A nuclear magnetic resonance study of the ferroelastic phase transitions of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ single crystals

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Ae Ran Lim

Department of Science Education, Jeonju University, Jeonju 560-759, Korea

E-mail: aeranlim@hanmail.net and arlim@jj.ac.kr

Abstract
Nuclear magnetic resonance (NMR) measurements were carried out for $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals over a range of temperatures. Two and three groups were observed in the ^{23}Na spectra of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals, respectively, which were found to become one group at the ferroelastic phase transition temperature, T_{C1}. These transitions to one resonance line from two and three resonance lines are associated with the crystals' ferroelastic phase transitions. The changes in the spin–lattice relaxation times, T_1, for the ^{23}Na and ^{39}K nuclei in two crystals indicate that there is a structural phase transition from the trigonal phase to the monoclinic phase in these crystals at T_{C1}. Further, our results for the shifts in the resonance frequencies for the ^{39}K central resonance lines show that these ferroelastic phase transitions are accompanied by shifts of the two crystallographically independent K^+ cations, and mainly affect the environment of K(2), which is the most loosely bound cation in the crystal structures. We conclude that shifts of the oxygen atoms in the chromate and selenate groups around the Na and K atoms also play important roles in these phase transitions. Therefore, the ferroelastic phase transitions in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals at $T_{C1} = 239$ K and $T_{C1} = 334$ K, respectively, are accompanied by slight changes in the respective geometries of the CrO_4 and SeO_4 tetrahedra around the Na and K atoms.

1. Introduction

Tripotassium sodium chromate, $K_3Na(CrO_4)_2$, and tripotassium sodium selenate, $K_3Na(SeO_4)_2$, belong to a family that can be described with the chemical formula $A_3C(BX_4)_2$, where A, C = Li, Na, K, Rb, or Cs, and BX_4 = SO_4, SeO_4, CrO_4, or MoO_4. Members of this family have been examined in many investigations into ferroelastic phase transitions [1–6]. $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals undergo several successive structural phase transitions [4, 6, 7]. In the case of $K_3Na(CrO_4)_2$ crystals, the melting point is 1160 K, with a high-temperature phase transition at 853 K and a low-temperature phase transition at 239 K. At $T_{C2} = 853$ K, the crystal undergoes a transition from a phase with $6/mmm$ symmetry to a phase with $\bar{3}m$ symmetry. Further, at $T_{C1} = 239$ K the crystallographic system changes from trigonal $\bar{3}m$

to monoclinic $2/m$. Below 239 K, $K_3Na(CrO_4)_2$ exhibits ferroelastic properties [8, 9]. In contrast, $K_3Na(SeO_4)_2$ crystals have a melting point of 1170 K, two high-temperature phase transitions, at 730 and 758 K, and two low-temperature phase transitions, at 334 and 346 K [10, 11]. On decreasing the temperature below 758 K, the crystal undergoes a transition from a phase with $6/mmm$ symmetry to a phase of unknown symmetry. On further lowering of the temperature, the crystal undergoes a transition at 730 K to a phase with $\bar{3}m$ symmetry. At $T_{C2} = 346$ K, the crystal symmetry decreases to $\bar{3}$ or 32, and then at $T_{C1} = 334$ K the crystallographic system changes from trigonal to monoclinic $2/m$. $K_3Na(SeO_4)_2$ exhibits ferroelastic properties at room temperature [12]. The respective high- and low-temperature phases of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ are isomorphous.

Nuclear magnetic resonance (NMR) is one of the most fruitful tools for the study of structural phase transitions. A wealth of information about the lattice dynamics of a system can be obtained from changes in the NMR spectra and relaxation times. Thus, to obtain information about the structural phase transitions that occur in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$, it is useful to measure their NMR spectra, the spin–lattice relaxation times, T_1, and the spin–spin relaxation times, T_2, for their ^{23}Na and ^{39}K nuclei as functions of temperature. However, very little experimental investigation of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ has been performed; only Raman scattering results for the ferroelastic phase transition [13], elastic constants [3, 14], and electron paramagnetic resonance (EPR) measurements [15–17] have been reported.

In the present study, we used a pulse NMR spectrometer to investigate the temperature dependences of T_1 and T_2 for the ^{23}Na and ^{39}K nuclei in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals grown via the slow evaporation method, with the aim of comparing their dynamic behaviors. The changes in the ^{23}Na and ^{39}K NMR relaxation behaviors near the phase transition temperatures are reported here. The focus of the present research was the investigation of the mechanism of the ferroelastic phase transitions in these crystals. In this paper, we compare our results for $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals, which have similar structures.

