^{35}Cl NQR Study of Phase Soliton Formation and Residual Commensurations in K_2ZnCl_4

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In order to investigate the dynamics of the $ZnCl_4$ tetrahedra in K_2ZnCl_4, ^{35}Cl nuclear quadrupole resonance was employed for the spin-lattice relaxation measurements of each of the triplicated Cl sites in the lock-in phase. The temperature dependence of the spin-lattice relaxation rate ($1/T_{1Q}$) indicates that the domain peak observed in the incommensurate phase arises from the $ZnCl_4$ tetrahedral site with a negligible reorientational motion. On the other hand, an activated reorientational motion of the other two $ZnCl_4$ tetrahedral sites appears to lead to the phase solitons. Molecular motions in Rb_2ZnCl_4 and in Cs_2ZnCl_4, undergoing an incommensurate an not incommensurate phase transition, respectively, were also compared.

Key words: K_2ZnCl_4; ^{35}Cl NQR; Phase Soliton Formation; Residual Commensurations.

1. Introduction

K_2ZnCl_4 (KZC) shows one-dimensional incommensurate lattice modulation [1 - 3] and undergoes a phase transition at T_c = 403 K from the lock-in or improper ferroelectric (FE) to the incommensurate (IC) phase, and successively turns into a paraelectric normal (N) phase at T_I = 533 K. The low temperature polar (P) monoclinic phase arises below 145 K, and a very narrow IC phase in an interval of 0.027 K near (146.956 ± 0.002) K was reported recently [4].

The incommensurate lattice modulations along the pseudohexagonal symmetry axis, the c-axis [1, 2], can be described by a wavevector $\vec{q} = \frac{1}{3}(1 + \delta)\vec{c}^*$ [5 - 7]. Undergoing the lock-in transition, the incommensurate modulation commensurately locks in to $\delta = 0$, which leads to a unit cell triplication in the direction of the c-axis [7] with a spontaneous polarization along the a-axis, so that the crystal shows ferroelectricity [5]. It is well known that the important eigencomponents of such a lattice modulation are the rotation of the $ZnCl_4$ tetrahedra around the c-axis, and the translation of the $ZnCl_4$ group and the K^+ ion [8]. Thus, studies of the rotational motion of the tetrahedral group are important for understanding the lattice modulation and the incommensurability in A_2BX_4 systems.

A small rotational or translational displacement from the lattice modulation can be sensitively reflected by the quadrupole-perturbed NMR or NQR resonance condition of each local site. Therefore, ^{35}Cl and ^{81}Br NQR studies of some A_2BX_4 halide crystals have been extensively carried out to investigate the configuration and the dynamics of the tetrahedral anion group [6, 8 - 11]. In the "plane wave limit" with nearly harmonic incommensurate lattice modulations, the anomalous resonance line arising from the EFG modulation can be analyzed theoretically by the superposition of the spatially distributed NQR peaks. It can be expanded as a power series of the lattice displacement or, more precisely, the amplitude and phase of the lattice modulation which acts as a primary order parameter of the incommensurate to paraelectric transition [7].

In the "soliton limit" near the lock-in transition, on the other hand, the domains walls (discommensuration) coexist with the commensurate domains (residual commensuration). Such domain walls, in which

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the phase of the lattice modulation changes rapidly, are referred to as "phase solitons". Thus, the lock-in transition can be understood in terms of the formation and annihilation of such phase solitons [7]. In fact, Topič et al. observed the change of the phase soliton density through the phase transition by analyzing the resonance lines of quadrupole-perturbed ^{39}K (+1/2 → –1/2) NMR of K_2ZnCl_4 and K_2SeO_4 [12, 20].

Recently relaxation studies of NQR and quadrupole-perturbed NMR have been extensively carried out in order to investigate the dynamics of the incommensurate modulation [14 - 19, 23] and of the tetrahedral groups [8]. By employing NQR techniques, the shape and depth of the potential confining the tetrahedral anion and hindering its rotational motion can be estimated from the dynamics reflected in the temperature dependence of the spin-lattice relaxation [8]. It is the purpose of the present work to throw some light onto the detailed processes and dynamics concerning the formation of the phase solitons and commensurate domains by probing the dynamics of the triplicated $ZnCl_4$ tetrahedral groups in the lock-in phase by means of ^{35}Cl NQR spin-lattice relaxation measurements.

