NQR Investigation of Anion Dynamics in Rb$_2$Zn(Cl$_{1-x}$Br$_x$)$_4$ *

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The structural stability of Rb$_2$Zn(Cl$_{1-x}$Br$_x$)$_4$ (x = 1% and 3%) is investigated using the $^{35}$Cl quadrupole resonance frequency and spin lattice relaxation time ($T_1\Omega$) in the paraelectric (PE) phase. The PE to incommensurate (IC) phase transition temperature $T_1\Omega$ observed at 302 K in the pure compound, is lowered to 300 K for x = 1% and to 293 K for x = 3%. These effects are smaller than in the earlier reported case of 3% Cs substitution in Rb$_2$ZnCl$_4$, which reduces $T_1\Omega$ by 25 K. While bigger cation substitution affects only the barrier for anion dynamics about directions perpendicular to the a-axis (direction of low temperature IC modulation wave), bigger anion substitution is found to affect the barrier for anion dynamics about the a-axis as well. The present study also indicates that the cusp like dip in $T_1\Omega$ observed while approaching $T_1\Omega$ from above (characterizing the soft mode condensation associated with the structural phase transition) is essentially unaffected by anion impurity substitution, in contrast to the case where bigger cation substitution tends to smear the transitional effects. These results seem to suggest the dominant role played by cations in stabilizing the PE phase of these A$_2$BX$_4$ systems, in comparison to anions.

Key words: NQR, A$_2$BX$_4$ systems, Anion dynamics, Structural stability, Incommensurate phases.

1. Introduction

The structural stability of compounds belonging to the A$_2$BX$_4$ family (A = Alkali; B = Metal; X = Halogen) and their correlation to the BX$_4$ anion dynamics has recently attracted considerable attention [1–5]. Most of the compounds belonging to this family undergo a second order phase transition from their high temperature paraelectric (PE) phase to an incommensurate (IC) phase at a temperature $T_1\Omega$. It is widely believed that the size of the cation (A) in relation to the anion (BX$_4$) plays a major role in these phase transitions [4, 5]. For example, while an increase in the cation size leads to a dramatic reduction in $T_1\Omega$ (for a given anion), an increase in the anion size results in an increase in $T_1\Omega$ (for a given cation), though not as dramatic as in the earlier case [6, 7]. The primary role of the cation in deciding the phase transition temperature is rather well established [4], but the subtleties of the phase transition phenomena are usually related to the rotational dynamics of the BX$_4$ anion. In order to understand the role of cation/anion on the structural stability of the PE phase, an investigation of the influence of substitutional disorder in the cation/anion sites seems to be necessary. Such an attempt could be undertaken by substituting the cation/anion in a well studied incommensurate system, for example Rb$_2$ZnCl$_4$, and by studying the influence of substitution on the phase transition temperature and associated changes in the anion dynamics.

Recent attempts to substitute Cs (a bigger cation) in Rb$_2$ZnCl$_4$ as an impurity lead to a significant suppression of the transition temperature $T_1\Omega$, in addition to stabilizing the incommensurate phase remarkably, as evidenced by $^{35}$Cl NQR studies [2, 3]. For x = 5% of this mixed system with bigger cation impurity, (Rb$_{1-x}$Cs$_x$)$_2$ZnCl$_4$, $T_1\Omega$ was suppressed by about 45 K. Interestingly, these studies in the PE phase have indicated that the potential barrier for anion dynamics about the crystallographic a-axis (incommensurate modulation wave propagates along this direction in the low temperature incommensurate phase) remains insensitive to cation substitution [2]. On the other hand, for dynamics about directions perpendicular to the a-axis (perpendicular motions), the potential is found to become increasingly anharmonic with Cs substitution, suggesting a strong correlation of perpendicular motions with the phase stability.

Since it is the rotational dynamics of the anion which is crucially involved in mediating this transition, an attempt to substitute the anion itself could perhaps yield interesting results, especially regarding the dynamic processes near the transition tempera-
nature. In this context, the present work is concerned with an investigation of anion dynamics in the mixed system \( \text{Rb}_2\text{Zn(Cl}_{1-x}\text{Br}_x\text{)}\text{Cl}_4 \) (for \( x = 1\% \) and \( 3\% \)) in the PE phase. The PE to IC transition temperature \( T_i \) is 302 K in \( \text{Rb}_2\text{ZnCl}_4 \) and 347 K in \( \text{Rb}_2\text{ZnBr}_4 \), and curiously both systems undergo a lock-in transition from the incommensurate phase to a commensurate phase (wherein the commensurability is restored) at the same temperature, \( T_C \) (192 K), suggesting a negligible role of anions in affecting the lock-in transition temperature. In the present work the details of such dynamics processes are studied using \( ^{35}\text{Cl} \) quadrupole resonance and relaxation as a function of temperature.