2. Crystal structures

2.1. K3Na(CrO4)2

The structure of $K_3Na(CrO_4)_2$ single crystals at 290 K is trigonal $P\bar{3}m1$ and the cell parameters are $a = 5.857$ Å and $c = 7.521$ Å [8]. There is one molecule per unit cell. Below T_{C1} (=239 K), this crystal exhibits ferroelastic properties, and the crystals have three domains oriented at 120° intervals. This crystal consists of CrO_4^{2-} tetrahedral anions, Na cations coordinated with six oxygen atoms in deformed octahedra, and two crystallographically inequivalent K(1) and K(2) cations with 10 and 12 oxygen atom coordination respectively. The two CrO4 tetrahedra inside each unit cell are oriented with their apices in opposite directions [18]. The trigonal structure of $K_3Na(CrO_4)_2$ is shown in figure 1. At 230 K, the space group of this phase is $C2/c$ with a monoclinic structure that has lattice constants $a = 10.128$ Å, $b = 5.8437$ Å, $c = 15.022$ Å, and $\beta = 89.97°$, and there are four molecules per unit cell. The Na–O distances in the NaO_6 octahedra are symmetry-restricted to a single value of 2.364 Å. The mean distances in the K(1)–O and K(2)–O polyhedra are 2.969 Å and 3.155 Å respectively, i.e. the K(1)–O bond is significantly shorter than the K(2)–O bond.

2.2. K3Na(SeO4)2

The structure of $K_3Na(SeO_4)_2$ single crystals at 291 K is monoclinic $2/m$ and the cell parameters are $a = 10.162$ Å, $b = 5.867$ Å, $c = 15.021$ Å, and $\beta = 90.00°$ [5, 10]. There are four molecules per unit cell. At room temperature, this crystal exhibits ferroelastic properties, and the crystals
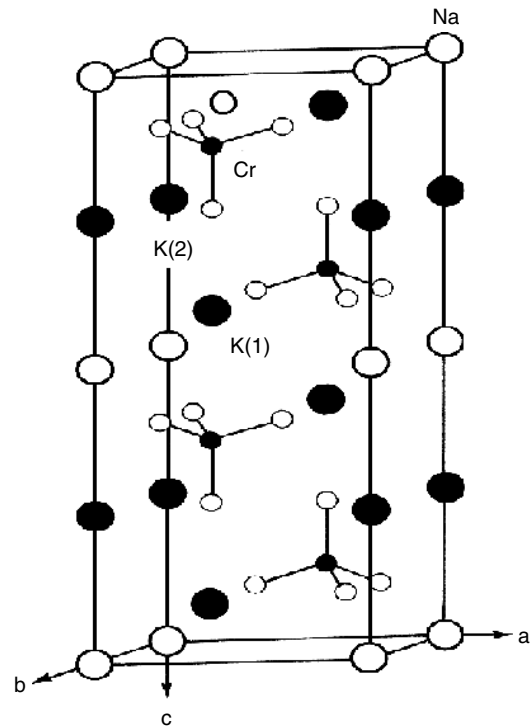

Figure 1. The trigonal phase of the $K_3Na(CrO_4)_2$ crystal. Two unit cells linked by the lattice transition along the c-axis are depicted.

are triple-twinned with a 120° domain structure. This crystal consist of SeO_4^{2-} tetrahedral anions, Na cations coordinated by six oxygen atoms in deformed octahedra, and two crystallographically inequivalent K(1) and K(2) cations with 10 and 12 oxygen atom coordination respectively. The symmetry of the phase (334–346 K) that is intermediate between the paraelastic $\bar{3}m$ and ferroelastic $2/m$ phases is trigonal with point group $\bar{3}$ [19]. The space group of this phase is $P\bar{3}c1$ with $a = 5.8725$ Å and $c = 7.5092$ Å, and there is one molecule per unit cell. The crystal structure of $K_3Na(SeO_4)_2$ in the paraelastic phase is similar to that shown in figure 1. Further, the crystal structure of $K_3Na(SeO_4)_2$ at 390 K is trigonal $\bar{3}m1$ with lattice parameters $a = 5.906$ Å and $c = 7.552$ Å [5], and there is one molecule per unit cell. The observed SeO4 tetrahedra are slightly distorted from ideal tetrahedra in all three phases [20].