The existence of nearly commensurate domains regularly separated by phase solitons in the incommensurate Rb_2ZnCl_4 and Rb_2ZnBr_4 near the lock-in transition [13] has been evidenced by the appearance of additional domain components in an incommensurate continuum of the NQR spectrum while lowering the temperature to T_C. The incommensurate NQR line of solitons continuously turned into the discrete lines of the lock-in phase, which can be explained by the "narrowing" of the phase soliton width from the initially broader one [7]. However, the important issue of the origin of the residual commensuration has not yet been addressed, especially from the dynamical point of view. While there is little direct ^{35}Cl NQR observation of the formation of the phase soliton and the lock-in transition into discrete commensurate lines in K_2ZnCl_4, Milia et al. reported a domain peak [6], or a residual commensurate line extended to the IC phase from the NQR peaks in the lock-in phase. Nonetheless, the incommensurate NQR line of the phase soliton was presumably too weak to be observed, which was explained by the spreading of the incommensurate NQR line, as is supported by the large lock-in phase rotational amplitudes of the $ZnCl_4$ tetrahedra around the *c*-axis (±77.5°, ±40.0°, and ±42.5°, respectively) [6].

2. Experiment

A K_2ZnCl_4 single crystal was grown for this work by the Czochralski method in an Ar atmosphere, using a melt of potassium chloride and zinc chloride as the starting material. A portion of the single crystal was crushed for a powder sample for detection of all the NQR lines at the same time.

In the A_2BX_4-type crystals there are three inequivalent X (or Cl in the current case) sites in the commensurate paraelectric phase reflecting the crystal structure and molecular group configuration. For the commensurate lattice modulation, the NQR signal from those inequivalent sites will be multiplicated in the lock-in phase, resulting in three distinct NQR lines, labeled Cl(1), Cl(2), and Cl(3), respectively [6, 9, 11, 13]. Our measurements, employing a home-built pulsed NQR spectrometer, basically reproduced previously reported the temperature dependence of the ^{35}Cl NQR frequencies, and the measurements in the current work were made on the Cl(1) lines in the lock-in phase with a temperature stability within 10 mK.

The temperature dependence of the spin-lattice relaxation times (T_{1Q}) for each of the three distinct Cl(1) NQR lines resulting from the triplication of the unit cell in the lock-in phase was measured using the inversion recovery method in order to separately characterize the dynamics of the $ZnCl_4$ tetrahedra in each of the triplicated unit cells. The separations between the resonance peaks were too small in general for direct magnetization recovery measurements in the time domain. Therefore we obtained the spin-lattice relaxation time in the frequency domain by integrating each peak in a suitable window. Such a process was realized by including a Fourier transformation and integral routine in our automated T_1 measurement program.

The magnetization recovery was well fitted into a single-exponential form, thus defining a unique T_{1Q} at all temperatures investigated. The Cl(1) lines with the highest resonance frequencies, arise from the "polar site", for which the EFG (or Zn-Cl bond) axis is almost parallel to the direction of the lattice modulation, and were of our interest because of the better signal-to-noise ratio (S/N) and because of the apparent domain peak component which is extended to the incommensurate phase [6].

