Temperature-dependent nuclear magnetic resonance study of ^{133}Cs in an LiCsSO$_4$ single crystal

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Abstract. Temperature dependence of the ^{133}Cs nuclear magnetic resonance in an LiCsSO$_4$ single crystal grown by the slow evaporation method has been investigated by employing an FT NMR spectrometer. From the experimental data, the quadrupole coupling constant, asymmetry parameter and direction of the EFG tensor were determined in the temperature range from 180 K to 400 K. The ^{133}Cs NMR spectra shows a phase transition at 200 K which is connected with the formation of three kinds of ferroelastic domain. The obtained results are explained by the existence of these three domains, rotated with respect to each other by 60° around the c-axis. The nuclear quadrupole coupling constant and asymmetry parameter obtained as functions of temperature for ^{133}Cs in an LiCsSO$_4$ single crystal are described by the linear equations $e^2qQ/h = 178 + 1.05 \times 10^{-1}(T - T_r)$ kHz and $\eta = 0.9221 - 2.33 \times 10^{-4}(T - T_r)$, respectively, in the temperature range 180–400 K.

1. Introduction

LiCsSO$_4$ single crystals undergo a phase 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 space group of the high temperature phase and that of the low temperature phase are $Pcmn$ and $P112_1/n$, respectively, without cell multiplication. 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 [3]. LiCsSO$_4$ crystals have been studied by x-ray diffraction [4, 5], Raman spectroscopy [6–8], EPR [9–13], NMR [14–16] and optical properties [17].

In this paper, we discuss the ^{133}Cs nuclear magnetic resonance (NMR) in an LiCsSO$_4$ single crystal grown by the slow evaporation method. The temperature dependence of 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 ^{133}Cs ($I = 7/2$) were determined with a pulse NMR spectrometer. Based on these results, we examine the phase transition and the ferroelastic property of an LiCsSO$_4$ single crystal.

2. Crystal structure

LiCsSO$_4$ is an orthorhombic structure with four molecular units per unit cell. The space group is $Pcmn$ and the point group is mmm, and the lattice constants $a = 9.456$ Å, $b = 5.456$ Å and

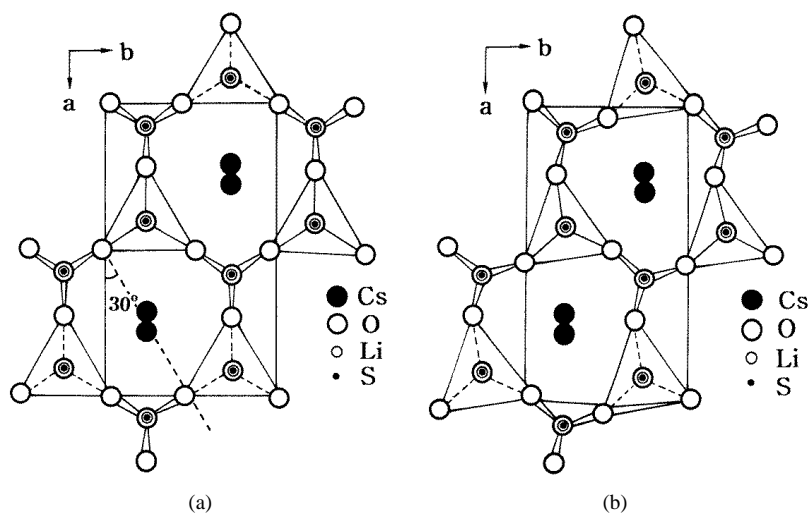‖ To whom all correspondence should be addressed.

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.

$c = 8.820$ Å. 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 ranging from 1.849 to 1.954 Å [4]. Figure 1(a) shows the projections of the atomic positions in the $Pcmn$ phase 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 $2/m$ [12]. The lattice parameters are $a = 9.379$ Å, $b = 5.423$ Å, $c = 8.834$ Å and $\gamma = 89.75°$. 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

Clear single crystals of LiCsSO$_4$ were grown at room temperature by slow evaporation from aqueous solution containing equimolar amounts of Li$_2$SO$_4 \cdot$H$_2$O and Cs$_2$SO$_4$. The transparent and colourless single crystals prepared were about $5 \times 5 \times 6$ mm^3. The crystals are hexagonal in shape and display a 60° twin structure. As samples for measurements, untwinned parts were selected from these crystals. The orientation of the crystal was identified using an 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.