3. Experimental method

Single crystals of $K_3Na(BX_4)_2$ ($BX_4 = CrO_4$, SeO_4) were grown at room temperature by slow evaporation from aqueous solutions containing K_2BX_4 and Na_2BX_4 in a molar ratio of 3:1. The $K_3Na(CrO_4)_2$ crystals have hexagonal and rectangular shapes, and are yellow-orange in color. The $K_3Na(SeO_4)_2$ crystals are colorless and transparent, and have hexagonal shapes.

The NMR signals of the ^{23}Na and ^{39}K nuclei in the $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ single crystals were measured
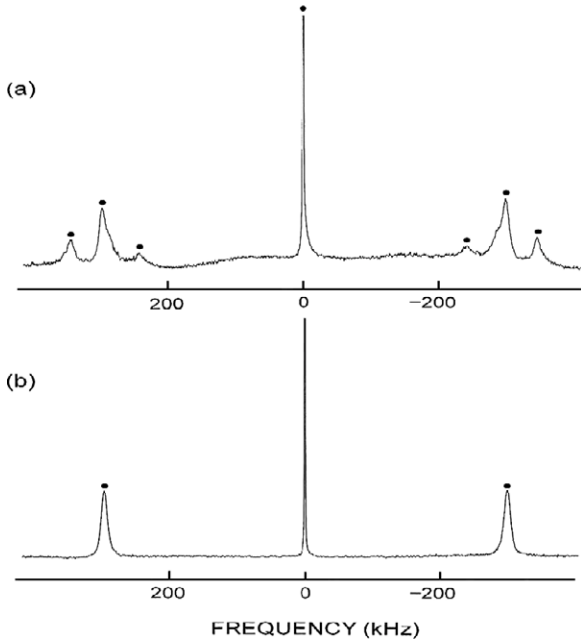
Figure 2a. ^{23}Na NMR spectra for $K_3Na(CrO_4)_2$ crystals: (a) below T_{C1} (=239 K) and (b) above T_{C1} (=239 K).

Figure 2b. ^{23}Na NMR spectra for $K_3Na(SeO_4)_2$ crystals: (a) below T_{C1} (=334 K) and (b) above T_{C1} (=334 K).

using the Bruker 400 FT NMR spectrometer at the Korea Basic Science Institute. The static magnetic field was 9.4 T, and the central radio frequency was set at $\omega_o/2\pi = 105.84$ MHz for the ^{23}Na nuclei, and at $\omega_o/2\pi = 18.67$ MHz for the ^{39}K nuclei. For the T_1 measurements, a π-t-$\pi/2$ pulse sequence was used in the ^{23}Na experiments, whereas a $\pi/2$-t-$\pi/2$ pulse sequence was used in the ^{39}K experiments. The spin–spin relaxation time, T_2, is defined as the characteristic time decay of the echo height in a spin-echo sequence. The widths of the π pulse were 7.14 μs for ^{23}Na and 9.5 μs for ^{39}K. The NMR measurements are temperature-dependent and were obtained over the temperature range 180–420 K. The samples were maintained at a constant temperature (accuracy, ±0.5 K) by controlling the nitrogen gas flow and the heater current.

4. Experimental results and analysis

The nuclear spin–lattice relaxation times were measured by monitoring the return to the equilibrium value of the nuclear magnetization following the π-t-$\pi/2$ and $\pi/2$-t-$\pi/2$ pulse sequences for the ^{23}Na and ^{39}K nuclei, respectively. The recovery laws for quadrupole relaxation in ^{23}Na ($I = 3/2$) and ^{39}K ($I = 3/2$) nuclear spin systems are nonexponential functions. The temperature dependence of the relaxation time is indicative of fluctuations in the electric field gradient (EFG) tensor that are driven by thermally activated hopping motion [21, 22]. For $I = 3/2$, the relaxation transition probabilities can be expressed as follows [23–25]:

$$W_1 = \frac{1}{12}\left[\frac{eQ}{\hbar}\right]^2 \int_{-\infty}^{-\infty} \langle V_1(0)V_{-1}(t)\rangle \exp(i\omega_L t)\,\mathrm{d}t$$
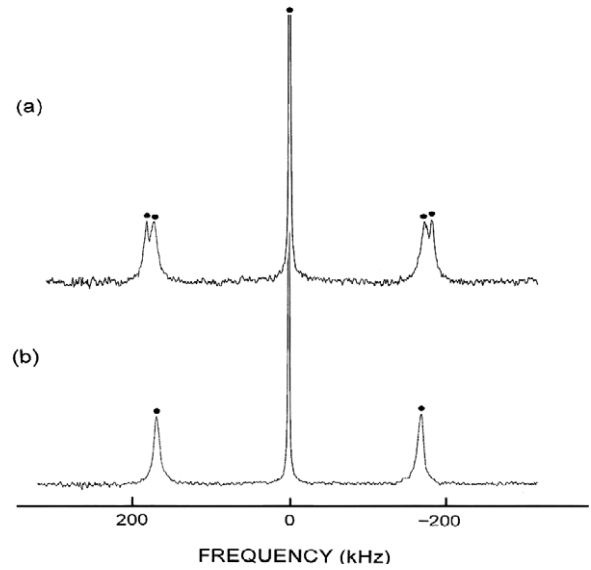$$W_2 = \frac{1}{12}\left[\frac{eQ}{\hbar}\right]^2 \int_{-\infty}^{-\infty} \langle V_2(0)V_{-2}(t)\rangle \exp(i2\omega_L t)\,\mathrm{d}t \tag{1}$$

where W_1 and W_2 ($n = 1, 2$) denote the ^{23}Na and ^{39}K spin–lattice transition rates corresponding to the $\Delta m = \pm1$ and $\Delta m = \pm2$ transitions, respectively.

The inversion recovery function can be described with the following equation when the central line is saturated [26, 27]:

$$[M(t) - M(\infty)]/M(\infty) = 0.5(\exp(-2W_1 t)$$
$$+\ 0.5\exp(-2W_2 t)) \tag{2}$$

where $M(t)$ is the nuclear magnetization corresponding to the central transition at time t after saturation. The spin–lattice relaxation time is given by

$$T_1^{-1} = [2(W_1 + 4W_2)]/5. \tag{3}$$

The ^{23}Na ($I = 3/2$) NMR spectra of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals usually consist of a central line and two satellite lines. The resonance lines of ^{23}Na were observed when the magnetic field was applied along the c-axis of the crystal. The ^{23}Na spectra of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ below and above their ferroelastic phase transition temperatures are shown in figures 2a and 2b, respectively. The zero point of the x-axis indicates the resonance frequency, 105.84 MHz, of the ^{23}Na nucleus. The satellite transitions are well resolved from the central line, and the signal intensity of the central line is stronger than those of the other lines, in both cases. The theoretical intensity ratio of the satellite lines and the central line is 3:4:3, as determined from the transition probabilities [26]. The experimentally observed intensity of the central line relative to the intensities of the satellite lines is much stronger than given by the theoretical ratio in both cases, due to the overlap of the central lines of the three or two groups. The central transition is virtually unshifted by the quadrupole interaction, and the splittings between the lines of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals were found to vary with temperature, as shown in figures 3(a) and (b), respectively. The ^{23}Na spectra do change near the phase
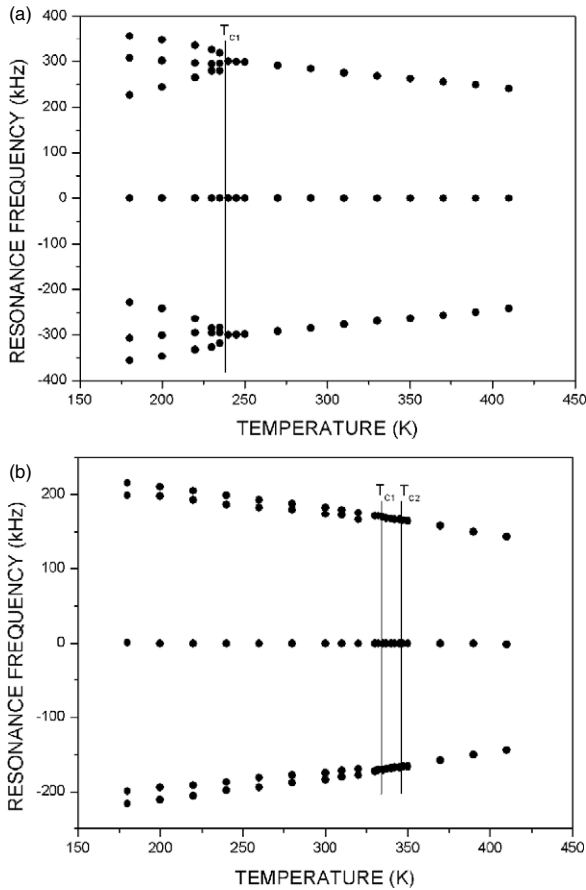
Figure 3. The splittings of the ^{23}Na resonance lines as functions of temperature: (a) $K_3Na(CrO_4)_2$ and (b) $K_3Na(SeO_4)_2$ crystals.
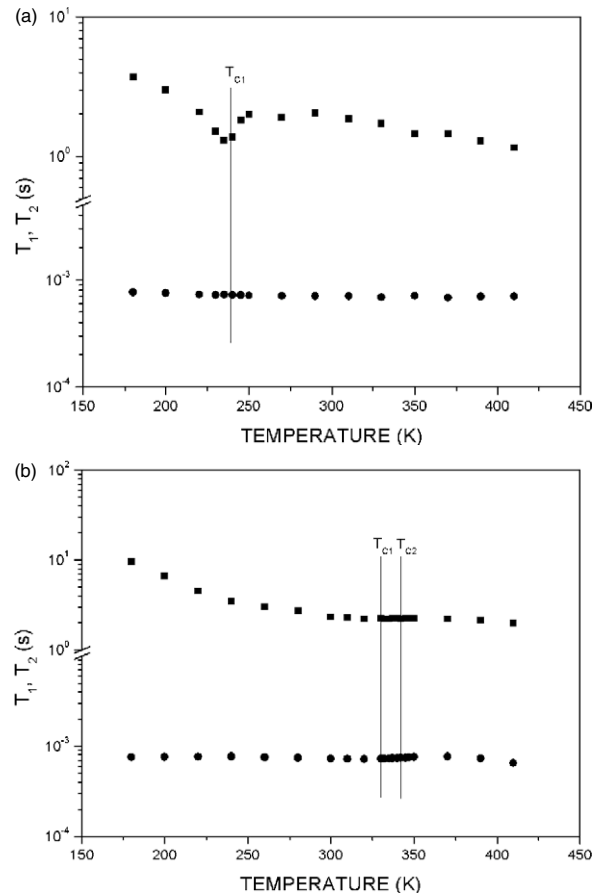