2. Experimental Details

Polycrystalline samples of \( \text{Rb}_2\text{Zn(Cl}_{1-x}\text{Br}_x\text{)}\text{Cl}_4 \) (with \( x = 1\% \) and \( 3\% \)) were grown by repeated recrystallization through slow vaporization of an aqueous solution containing the respective chlorides and bromides in stoichiometric ratios at about 310 K, and dried thoroughly to remove moisture. The value of \( x \) quoted represents the stoichiometric values of the compounds used in the preparation of the samples. The exact amount of impurity that is present in the system was not independently estimated. NQR studies were made using a home made pulsed NQR spectrometer. The temperature dependences of the NQR frequencies of these rather broad signals (typical \( T_i^* \approx 50 \mu \text{s} \)) were determined by employing a Hahn spin echo sequence, and the quadrupolar spin lattice relaxation time \( T_{1Q} \) measurements were made using an inversion recovery spin echo sequence \((\pi - \tau - \pi/2 - \tau' - \pi, \text{with } \tau' \text{ fixed at } 250 \mu \text{s})\). These measurements are accurate to within \( \pm 1 \) kHz in frequency and to within \( 5\% \) in \( T_{1Q} \). However, the \( T_{1Q} \) values for \( x = 3\% \) above 330 K are accurate only to within \( 10\% \) due to considerable line broadening arising due to Bromine substitution. The sample temperature was controlled to within 0.1 K, employing a gas-flow cryostat using dry air.

3. Results

As in the pure compound three \( ^{35}\text{Cl} \) NQR frequencies, corresponding to an inequivalence among the different chlorine sites, were observed in the mixed compounds [1, 2], and the intensities of all the lines decreased appreciably on doping substitution. The assignment of these frequencies arising from the three inequivalent chlorines, due to different Zn-Cl bond lengths in the Zn\( \text{Cl}_4 \) tetrahedron (Fig. 1), is rather well established.

The temperature \((T)\) variation of all the frequencies is essentially linear. The PE to IC transition is characterized by a sudden line broadening, with a quasi-continuous distribution of the NQR frequency at lower temperatures. On approaching the paraelectric to incommensurate transition temperature \((T_i)\) from above, all the lines broaden considerably. While the distribution of the NQR frequency due to incommensurability for the \( v_H \) site could be followed into the incommensurate phase, \( v_M \) and \( v_L \) are broadened considerably making their observation below \( T_i \) very difficult. With increasing temperature, the NQR frequency of all the lines steadily decrease, and a typical fade out phenomenon is observed above 370 K for all the three lines. The temperature variation of \( v_H \) is faster than that of \( v_M \) and \( v_L \), both of which seem to vary similarly. With increasing Br impurity concentration, the temperature coefficients of NQR frequency, \( dv/dT \), of all the lines steadily decrease (Table 1). While \( dv_H/dT \) decreases from \(-2 \) kHz/K (pure compound) to \(-1.4 \) kHz/K for \( x = 3\% \), \( dv_L/dT \) decreases from \(-0.7 \) kHz/K to \(-0.5 \) kHz for \( x = 3\% \).

Figures 2 and 3 show the variation of \( T_{1Q} \) with temperature for the \( v_H \) and \( v_L \) lines, respectively, for all the three compounds \((x = 0, 1\% \) and \( 3\%) \). The salient
Table 1. NQR spectral parameters (dv/dT in kHz/K; E_a in kJ/mole; v(0) in MHz; T_i in K).

<table>
<thead>
<tr>
<th>Compound</th>
<th>High (perpendicular)</th>
<th>Low (parallel)</th>
<th>T_i</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dv/dT</td>
<td>E_a</td>
<td>v(0)</td>
</tr>
<tr>
<td>Rb_2ZnCl_4</td>
<td>-2.0</td>
<td>58</td>
<td>10.292</td>
</tr>
<tr>
<td>1% Br</td>
<td>-1.6</td>
<td>49</td>
<td>10.155</td>
</tr>
<tr>
<td>3% Br</td>
<td>-1.4</td>
<td>20</td>
<td>10.082</td>
</tr>
<tr>
<td>1% Cs</td>
<td>-1.7</td>
<td>48</td>
<td>10.082</td>
</tr>
<tr>
<td>3% Cs</td>
<td>-1.3</td>
<td>39</td>
<td>10.078</td>
</tr>
</tbody>
</table>

Fig. 2. Temperature (T) variation of spin lattice relaxation time (T_i Q) of v_H in Rb_2Zn(Cl_1-xBr_x)_4 for x = 0, 1% and 3%. The straight lines through the data points (of x = 1% and 3%) are fits to an Arrhenius behavior.

