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Phase transition by ^7Li NMR in an LiCsSO_4 single crystal

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Abstract. The temperature dependence of the ^7Li nuclear magnetic resonance in an LiCsSO_4 single crystal grown by the slow evaporation method has been investigated by employing an FT NMR spectrometer. The rotation patterns of the ^7Li NMR spectra were obtained in three mutually perpendicular planes under an applied magnetic field of 4.7 T. The ^7Li NMR spectra demonstrate the occurrence of the second-order phase transition at 200 K which is connected with a lowering of the Li^+ site symmetry. Two kinds of ferroelastic domain below 200 K were measured. In the temperature range of 140–380 K, the nuclear quadrupole coupling constants and asymmetry parameters of ^7Li in LiCsSO_4 decrease as the temperature increases. The temperature dependence of e^2qQ/h and η is satisfactorily explained with a single torsional frequency of the Li–O ion by simple Bayer theory.

1. Introduction

Lithium caesium sulphate, LiCsSO_4 , single crystals undergo a transition from the paraelastic phase with orthorhombic structure at room temperature to the ferroelastic phase with monoclinic structure below T_C ($= 202$ K) [1, 2]. The main changes in the structure as a result of this transition are described by rotation of the SO_4 tetrahedra about the c -axis through roughly 14° [3]. This crystal undergoes a second-order ferroelastic phase transition, and the ferroelastic character of this transition was established by direct observation of a stress–strain hysteresis loop [4–7]. LiCsSO_4 crystals have been studied by x-ray diffraction [8, 9], Raman spectroscopy [10–12], EPR [13–17], NMR [18, 19] and optical properties [20].

In this paper, we present the ^7Li nuclear magnetic resonance (NMR) in a LiCsSO_4 single crystal grown by the slow evaporation method. The quadrupole coupling constant, e^2qQ/h , the asymmetry parameter, η , 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 e^2qQ/h and η of ^7Li in a LiCsSO_4 single crystal was analysed by means of experimental data obtained with a pulse NMR spectrometer. Based on these results, we examine the phase transition and the ferroelastic property of a LiCsSO_4 single crystal. The temperature dependence of ^7Li NMR in a LiCsSO_4 single crystal is a new result.

2. Crystal structure

Lithium caesium sulphate, LiCsSO_4 , is a orthorhombic structure with four molecular units per unit cell. The space group is $Pcmn$ and the point group is mmm , and the lattice constant

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$a = 9.456 \text{ \AA}$, $b = 5.456 \text{ \AA}$ and $c = 8.820 \text{ \AA}$. The four Li and Cs atoms in a unit cell are crystallographically equivalent. The oxygen coordination around each Cs is 11-fold, and the Li^+ ion has a tetrahedral coordination with Li–O distance ranges from 1.849 to 1.954 \AA [8]. Figure 1(a) shows the projections of the atomic positions in the $Pcmn$ phase onto a (001) plane.

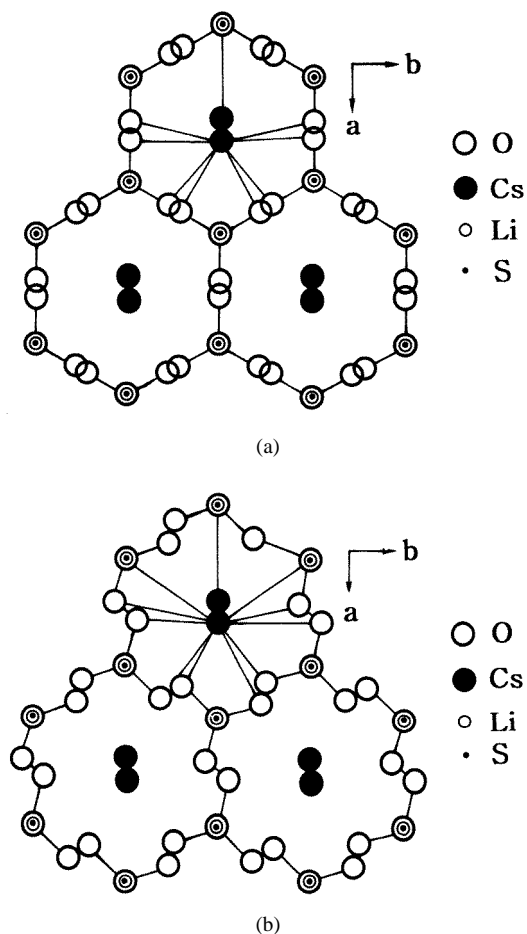


Figure 1. (a) Projections of the atomic positions in the orthorhombic $Pcmn$ phase of LiCsSO_4 onto a (001) plane. (b) Projections of the atomic positions in the monoclinic $P2_1/n$ phase of LiCsSO_4 onto a (001) plane.