Figure 4. Temperature dependences of the spin–lattice relaxation time, T_1, and spin–spin relaxation time, T_2, for ^{23}Na (■: T_1 and ●: T_2): (a) $K_3Na(CrO_4)_2$ and (b) $K_3Na(SeO_4)_2$ crystals.

transition temperatures; there are two and three resonance lines for $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals, respectively, due to the number of orientations of their respective ferroelastic domains, i.e. two and three respectively. Above the phase transition temperatures, the splittings between the resonance lines decrease slightly with increasing temperature. The transitions to one resonance line from two and three resonance lines for the crystals indicate that their ferroelastic character has disappeared, and are associated with their ferroelastic phase transitions.

The nuclear magnetization recovery curves of the ^{23}Na nuclei in the two crystals were obtained by monitoring the nuclear magnetization after a saturation pulse at several temperatures. The spin–lattice relaxation time, T_1, in equation (2) was determined directly from the slope of a plot of $\log[(M(\infty) - M(t))/2M(\infty)]$ versus time t. The traces could be satisfactorily fitted with the double exponential function in equation (2). T_1 for ^{23}Na was obtained in terms of W_1 and W_2 using equation (3), and the temperature dependences of T_1 and T_2 for the ^{23}Na nuclei in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ are shown in figures 4(a) and (b), respectively. T_1 for the ^{23}Na nuclei in $K_3Na(CrO_4)_2$ crystals undergoes significant changes near 239 K, whereas T_2 for the ^{23}Na nuclei is nearly constant in the investigated temperature range, as shown in figure 4(a). Abrupt changes in relaxation times near temperatures associated with structural phase transitions have

been reported for a large number of compounds [28–30]. The transition at T_{C1} is due to the critical slowing down of the soft mode as the trigonal structure is converted to the monoclinic structure in this crystal. The relaxation times of the ^{23}Na nuclei undergo significant changes near 239 K, indicating that there are drastic alterations in the spin dynamics at the transition temperature. The changes in the T_1 curve near 239 K are associated with the second-order phase transition. In the case of $K_3Na(SeO_4)_2$ crystals, the relaxation times of the ^{23}Na nuclei do not undergo significant changes near T_{C1} and T_{C2}, as shown in figure 4(b). T_1 slowly decreases with increasing temperature. The spin–spin relaxation times, T_2, of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals were found to be nearly constant, on the order of 10^{-3} s. Here, T_2 was estimated from a single exponential fit $[M(t) \propto \exp(-t/T_2)]$ of the echo decay. T_2 is directly related to the line-width (narrower lines indicate a longer T_2), which can be linked to liquid-like behavior.