Nuclear magnetic resonance signals of ^{133}Cs in the LiCsSO$_4$ single crystal were measured using a Varian 400 FT NMR spectrometer at the Korea Basic Science Institute in Taejon. The static magnetic field was 9.4 T and the central rf frequency was set at $\omega_0/2\pi = 52.484$ MHz. The NMR spectra of ^{133}Cs were recorded with a sequence of one 90° pulse, 60 scans and a repetition time of 10 s. A ring-down delay time of 3 μs was used to remove the effect of the pulse. The temperature-dependent NMR measurements were obtained using a previously reported method [18].
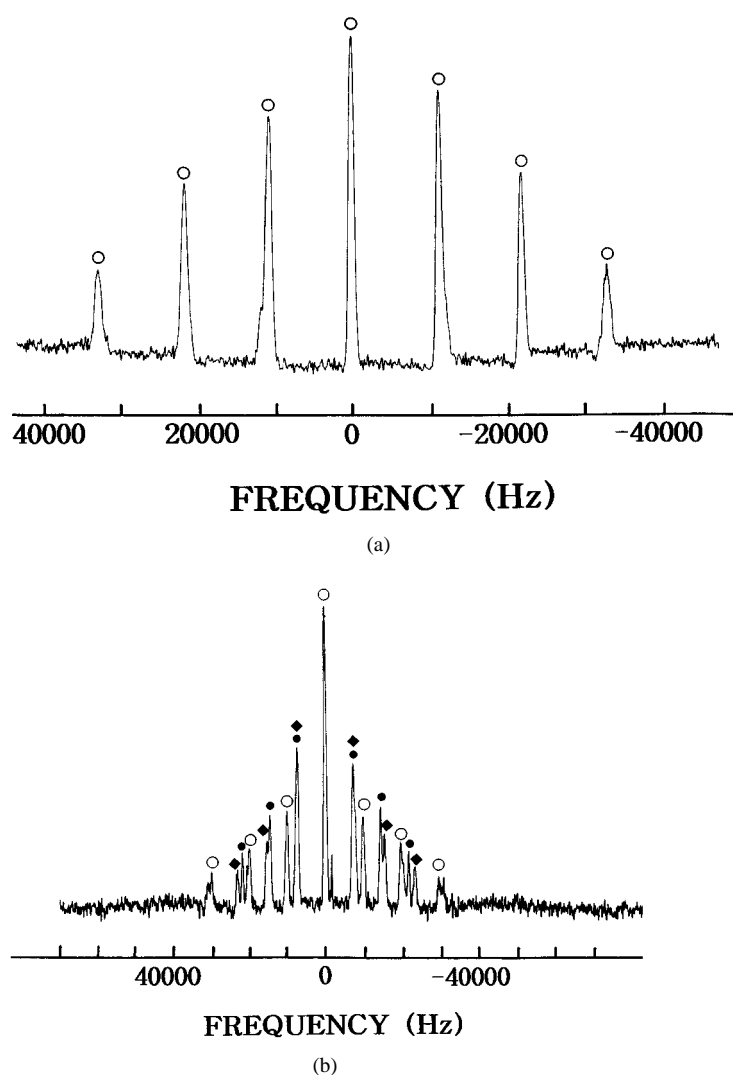
Figure 2. ^{133}Cs NMR spectra in the LiCsSO$_4$ crystal: (a) room temperature; (b) 180 K.