The orthorhombic to monoclinic transition is characterized by the disappearance of the b -mirror symmetry and an ordering of the sulphate groups. At 163 K, the space group is monoclinic $P2_1/n$ and the point group is $2/m$ [16]. The lattice parameters are $a = 9.379 \text{ \AA}$, $b = 5.423 \text{ \AA}$ and $c = 8.834 \text{ \AA}$ and $\gamma = 89.75^\circ$. In the monoclinic phase, there are still four molecular units in a unit cell and all the atoms are crystallographically equivalent. Figure 1(b) shows the projections of the atomic positions at 163 K onto a (001) plane.

3. Experimental procedure

Good optical quality single crystals of LiCsSO_4 were grown by slow evaporation from aqueous solution containing equimolar amounts of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and Cs_2SO_4 . The transparent and colourless single crystals prepared were about $5 \times 5 \times 6 \text{ mm}^3$. The crystals are hexagonal plates in shape and show a 60° twin structure as shown in figure 2. As samples for measurements, untwinned parts were selected from as-grown crystals. The orientation of the crystal was identified from the optical polarizing microscope and the x-ray Laue method. The angular dependence of the NMR spectra was measured on the crystallographic ab -, bc - and ca -planes, respectively.

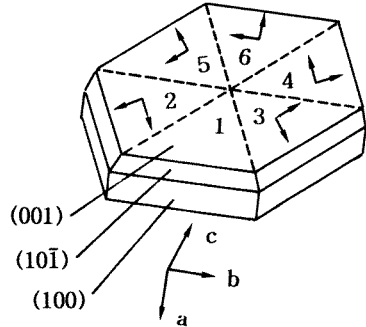


Figure 2. The room temperature crystal growth habit of LiCsSO_4 crystals, composed of six twin-domains. The orientations of the crystal a -, b -axes for domain 1 are indicated below the figure, while those for domains 2–6 are indicated by small arrows in the domains themselves.

Nuclear magnetic resonance signals of ${}^7\text{Li}$ in the LiCsSO_4 single crystal were measured using a Bruker MSL 200 FT NMR spectrometer. The static magnetic field was 4.7 T and the central rf frequency was set at $\omega_0/2\pi = 77.777 \text{ MHz}$. The NMR spectra of ${}^7\text{Li}$ were recorded with a sequence of one 90° pulse, 20 scans and a repetition time of 3 s. A ring-down delay time of $7 \mu\text{s}$ was used to remove the effect of the pulse. The temperature-dependent NMR measurements were taken by the previously reported method [21].

4. Experimental results and analysis

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

$$H = H_Z + H_Q \quad (1)$$

where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction of the ${}^7\text{Li}$ nucleus, which has the nuclear spin $I = 3/2$ with 92.58% natural abundance. The quadrupole Hamiltonian in the principal axis system of the EFG tensor is given by [22, 23]

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

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 $0 \leq \eta \leq 1$. Because the spacings between adjacent lines are equal, the first-order perturbation of H_Q with respect to H_Z is sufficient. The energy eigenvalues are then given by

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

where

$$E_m^{(0)} = -g_n \beta_n B m \quad (4)$$

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

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):

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

All resonance spectra and the parameters were calculated by numerically diagonalizing the 4×4 matrix using a computer program to analyse the experimental data. The computer program used also included the Eulerian transformation of the magnetic field vector with respect to the coordinate system made up of principal axes of the electric field gradient (EFG) tensor. The Eulerian angles Φ , Θ , Ψ are for a transformation of the crystal system (a , b , c) into the EFG system (X , Y , Z).

In general, rotation patterns in three mutually perpendicular directions are required to determine the quadrupole interaction completely. The rotation patterns of ^7Li NMR spectra measured in the crystallographic planes at room temperature are displayed in figure 3; they were obtained by converting the resonance frequency into the resonance magnetic field. 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 may be sufficient for analysis. In figure 3, the satellite resonance lines did not show the 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