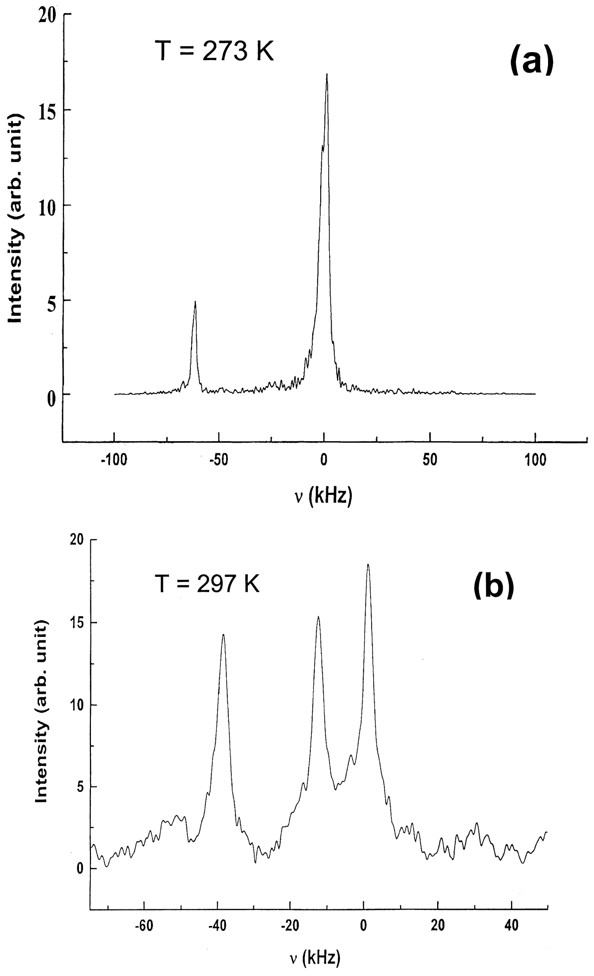

Fig. 1. ^{35}Cl NQR lineshapes of KZC obtained at (a) 273 K and (b) 297 K.

3. Results and Discussion

Figure 1 shows the ^{35}Cl NQR lineshapes obtained for the Cl(1) sites. Each of the ^{35}Cl(1) NQR lines, denoted as Cl(1)-1, Cl(1)-2, and Cl(1)-3, respectively, was carefully followed in the lock-in phase as shown in Fig. 2, reproducing the previously reported temperature dependence of the lines. The Cl(1)-1 line, previously seen as a domain peak or residual commensuration extended to the IC phase, exhibited a reasonable S/N ratio in the high temperature region.

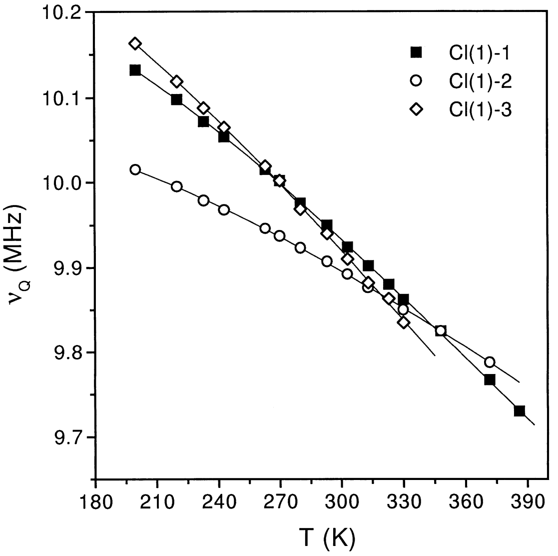

Fig. 2. Temperature dependence of the ^{35}Cl(1) NQR frequencies in KZC. The lines are guides for the eye.

Figure 3 shows the single-exponential spin-lattice relaxation patterns obtained for the T_{1Q} measurements of the Cl(1)-1 site, and the temperature dependence of our spin-lattice relaxation rate ($1/T_{1Q}$) on each of the Cl(1) sites in the lock-in phase is shown in Figure 4. Measurements of the spin-lattice relaxation times above 371 K were severely hampered by a significant line broadening [6].

In general, quadrupolar relaxation in symmetric molecular groups, corresponding to the $ZnCl_4$ tetrahedra in our case, can take place through two types of relaxation mechanisms. One is the random motion of librating molecules or any other type of vibration such as phonon modes, which is normally effective at relatively low temperatures and which follows a $1/T_{1Q} \propto T^m$ type temperature dependence of the spin-lattice relaxation rate [21, 22]. The other is molecular reorientations with the temperature dependence of $1/T_{1Q} \propto exp(-E_a/RT)$ for an Arrhenius type of dynamics, where E_a is the activation energy per mole. Thus, the temperature dependent NQR spin-lattice relaxation rate can be generally formulated as

$$T_{1Q}^{-1} = aT^2 + b\exp\left[-E_a/RT\right].$$

The Arrhenius type relaxation can be activated in the higher temperature region, where $T > E_a/R$. This activation, in general, enables one to find out the depth of the confining potential of the anion reorientation, which depends on the complex balance of the interatomic forces and the relative cation sizes hindering