4. Experimental results and analysis

The seven-line structure is a result of the quadrupole interaction of the ^{133}Cs ($I = 7/2$) nucleus. A typical NMR spectrum of ^{133}Cs is shown in figure 2(a). Rotation patterns in three mutually perpendicular directions are required to determine the quadrupole interaction completely. The rotation patterns of ^{133}Cs NMR spectra measured in the three crystallographic planes at room temperature are displayed in figure 3. Because the resonance frequency of the central line is almost constant and the spacings between adjacent lines are equal, the first-order perturbation of the nuclear electric quadrupole term with respect to the Zeeman term may be sufficient for analysis [19, 20]. The satellite resonance lines show an 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 lines are angle independent. At this time, the satellite resonance lines did not
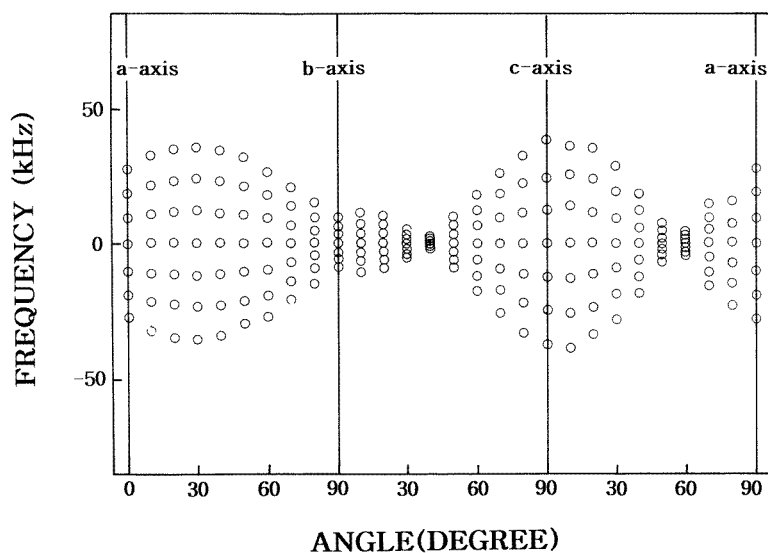
Figure 3. The rotation pattern of ^{133}Cs NMR measured in the *ab-*, *bc-* and *ca*-plane at room temperature.

show maximum or minimum separation in the crystallographic axis. The parameters were determined by a least-squares fit to the experimental data. The nuclear quadrupole coupling constant and asymmetry parameter of ^{133}Cs in a LiCsSO$_4$ crystal were determined as 181 kHz and 0.92 at room temperature. The direction of the principal EFG tensor for the Cs ion at 300 K is represented with the Eulerian angles $\Phi = 30°$, $\Theta = 10°$ and $\Psi = 30°$. These results are inconsistent with the previous report [14]. The geometric angles of the Cs–O bonds in the Cs–O polyhedra is approximately 30° to the *a*-axis as shown in figure 1. These directions are reasonably close to Eulerian angles $\Phi = 30°$.