The ^{39}K ($I = 3/2$) NMR spectra consist of a pair of satellite lines and a central line. When the crystals are rotated about the crystallographic axis, crystallographically equivalent nuclei give rise to three lines: one central line and two satellite lines. The ^{39}K resonance lines were observed when the magnetic field was applied along the c-axis of the crystal. Instead of two or three resonance groups for
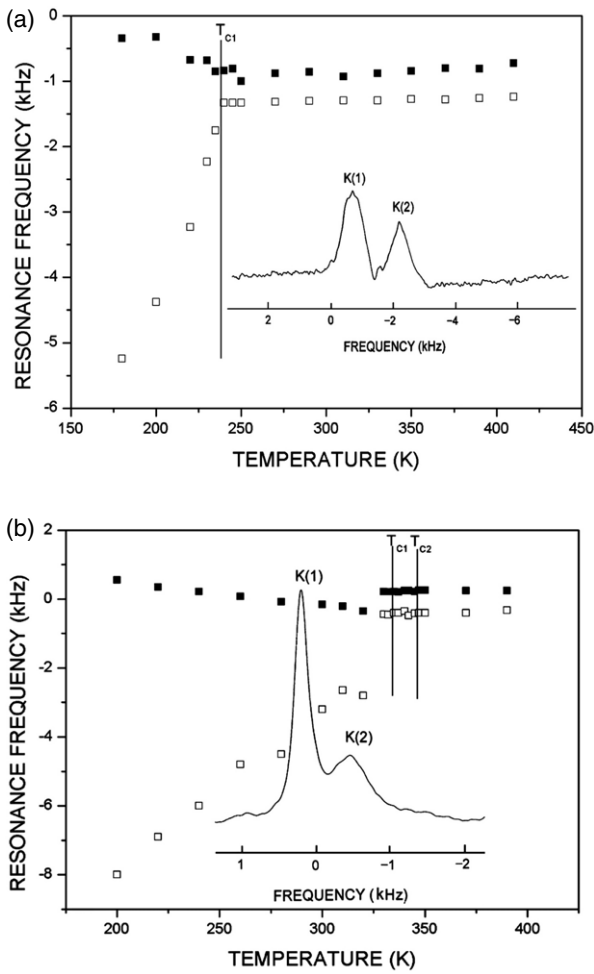
Figure 5. The variations with temperature of the central lines for the crystallographically inequivalent K(1) and K(2) nuclei in (a) $K_3Na(CrO_4)_2$ and (b) $K_3Na(SeO_4)_2$ crystals (■: K(1) and □: K(2)) (insets: ^{39}K NMR spectra).

Figure 6. Temperature dependences of the spin–lattice relaxation time, T_1, and spin–spin relaxation time, T_2, for K(1) and K(2) in (a) $K_3Na(CrO_4)_2$ and (b) $K_3Na(SeO_4)_2$ crystals.