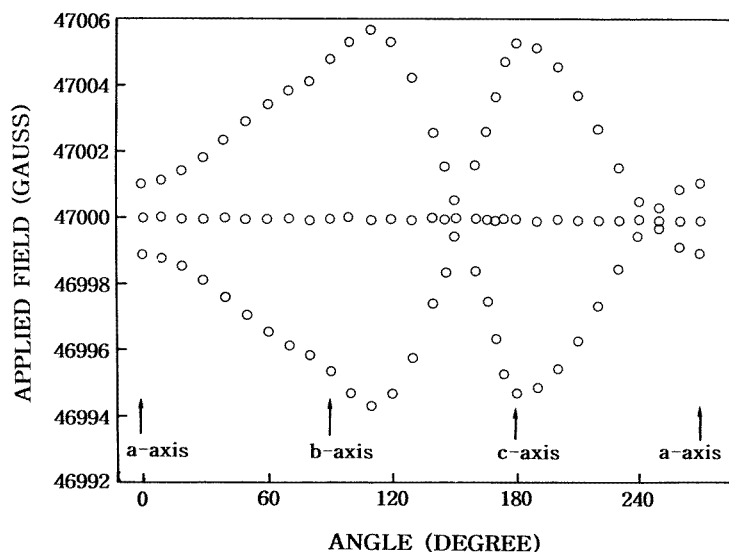


Figure 3. The rotation pattern of ^7Li NMR measured in the ab -, bc -, and ca -planes at room temperature.

axes. The EFG tensor of ^7Li was found to be non-axially symmetric, consistent with the crystal structure; the lithium ion is surrounded by oxygen atoms located at a slightly distorted tetrahedron.

The ^7Li NMR spectra were measured in the temperature range of from 140 K to 380 K. The ^7Li NMR spectrum consists of only three lines for all orientations of the crystal in the external magnetic field in the 205–380 K temperature range, as shown in figure 3. The splitting of ^7Li resonance lines slightly changed in the temperature range between 205 K and 380 K. While the central transition remained constant, the splitting between lines was found to decrease as the temperature increases. The parameters were determined by a least-squares fit to the experimental data. The nuclear quadrupole coupling constant and asymmetry parameter of ^7Li in an LiCsSO_4 crystal were determined as 22.35 kHz and 0.68 at room temperature. The direction of the principal EFG tensor for the Li ion at 300 K are represented with the Eulerian angles $\Phi = 90^\circ$, $\Theta = 20^\circ$ and $\Psi = 0^\circ$. These results are consistent with the previous report [18].

At the transition point of 200 K, the ^7Li NMR line splits into two lines. Two sets of ^7Li resonance lines indicates a phase transition takes place to a new phase with a lower symmetry than orthorhombic. The phase transition results in splitting of the ^7Li NMR line into two components demonstrating a change in the lithium site symmetry. Below 200 K, the ^7Li NMR spectra had only continuous quantitative changes in the quadrupole splitting distances, without any pattern changes or abrupt changes. One of the rotation patterns of the ^7Li NMR spectra measured in the ab -, bc - and ca -planes at 180 K is displayed in figure 4. The obtained results can be explained by the existence of two kinds of ferroelastic domain, rotated with respect to each other by 60° around the c -axis. From the experimental data, the principal axes of the ^7Li EFG tensor at room temperature are not the same as when it is below T_C . The principal axes X , Y and Z of the EFG tensor for the Li ion are found to lie along the Eulerian angles $\Phi = 70^\circ$, $\Theta = 15^\circ$ and $\Psi = 35^\circ$. The nuclear quadrupole coupling constant and asymmetry parameter of ^7Li in a LiCsSO_4 crystal were determined to be 26.90 kHz and 0.79 at 180 K.

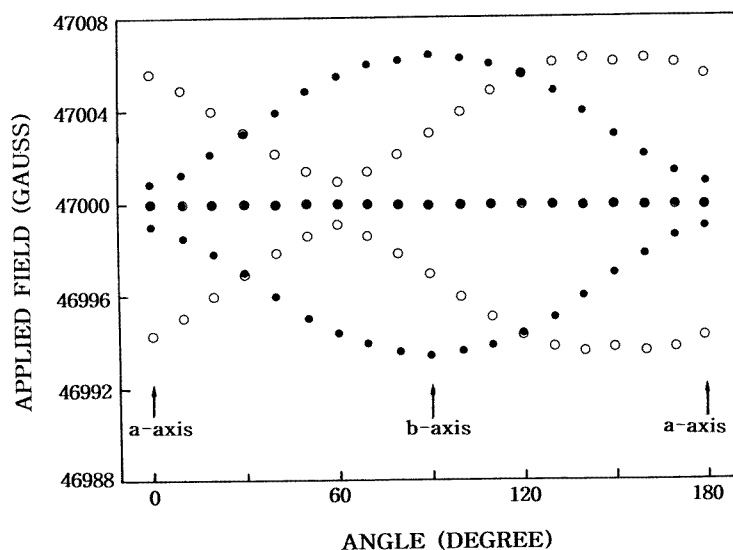


Figure 4. The rotation patterns of ^7Li NMR measured in the ab -plane at 180 K.