In order to examine the temperature dependence of e^2qQ/h and η for ^{133}Cs in the LiCsSO$_4$ single crystal, the resonance spectra were measured at several temperatures in the range 180–400 K including the phase transition temperature. Originally, the seven-line structure was a result of the quadrupole interaction of the ^{133}Cs ($I = 7/2$) nucleus. The ^{133}Cs NMR spectrum consists of only seven lines for all orientations of the crystal in the external magnetic field in the 205–400 K temperature range. However, the ^{133}Cs NMR line splits into three set lines below the transition point of 200 K as shown in figure 2(b). Here, the signal for one set showed very strong intensity, while another signal showed weak intensity. One signal labelled by closed diamonds in these three groups is shown to be of very weak intensity. One of the rotation patterns of the ^{133}Cs NMR spectra measured in the *ab*-plane at 180 K is displayed in figure 4. The ^{133}Cs NMR lines were a superposition of the resonance lines of one domain and the lines rotated by a 60° angle with respect to the *c*-axis. The domain wall makes an angle of 60° and 120° with respect to the *a*-axis. The obtained results can be explained by the existence of three kinds of ferroelastic domain. This indicates that the LiCsSO$_4$ crystal below T_C has characteristics of a twin structure crystal. The emergence of three sets of ^{133}Cs resonance lines indicates that a ferroelastic phase transition takes place to a new phase with lower symmetry than the orthorhombic. From the experimental data, three parameters were observed with the same magnitude of the quadrupole coupling constant and the asymmetry parameter. The nuclear quadrupole coupling constant and asymmetry parameter of ^{133}Cs in
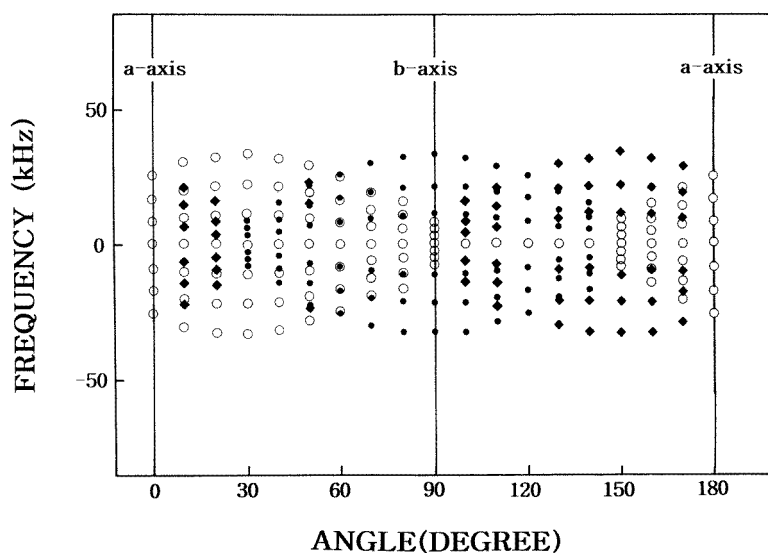
Figure 4. The rotation patterns of ^{133}Cs NMR measured in the *ab*-plane at 180 K.
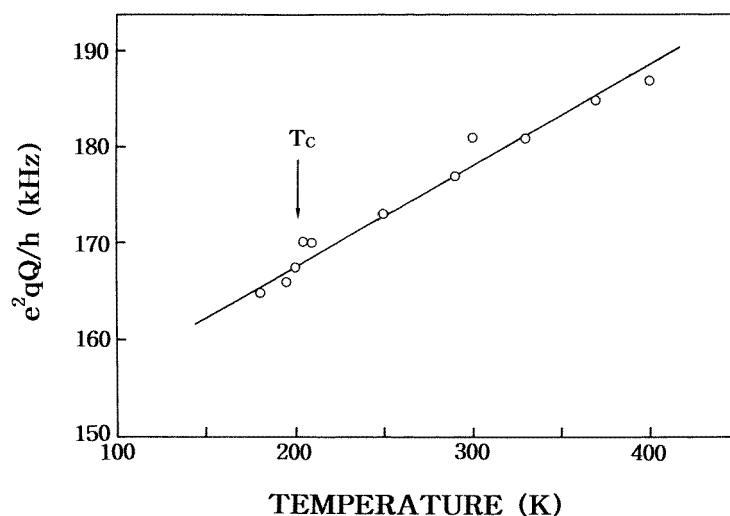

Figure 5. Temperature dependence of the nuclear quadrupole coupling constant, e^2qQ/h, for ^{133}Cs in an LiCsSO$_4$ single crystal.

an LiCsSO$_4$ crystal were determined to be 165 kHz and 0.953 at 180 K. The principal axes X, Y and Z of the EFG tensor for the Cs ion are found to lie along the Eulerian angles above T_C.