the K(1) and K(2) nuclei in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals, only two central resonance lines for ^{39}K are obtained in the investigated temperature range. The magnitudes of the quadrupole parameters of ^{39}K nuclei are of the order of megahertz, so usually only central lines are obtained. Thus, the two resonance lines are for the central transition of the ^{39}K NMR spectra. In the case of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals, the two resonance lines in their spectra are associated with two crystallographically inequivalent positions of the K nuclei, K(1) and K(2), with two and one ions per unit cell, respectively, as shown in the insets in figures 5(a) and (b), respectively. Two or three satellite resonance lines for the ^{39}K nucleus corresponding to transitions between the level $(+2/3 - +1/2)$ and $(-1/2 - -2/3)$ are out of the frequency range of the NMR probe. Thus, the satellite resonance lines for inequivalent K(1) and K(2) due to ferroelastic domains below T_C could not be detected in this frequency range. In order to check the ferroelastic properties for these crystals, the stress–strain hysteresis curves were measured, and confirmed that the phase of these crystal below T_C is ferroelastic and that the phase above T_C is paraelastic. The resonance frequencies
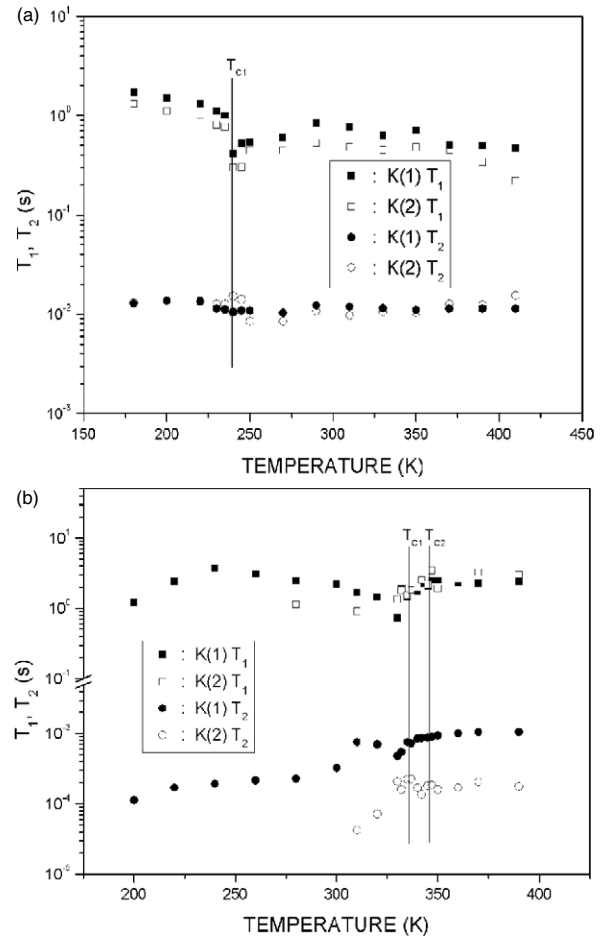
of the central lines for K(1) and K(2) change abruptly near the phase transition temperatures in both cases, as shown in figures 5(a) and (b). The change in the central line for the K(2) nuclei is larger than that for the K(1) nuclei, in both cases. Based on the second-order quadrupole shift in the central transition of the ^{39}K NMR spectra, two different K resonance groups with different resonance frequencies were obtained. From the shifts in the resonance frequencies of the central lines, we conclude that the quadrupole coupling constant of the K(2) nucleus changes significantly. Although the quadrupole coupling constant for K(1) below the phase transition temperature is significantly different to that of K(2), the quadrupole coupling constant for K(1) is similar to that of K(2) above the phase transition temperature, in both cases.

The nuclear magnetization recovery traces for ^{39}K in the two crystals were measured at several temperatures, and it was found that the saturation recovery traces of ^{39}K can be represented with the combination of two exponential functions, in both cases. T_1 for ^{39}K was obtained in terms of W_1 and W_2 using equation (2), and the temperature dependences of T_1 and T_2 for the ^{39}K nuclei in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals are shown in figures 6(a) and (b), respectively. In the case of $K_3Na(CrO_4)_2$ crystals, the values of T_1 for K(1)

and K(2) are nearly the same, and undergo significant changes near T_{C1} (=239 K). The phase transition at T_{C1} is second-order. This change in the temperature dependence of T_1 at T_{C1} for the ^{39}K nuclei coincides with the change in the behavior of T_1 for the ^{23}Na nuclei at this temperature. This type of anomalous decrease in T_1 around T_{C1} is usually indicative of a structural phase transition. The spin–spin relaxation time is nearly constant as the temperature is increased. The values of T_1 for K(1) and K(2) in $K_3Na(SeO_4)_2$ crystals are nearly the same within the experimental error, and the relaxation times for the ^{39}K nuclei undergo significant changes near T_{C1} (=334 K), indicating that there is a drastic alteration in the spin dynamics at this transition temperature. The trends for T_2 of K(1) and K(2) are very different; T_2 for K(1) is longer than that for K(2). T_1 and T_2 for the ^{39}K nuclei undergo significant changes near 334 K, whereas T_1 and T_2 for the ^{39}K nuclei do not vary significantly at 346 K. The transition at T_{C1} is due to the critical slowing down of the soft mode as the trigonal phase in this crystal is converted to the monoclinic phase. In the case of K(2), the potassium NMR line-width becomes narrower as the temperature increases. T_2 is directly related to the line-width, and thus T_2 increases above T_{C1}. Although the results for ^{23}Na relaxation provide no evidence of the phase transition at T_{C1}, ^{39}K relaxation changes abruptly at T_{C1}. Thus the T_1 of the ^{23}Na and ^{39}K nuclei depend on their local environments. The temperature dependences of T_1 and T_2 near T_{C2} are more or less continuous and are not affected by this phase transition.