Fig. 3. Temperature (T) variation of the spin lattice relaxation time (T_i Q) of v_L in Rb_2Zn(Cl_1-xBr_x)_4 for x = 0, 1% and 3%. The straight lines through the data points (of x = 1% and 3%) are fits to an Arrhenius behavior.

Features are: (i) T_i Q of v_H is longer than that of v_L; (ii) the T_i Q-values for both v_H and v_L exhibit a cusp-like minimum at T_i. The cusp-like behavior of T_i Q near T_i seems to become more pronounced and sharper with increasing Br impurity concentration; (iii) T_i Q tends to increase with increasing temperature above T_i, reaching a maximum at around 330 K; and (iv) above this temperature, the T_i Q values of both sites exhibit an Arrhenius type behavior. With increasing temperature, T_i Q becomes smaller, and ultimately the T_i Q values are too small to be measured above 370 K. From Figs. 2 and 3 it is seen that T_i Q of each site becomes longer with increasing Br substitution. For example, the T_i Q value which is about 1 ms for v_H at 360 K in the pure compound increases considerably to about 4 ms for x = 3%. T_i Q of v_L also becomes longer with substitution (0.6 ms and 1.5 ms in the pure and x = 3% compound, respectively, at 360 K).

Quadrupolar relaxation in these systems with a symmetric molecular group in this temperature range (above 330 K) is primarily due to sudden and infrequent rotational motions of the ZnCl_4 anion, overcoming their hindering potential barriers. This leads to a strong quadrupolar coupling between the spin system and the lattice, with a relaxation rate [8]

\[ T_i Q^{-1} = b \exp (-E_a / RT), \]

where E_a is the activation energy corresponding to this motion and b is an appropriate constant. Table 1 summarizes the values of E_a calculated at the v_H and v_L sites as a function of impurity concentration. It is seen that the E_a's measured at both sites decreased considerably with Br substitution. The variation of T_i with Br impurity concentration, measured from the cusp in the T_i Q-data and line broadening, is given in Figure 4. It is seen that T_i at 302 K in the pure system is suppressed to about 300 K for x = 1%, and to 293 K for x = 3%.

4. Discussion

The present study focuses on the influence of the substitution of a bigger anion (ZnBr_4) on the phase transition behavior of Rb_2ZnCl_4 and associated anion dynamics. Due to the tetrahedral symmetry of the ZnCl_4 anion (Fig. 1), NQR can in principle distinguish two types of processes, viz. anion dynamics about the crystallographic a-axis (say parallel motions) and about directions perpendicular to the a-axis (say per-
of torsional motions given by

$$\langle \Theta \rangle^2 = \frac{\hbar}{8\pi^2c} \sum (I_i v_i)^{-1} \sin^2 \alpha_i \coth \frac{hc v_i}{2kT}. \quad (3)$$

Here $v_i$ and $I_i$ are the frequency and moment of inertia, respectively, associated with the $i$th normal mode, and $\alpha_i$ is the angle between the quantizing axis of the field gradient and the axis about which the rotation of the Zn-Cl bond takes place. From (2), estimates of mean square amplitudes for torsional motions could be obtained from a known temperature variation of the NQR frequency. Over the limited temperature range employed here, and for the purpose of comparison of relative differences among inequivalent sites, the variation of NQR frequency with $T$ could be essentially considered linear, and the observed rate of variation can be directly correlated with mean square amplitudes $\langle \Theta \rangle^2$. Further, estimates of the barrier heights encountered for such motions are obtained from relaxation studies (as a function of temperature), provided such anion motions are effective in mediating the spin lattice relaxation processes in the appropriate temperature range.

