = 8.633$ Å at room temperature [3]. The projection of LiKSO$_4$ onto the (0001) plane is shown in figure 1. Since one of the S–O bonds lies along the c-axis, the projections of the tetrahedra are shown as equilateral triangles with Li at the centroid. The two lithium ions in the unit cell are displaced by $c/2$ along the c-axis [7]. The solid triangles represent the relative orientation of the tetrahedron in the C_6^6 phase. In this structure, the lithium ion is surrounded by tetrahedrally coordinated oxygens [14]. The Li$^+$ ion has a tetrahedral coordination with Li–O distances in the range 1.909–1.923 Å [15].
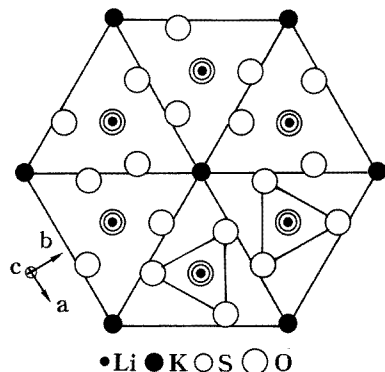
Figure 1. The hexagonal structure of LiKSO$_4$ projected onto the (0001) plane.

3. Experimental procedure

Single crystals of LiKSO$_4$ were grown by slow evaporation from an aqueous solution at 32 °C containing equimolar proportions of Li$_2$SO$_4$·H$_2$O and K$_2$SO$_4$. The optical axis (*c*-axis) was identified with a polarizing microscope, and the orientation of the *a*-axis was determined by the x-ray Laue method. The angular dependence of the NMR spectra was measured on the crystallographic *ac*- and *ab*-planes.
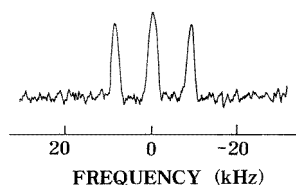

Figure 2. A typical NMR spectrum of ^{7}Li in a LiKSO$_4$ crystal recorded with the pulse NMR spectrometer. The static magnetic field B_0 is parallel to the *a*-axis. The zero point corresponds to the resonance frequency 77.768 MHz of the ^{7}Li nucleus.

Nuclear magnetic resonance signals of ^{7}Li in the LiKSO$_4$ single crystal, with the size of approximately $5 \times 5 \times 4$ mm^3, 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 ^{7}Li 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 μs was used to remove the effect of the pulse.

4. Experimental results and analysis

The Hamiltonian used for NMR to analyse the experimental results is as usual

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

where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction of the ^{7}Li nucleus, which has the nuclear spin $I = 3/2$ with 92.58% natural abundance.
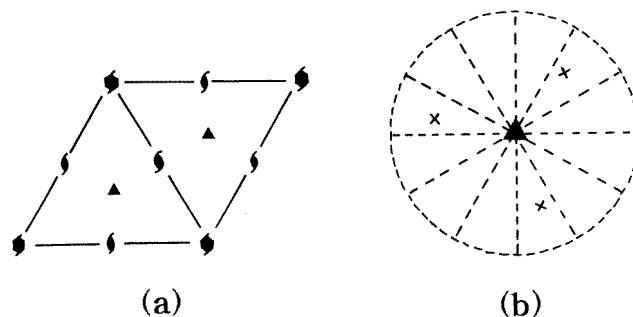
Figure 3. (a) A diagram of the symmetry element for C_6^6. (b) The stereographic projection for the symbol 3.

The quadrupole Hamiltonian in the principal axes system of the EFG tensor is given by [16, 17]

$$H_Q = e^2qQ[3I_Z^2 - I(I+1) + \eta(I_+^2 + I_-^2)/2]/4I(2I-1) \qquad (2)$$

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 $|V_{XX}| \leqslant |V_{YY}| \leqslant |V_{ZZ}| = eq$; also $0 \leqslant \eta \leqslant 1$. From the fact that the spacings between adjacent lines as shown in figure 2 are equal, the first-order perturbation of H_Q with respect to H_Z is sufficient for our purposes. Thus the energy eigenvalues are given by

$$E_m = E_m^{(0)} + E_m^{(1)} \qquad (3)$$

where

$$E_m^{(0)} = -g_n\beta_n Bm \qquad (4)$$

$$E_m^{(1)} = e^2qQ\{[3m^2 - I(I+1)]/4I(2I-1)\}[(3\cos^2\theta - 1) + \eta\sin^2\theta\cos 2\phi]/2. \qquad (5)$$