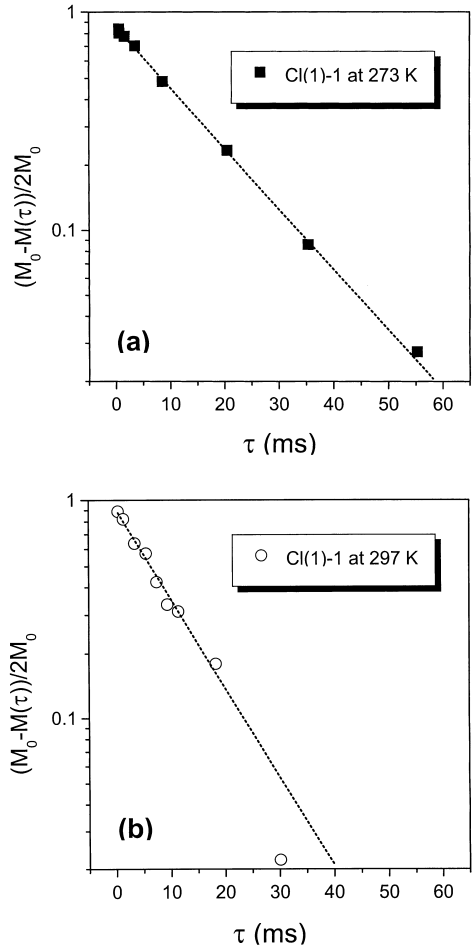

Fig. 3. ^{35}Cl NQR spin-lattice relaxation patterns of the KZC Cl(1)-1 site obtained at (a) 273 K and (b) 297 K.

the torsional motion around the axis of lattice modulation (the *c*-axis in our case) [8].

Among the three Cl(1) lines, distinct temperature dependences of the spin-lattice relaxation rate are noticed in Figure 4. One of them, the Cl(1)-1, which is the only line that was extended through T_C, shows a temperature dependence of T^m with $m = 4$ for most of the temperature range. On the other hand, the other lines obviously cannot be described by the simple power law dependence alone, but are shown to be dominated by the activation mechanism for most of the temperature range. The activation energy E_a for the reorientational motion of the $ZnCl_4$ tetrahedra, obtained from the fitting to (1), is 60 kJ/mol for Cl(1)-2 and 47 kJ/mol for Cl(1)-3, respectively.

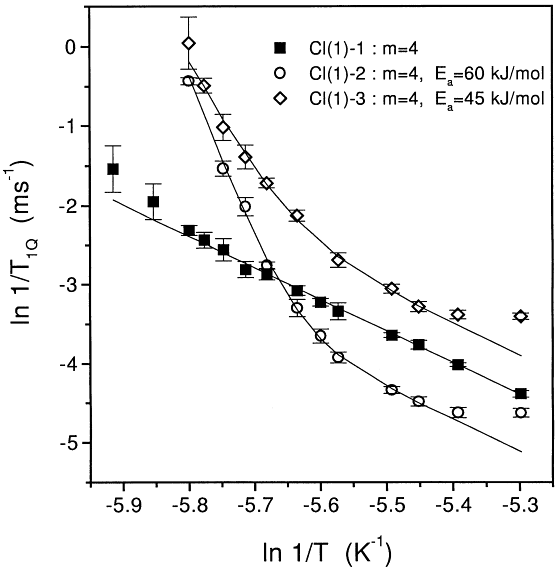

Fig. 4. Temperature dependence of the spin-lattice relaxation rate ($1/T_{1Q}$) for each of the triplicated Cl(1) sites. The temperature dependence of the Cl(1)-1 (■) spin-lattice relaxation was fitted to the simple power law of T^m, whereas those for Cl(1)-2 (○) and Cl(1)-3 (◇) were fitted to the form of $T_{1Q}^{-1} = aT^m + b\exp[-E_a/RT]$ in the view of the similar environments concerning the random motion, and the presence of the reorientational motions for those sites.

The simple power law behavior of the spin-lattice relaxation for the Cl(1)-1 site indicates that the reorientational motion of the Cl(1)-1 tetrahedral group is negligible in most of the temperature range of the lock-in phase, in contrast to the cases of Cl(1)-2 and Cl(1)-3. This relative reorientational immobility appears to offer an understanding of the origin of the domain peak arising from the Cl(1)-1 line, which showed a residual commensuration in the incommensurate phase near T_C.