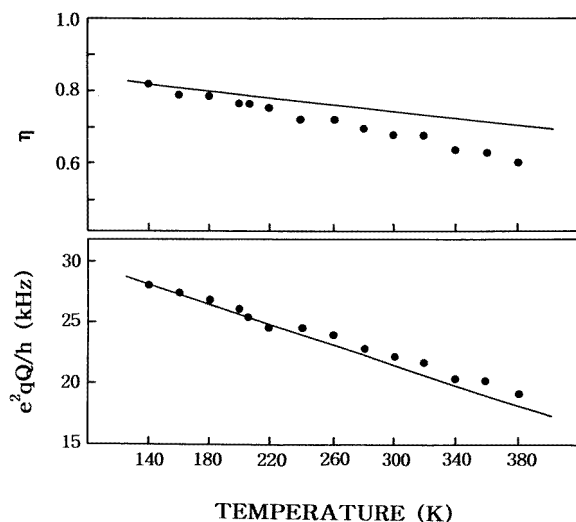


Figure 5. Temperature dependence of the nuclear quadrupole coupling constant and asymmetry parameter for ${}^7\text{Li}$ in a LiCsSO_4 single crystal. Measurements are indicated by the points. The solid lines are the predictions based on the theory of Bayer and of Wang.

The temperature dependence of e^2qQ/h and η in the temperature range of 140–380 K is shown in figure 5. From the experimental data, e^2qQ/h and η above and below 200 K were found to decrease almost linearly as a function of increasing temperature in this study. Only the principal axes of the ${}^7\text{Li}$ EFG tensor at room temperature are not same as when it is below T_C . This means that the phase transition is a second-order phase transition. A simple model by Bayer [24] and Wang [25], which ascribes the temperature dependence to a torsional oscillation of the Li–O group in LiCsSO_4 , was adopted in this study to better explain the temperature dependence of e^2qQ/h and η for ${}^7\text{Li}$. The temperature dependence of e^2qQ/h and η may be explained with a single torsional mode about the X -axis of the EFG tensor. If the terms of the second order in the angular displacement are retained, then the following equation holds [26]:

$$\begin{aligned} q' &= q[1 - (3 + \eta)\langle\theta_X^2\rangle/2] \\ \eta' &= \{\eta - (3 + \eta)\langle\theta_X^2\rangle/2\}/\{1 - (3 + \eta)\langle\theta_X^2\rangle/2\} \end{aligned} \quad (7)$$

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

$$I_i w_i^2 \langle\theta_i^2\rangle = \hbar w_i [1/2 + 1/\{\exp(\hbar w_i/kT) - 1\}] \quad (8)$$

where w_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, both e^2qQ/h and η decrease with the increasing temperature. The solid line in figure 5 is the prediction of e^2qQ/h and η for ${}^7\text{Li}$ with $I_x = 1.67 \times 10^{-45} \text{ kg m}^2$ and $w_x = 4.5 \times 10^{12} \text{ rad s}^{-1}$. Therefore, the theory of Bayer and Wang can explain our data in the temperature range of 140–380 K.

5. Discussion and conclusion

The phase transition by ^7Li NMR in a LiCsSO_4 single crystal grown by the slow evaporation method was investigated by employing a Bruker FT NMR spectrometer. From the experimental data, the quadrupole coupling constant, asymmetry parameter and the direction of EFG tensor were determined in the temperature range from 140 K to 380 K. In the temperature range between 140 K and 380 K, which includes the phase transition, there is no abrupt change in the parameter of ^7Li NMR. Only e^2qQ/h and η of the ^7Li nucleus decrease as temperature increases. However, the principal axes of the ^7Li EFG tensor below T_C are not the same as above T_C . The ^7Li NMR spectra demonstrate the occurrence of a second-order phase transition at 200 K which is connected with a lowering of the Li^+ site symmetry and formation of two kinds of ferroelastic domain.

In addition, the quadrupole coupling constants and asymmetry parameters of ^7Li in an LiCsSO_4 single crystal decrease as the temperature increases. The solid lines are the predicted values of e^2qQ/h and η for ^7Li with $w_x = 4.5 \times 10^{12}$ rad s $^{-1}$. The temperature dependence of e^2qQ/h and η is explained by a single torsional frequency of the Li–O group by the simple Bayer theory.

Acknowledgments

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