In equation (4) g_n is the nuclear g-factor, β_n the nuclear magneton, and m the magnetic quantum number. In equation (5) θ and ϕ are the polar and azimuthal angle, respectively, of the applied magnetic field B with respect to the principal axes of the EFG tensor. The resonance condition of the allowed transition of $\Delta m = \pm 1$ is derived from equations (4) and (5):

$$\nu_{m\to m-1} = (g_n\beta_n/h)B - 3e^2qQ(m-1/2)[(3\cos^2\theta - 1) + \eta\sin^2\theta\cos 2\phi]/4I(2I-1)h. \qquad (6)$$

Table 1. Quadrupole parameters of ^7Li in LiKSO$_4$ at room temperature.

e^2qQ/h (kHz)	η	Principal axes	References
25 ± 1	0.15 ± 0.01	$X = a$, $Y = b$, $Z = c$	Present work
35.8	0		Guo and Cao [4]

The three-line structure is a result of the quadrupole interaction of the ^7Li ($I = 3/2$) nucleus. A typical NMR spectrum of ^7Li is shown in figure 2, where the signals were obtained with the magnetic field applied along the crystallographic a-axis. It is a Fourier transform of the free-induction decay for the ^7Li NMR. The central transition is stronger
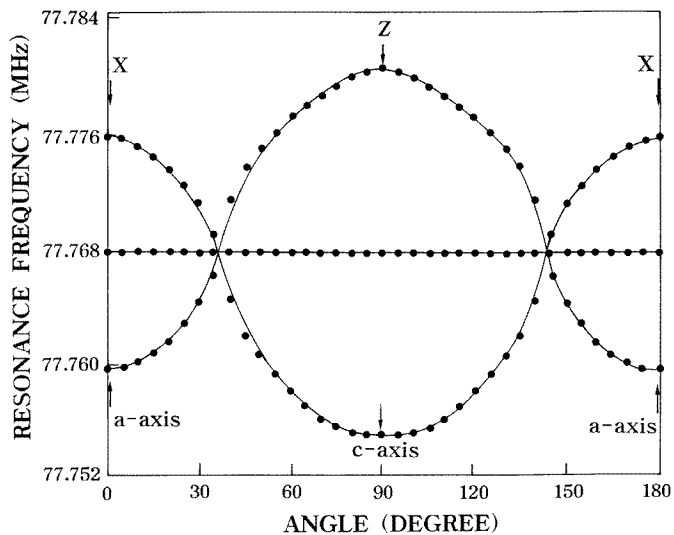
Figure 4. The rotation pattern of ^{7}Li NMR measured in the *ac*-plane at room temperature. The circles show experimental data and the lines show calculations based on the best-fit parameters.

Figure 5. The rotation pattern of ^{7}Li NMR measured in the *ab*-plane at room temperature. The circles show experimental data and the lines show calculations based on the best-fit parameters.
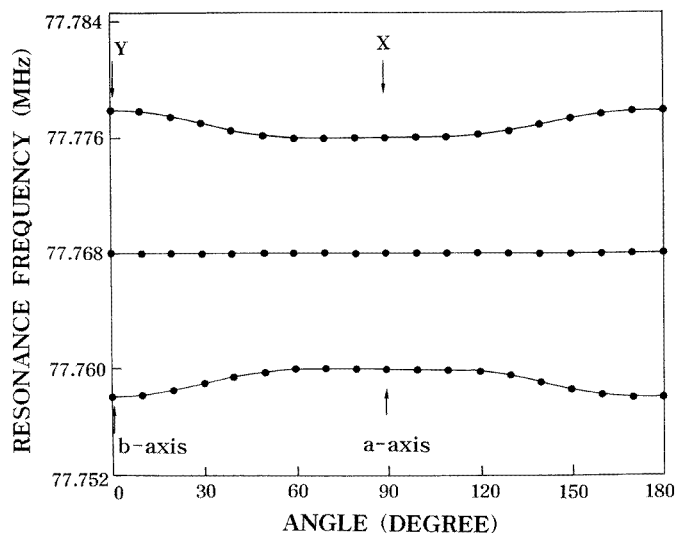
than the satellite lines, and the separations between adjacent lines are almost equal. Even though there are two lithium nuclei per unit cell, only one set of NMR spectra of ^{7}Li is obtained. A diagram of the symmetry elements and of the general position for C_6^6 is shown in figure 3(a). The following positions (Wyckoff notation and point symmetry) are occupied: 2Li(b, 3), 2K(a, 3), 2S(b, 3), and 6O(c, 1) [18]. The local symmetry at the Li site in LiKSO$_4$ has 3 symmetry. The stereographic projection for the symbol 3 is shown in