It may be illuminating to compare the spin-lattice relaxation time measurements in other A_2BX_4 systems. Figure 5 shows the temperature dependence of T_{1Q} in the paraelectric phase for Rb_2ZnCl_4 (RZC), also undergoing a commensurate - incommensurate phase transition, and for Cs_2ZnCl_4 (CZC) with a large cation size, which does not undergo a commensurate - incommensurate phase transition. It is noticed that the spin-lattice relaxation in RZC can describe the molecular reorientations without the phonon terms, whereas in the case of CZC both terms are necessary. Thus, it appears that the molecular reorienations play a more important role in RZC, which may be relevant

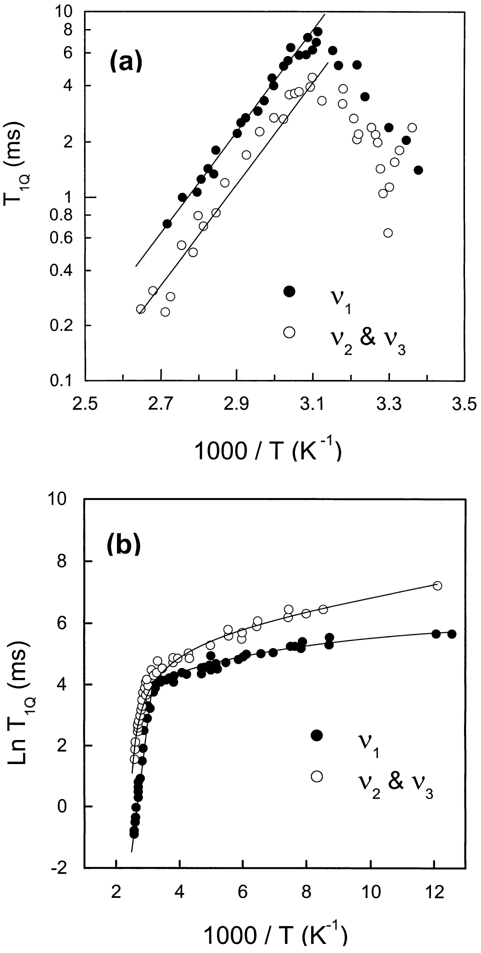

Fig. 5. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time for (a) Rb_2ZnCl_4 and (b) Cs_2ZnCl_4 (from [8]).

for the occurrence of the incommensurate phase in agreement with our arguments. The absence of NQR signals in the incommensurate phase of KZC can be attributed to the small cation size leading to very active $ZnCl_4$ tetrahedra.

As it appears that the incommensurate modulation arises mainly from the rotation of the $ZnCl_4$ tetrahedra, our results suggest that the formation of the phase solitons originates from the relatively active reorientation of the Cl(1)-2 and Cl(1)-3 sites. The relatively strong reorientational hindrance of the sites corresponding to the Cl(1)-1 line is believed to lead to the extension into the IC phase as a domain peak. In other words, the rotational motion of the Cl(1)-1 sites appears to be activated only at higher temperatures approaching T_C, as shown in Fig. 4, turning into the "plane wave limit". The rotational dynamics of each tetrahedral group in the lock-in phase appears to explain the residual commensuration from the Cl(1)-1, and the phase soliton formation from the other sites through the lock-in to incommensurate phase transition, in spite of no direct observation of the NQR signals in the incommensurate continuum. In the dynamics of the $ZnCl_4$ tetrahedra of the triplicated lattice the rotational motion about the Zn-Cl(1) axis is dominant, whereas the rotational or torsional motion about the other axes is comparatively small in amplitude and considered unimportant [23]. It can also be noticed that, while significant line broadening takes place between 371 and 386 K, no corresponding change takes place in T_{1Q}, supporting the previous observation that the line broadening is not due to the T_1 mechanism [6].

In summary, ^{35}Cl NQR spin-lattice relaxation measurements were employed in order to study the dynamics of the $ZnCl_4$ tetrahedra in the lock-in phase of K_2ZnCl_4. As a result, the origin of the residual commensuration in the incommensurate phase was attributed to the relative immobility of one of the $ZnCl_4$ tetrahedral sites. Besides, the molecular motions in Rb_2ZnCl_4 undergoing an incommensurate phase transition and Cs_2ZnCl_4 undergoing no incommensurate phase transition, were compared in view of the origin of the incommensurate phases.

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