Table 1 presents the $dv/dT$ and $E_a$ values for the $v_H$ and $v_L$ sites as a function of Br impurity concentration. It is observed that the barrier heights, which are almost equal for both types of motions in the pure compound, steadily decrease with increasing Br concentration, though the value for perpendicular motions seems to decrease more rapidly than that for parallel motions. It is also observed that the mean square amplitudes characterizing parallel and perpendicular motions ($dv/dT$ values of $v_L$ and $v_H$, respectively) decrease with increasing Br substitution. Interestingly, earlier studies with a bigger cation, Cs, in Rb$_2$ZnCl$_4$, although leading to a dramatic reduction in $T_1$ (Fig. 4), indicated a reduction in the barrier height and mean square amplitude of perpendicular motions only [2] with almost no change in corresponding parameters of parallel motions. Figures 5 and 6 show the temperature ($T$) variation of $T_{1Q}$ of $v_H$ and $v_L$ (characterizing perpendicular and parallel motions, respectively) for (Rb$_{1-x}$Cs$_x$)$_2$ZnCl$_4$ ($x = 3\%$) and Rb$_2$Zn(Cl$_{1-x}$Br$_x$)$_4$ ($x = 3\%$). For the sake of comparison, the data of pure Rb$_2$ZnCl$_4$ are also presented in the same figures.) While Cs substitution does not lead to any change in the $T_{1Q}$ values of $v_L$, those of $v_H$ are significantly increased. On the other hand, Br substitution makes the $T_{1Q}$ values of both $v_H$ and $v_L$ longer (hence a reduction in $E_a$ for both motions). This
observation is also quantified in Figs. 7 and 8, wherein the Br/Cs impurity concentration (x) dependence of £ for parallel and perpendicular motions is presented. It is noted that £ for both motions is reduced by Br substitution, while only the £ for perpendicular motions is affected (reduced) with Cs substitution. It is particularly interesting to relate this observation with the experimental fact that the reduction in £ with Br substitution is smaller than with Cs substitution (Figure 4). For example, while 3% Cs in Rb$_2$ZnCl$_4$ suppressed $T_i$ by 25 K, 3% Br in Rb$_2$ZnCl$_4$ suppresses $T_i$ only by 9 K. A linear fit of the observed variation of $T_i$ with x for the Br/Cs substitution in Rb$_2$ZnCl$_4$ yields a $dT_i/dx$ value of $-860$ K/at.% for Cs substitution and a $dT_i/dx$ value of only $-307$ K/at.% for Br substitution, perhaps suggesting that the influence of substitution on the relative changes in the spectral parameters of both motions has to be properly accounted for in explaining the variation of $T_i$ with x.
To put these observations in perspective, earlier studies with a bigger cation impurity suggested that such a substitution affects only the perpendicular motions, leaving the barrier for parallel motions to be totally decided by the host system [2]. If this scenario were to be acceptable, the present study (with a bigger anion substitution), wherein the barrier height for perpendicular motions has decreased considerably from 58 kJ/mole to 20 kJ/mole for x = 3% Br, should have resulted in a much more dramatic reduction in $T_I$, keeping in view that 3% Cs reduces such a barrier height only to 39 kJ/mole (Figure 7). But, while Cs substitution leaves the barrier height for parallel motions almost unchanged (Fig. 8), Br substitution reduces such a barrier height also (59 kJ/mole to 39 kJ/mole for 3% Br). Thus, Br substitution seem to result in a change in the crystal structure in all three directions, while Cs substitution preferentially affects only the coupling of anions along the axis of interest, viz., the a-axis. Since the IC modulation wave propagates along the a-axis, the dominant role played by the Cs impurity cation on the PE phase stability is now understood.

Another interesting observation from the present study is the cusp like dip in $T_{1Q}$ observed near $T_I$. On approaching $T_I$ from above, the $T_{1Q}$ values start decreasing rapidly, thereby indicating a structural phase transition associated with a soft mode condensation [11]. From Figs. 5 and 6, it is seen that Br substitution essentially leaves the dip almost unaffected, while Cs substitution seem to make the dip distinctly shallower, thereby indicating a smearing out of the transition. Coupled with the above observation that Cs substitution preferentially affects the perpendicular motions of anion dynamics in contrast to the uniform changes in all directions with Br substitution, this smearing out of the transition with Cs impurity suggests again the dominant role played by cations on the PE phase stability.

5. Conclusions

The presence of a bigger cation/anion (Cs/Br) impurity in Rb$_2$ZnCl$_4$ leads to, in general, a reduction in the PE to IC phase transition temperature ($T_I$), but for a comparable concentration level of impurities, cation substitution leads to a more dramatic reduction in $T_I$. Interestingly, such an impurity preferentially distorts the coupling of anions along the a-axis, while similar anion substitution distorts the coupling of anions about directions perpendicular to the a-axis as well. Keeping in view the one dimensional nature of the IC modulation wave in the low temperature IC phase, the observations signify the importance of coupling of anions about the a-axis in mediating the phase transition. Further, a bigger anion impurity seems to leave the signatures of the phase transition essentially unaffected, while a bigger cation impurity discernibly smears out the transition effects.

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