The ^{133}Cs NMR spectra had only continuous quantitative changes in the quadrupole splitting distances. The temperature dependence of e^2qQ/h for the ^{133}Cs nucleus is shown in figure 5 as open circles. The value of e^2qQ/h was found to increase as a function of increasing temperature, where the experimental data are described by the linear equation $e^2qQ/h = 178 + 1.05 \times 10^{-1}(T - T_r)$ kHz, as represented by the solid line. Here, T (K) is temperature and T_r (K) is room temperature. Generally, e^2qQ/h decreases as a function of
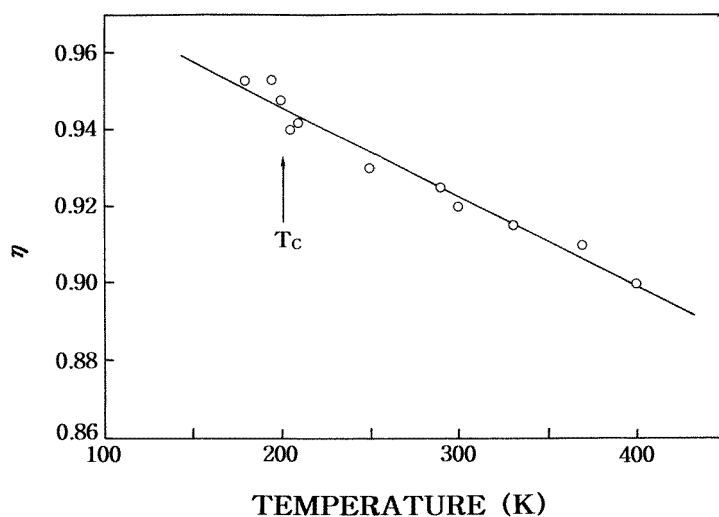
Figure 6. Temperature dependence of the asymmetry parameter, η, for ^{133}Cs in an LiCsSO$_4$ single crystal.

increasing temperature in many substances: that is, the slope $d\nu_Q/dT$ is negative. Conversely, however, e^2qQ/h for ^{133}Cs in LiCsSO$_4$ increases as the temperature increases. Figure 6 shows the temperature dependence of η, which decreases as the temperature increases. The solid line is the linear fit of η with a linear equation $\eta = 0.9221 - 2.33 \times 10^{-4}(T - T_r)$. This trend is similar to the temperature dependence of the ^{9}Be NMR in BeAl$_2$O$_4$ single crystals previously reported [21].

5. Discussion and conclusion

The phase transition by ^{133}Cs NMR in an LiCsSO$_4$ single crystal grown by the slow evaporation method was investigated by employing a Varian 400 FT NMR spectrometer. From the experimental data, the quadrupole coupling constant, asymmetry parameter and direction of the EFG tensor were determined in the temperature range from 180 K to 400 K. In the temperature range between 180 K and 400 K, which includes the phase transition, there is no abrupt change in the parameters of the ^{133}Cs nucleus. The principal axes of the EFG tensor for the Cs ion below T_C are same as above T_C. According to the ^{7}Li NMR results in LiCsSO$_4$ single crystals, in the temperature range between 140 K and 380 K, there is no abrupt change in the parameter of ^{7}Li NMR. Only the e^2qQ/h and η of the ^{7}Li nucleus decrease as temperature increases. However, the principal axes of the ^{7}Li EFG tensor below T_C are not the same as above T_C [16]. A change in the EFG tensor in ^{7}Li at T_C indicates that the LiO$_4$ tetrahedra are significantly affected during this transition. This is consistent with the observation that larger changes in the EFG tensor are obtained at the site of ^{7}Li than at ^{133}Cs at T_C. We conclude that the Cs ion plays only a minor role in this transition mechanism.

The ^{133}Cs NMR spectra demonstrate the occurrence of a phase transition at 200 K which is connected with the formation of these three domains. The obtained results can be explained by the existence of three kinds of ferroelastic domain, rotated with respect to each other by 60° around the c-axis. The quadrupole coupling constant of ^{133}Cs in an LiCsSO$_4$ crystal increases as the temperature increases. However, the asymmetry parameter decreases with increasing

temperature. The nuclear quadrupole coupling constant and asymmetry parameter obtained as functions of temperature for ^{133}Cs in LiCsSO$_4$ single crystals can be described by the linear equations $e^2qQ/h = 178 + 1.05 \times 10^{-1}(T - T_r)$ kHz and $\eta = 0.9221 - 2.33 \times 10^{-4}(T - T_r)$, respectively, in the temperature range 180–400 K.

Acknowledgments

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