5. Discussion and conclusion

NMR measurements were carried out at a range of temperatures for $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ single crystals grown using the slow evaporation method. $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals are isostructural in the paraelastic phase and undergo identical changes in space group symmetry at their ferroelastic phase transitions [5, 10–12]. $K_3Na(CrO_4)_2$ crystals undergo phase transitions at 239 and 853 K, whereas $K_3Na(SeO_4)_2$ crystals undergo successive phase transitions at 334, 346, 730, and 758 K. The mechanisms of the phase transitions of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals were investigated by means of ^{23}Na and ^{39}K NMR, and these NMR observations were found to provide a consistent description of the dynamics of the ^{23}Na and ^{39}K nuclei in these materials. The relaxation processes of ^{23}Na and ^{39}K in $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ single crystals were studied between 180 and 420 K. The ^{23}Na spectra of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals contain two and three groups, respectively, but at the ferroelastic phase transition temperatures there is only one group; thus these transitions to one resonance line from two and three resonance lines are associated with the crystals' ferroelastic phase transitions. The recovery traces for the central lines of ^{23}Na and ^{39}K with dominant quadrupolar relaxation cannot be represented with single exponential functions, but can be represented with combinations of two exponential functions. In $K_3Na(CrO_4)_2$ crystals, there are significant changes in T_1 for ^{23}Na and ^{39}K at T_{C1}, whereas T_2 is nearly constant at T_{C1}. These abrupt changes in the spin–lattice relaxation

times around T_{C1} are associated with the structural phase transition. In the case of $K_3Na(SeO_4)_2$, the relaxation times of the ^{23}Na nuclei do not undergo significant changes near T_{C1} and T_{C2}. There are significant changes in T_1 and T_2 for ^{39}K at T_{C1}, whereas T_1 and T_2 do not change significantly at T_{C2}. Although the results for ^{23}Na relaxation provide no evidence for the phase transition at T_{C1}, the ^{39}K relaxation changes abruptly at T_{C1}. This result indicates that the T_1 of the ^{23}Na and ^{39}K nuclei depend on their local environments. The role of structural changes is indeed relatively minor at T_{C2}. T_1 of the ^{23}Na and ^{39}K in both crystals are of the same order of magnitude, and have very similar trends with temperature. Although T_2 of the ^{39}K in the two crystals have similar trends, the order of magnitude of the T_2 values is different. The line-width for the ^{39}K nucleus in $K_3Na(CrO_4)_2$ crystals is narrower than that for ^{39}K in $K_3Na(SeO_4)_2$. This means that the motional narrowing of K ions in $K_3Na(CrO_4)_2$ is greater than that of K ions in $K_3Na(SeO_4)_2$. Thus, although the two crystals considered here have similar structures, their ^{39}K spin–spin relaxation times have different temperature dependences. Further, the phase transitions of the two crystals are accompanied by shifts in the resonance frequencies of the central lines of their K(1) and K(2) cations. The phase transitions mainly affect the K(2) environments. In the $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ single crystals, the changes in the EFG at the Na and K sites that are responsible for the observed T_1 anomalies originate mainly from variations in the motions of the nearest neighboring oxygen atoms. Further, the oxygen atoms linked by Cr and Se in the two crystals are also linked by Na and K atoms. From the NMR experimental results, the Na and K nuclei linked by oxygen atoms play an important role in the phase transitions. Thus these results suggest that shifts of the oxygen atoms in the chromate and selenate groups around the Na and K atoms also play an important role in the crystals' phase transitions. The ferroelastic phase transitions of $K_3Na(CrO_4)_2$ and $K_3Na(SeO_4)_2$ crystals occur at T_{C1} = 239 K and T_{C1} = 334 K, respectively, and are accompanied by slight changes in the geometries of the CrO_4 and SeO_4 tetrahedra around the Na and K atoms.

Acknowledgments

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