figure 3(b). The symbol 3 signifies that the principal axis is a triad. Starting with the initial pole of a general face, we obtained three poles related to each other by the rotation axis. This means that two sites are crystallographically and magnetically equivalent. Therefore, only one set of the NMR spectra of ^7Li is obtained even though there are two lithium nuclei per unit cell.

In general the rotation patterns in three mutually perpendicular planes are required to determine the quadrupole interaction completely. The rotation pattern of Li, measured in the crystallographic *ac*-plane at room temperature, is shown in figure 4. 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 rotation pattern in the *ab*-plane is shown in figure 5. The frequency difference between the maximum and minimum separation was about 3300 Hz. However, this pattern turns out to be slightly different from that in an earlier report, which indicated axial symmetry [4]. Therefore, the electric field gradient tensor of Li is non-axially symmetric. Accordingly, the quadrupole parameters are determined by the least-squares fit using the experimental data of figures 4 and 5; the quadrupole coupling constant $e^2qQ/h = 25 \pm 1$ kHz and the asymmetry parameter $\eta = 0.15 \pm 0.01$ are determined at room temperature. The parameters analysed for the ^7Li nucleus are summarized in table 1 together with those from the earlier report.

5. Discussion and conclusion

By the local symmetry at Li sites, only one set of NMR spectra of ^7Li is obtained, even though there are two lithium nuclei per unit cell. From the NMR results, 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 quadrupole coupling constant, $e^2qQ/h = 25 \pm 1$ kHz, and the asymmetry parameter, $\eta = 0.15 \pm 0.01$, of ^7Li at room temperature are determined. The EFG tensor of ^7Li is found to be non-axially symmetric, which is consistent with the crystal structure. The lithium ion is surrounded by oxygen atoms located on a slightly distorted tetrahedron. Further studies on the temperature dependence are currently being conducted.

Acknowledgments

References

[1] Hiraishi J, Taniguchi N and Takahashi H 1976 *J. Chem. Phys.* **65** 3221
[2] Oliveira A J, Germano F A, Filho J M, Melo F E A and Moreira J E 1988 *Phys. Rev.* B **38** 12 633
[3] Pimenta M A, Echegut P, Luspin Y, Hauret G, Gervais F and Abelard P 1989 *Phys. Rev.* B **39** 3361
[4] Guo Q and Cao Q J 1981 *Wultal Wu Li* **10** 475
[5] Meng Q A and Cao Q J 1982 *Acta Phys. Sinica* **31** 1045

[6]   Topic B, Haeberlen U and Blinc R 1990 *Z. Phys.* B **79** 275
[7]   Bansal M L, Deb S K, Roy A P and Sahni V C 1980 *Solid State Commun.* **36** 1047
[8]   Holuj F and Drozdowski M 1981 *Ferroelectrics* **36** 579
[9]   Teeters D and Frech R 1982 *Phys. Rev.* B **26** 4132
[10] Cach R, Tomaszewski P E and Bornarel J 1985 *J. Phys. C: Solid State Phys.* **18** 915
[11] Sorge G and Hempel H 1986 *Phys. Status Solidi* a **97** 431
[12] Balagurov A M, Popa N C and Savenko B N 1986 *Phys. Status Solidi* b **134** 457
[13] Frech R and Teeters D 1984 *J. Phys. Chem.* **88** 417
[14] Bradley A J 1925 *Phil. Mag.* **49** 1225
[15] Karppinen M, Lundgren J O and Liminga R 1983 *Acta Crystallogr.* C **39** 34
[16] Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford : Oxford University Press) ch VII
[17] Slichter C P 1989 *Principles of Magnetic Resonance* (Berlin: Springer) ch 10
[18] Hahn T 1987 *Space-group Symmetry (International Tables for Crystallography A)* (The International Union of Crystallography)