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The influence of impurity cation size on the structural stability of $(\text{Rb}_{1-x}\text{M}_x)_2\text{ZnCl}_4$ ($x = 0.03$; $\text{M} = \text{Na}, \text{K}, \text{NH}_4$, Rb and Cs)—a ^{35}Cl NQR study

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Abstract. The influence of the size of the cation impurity (M) on the dynamics of the ZnCl_4 anion and on the structural stability of the $(\text{Rb}_{1-x}\text{M}_x)_2\text{ZnCl}_4$ system ($\text{M} = \text{Na}, \text{K}, \text{NH}_4$ and Cs) is investigated through ^{35}Cl NQR frequency and relaxation studies as a function of temperature. The mean square amplitude of torsional motions of ZnCl_4 tetrahedra about an axis parallel to the a -axis of the crystal structure and about axes perpendicular to this direction, as well as the corresponding activation energies, are estimated from the experimental data. The results show that, while parallel motions are insensitive to the presence of impurity, the perpendicular motions develop an anharmonic potential when the impurity cation is larger than the host cation, which also suppresses the structural phase transition temperature. Smaller impurity cations, on the other hand, have minimal effect on the anion dynamics and on the phase transition temperature.

1. Introduction

A large number of compounds belonging to the A_2BX_4 family ($\text{A} = \text{K}, \text{NH}_4, \text{Rb}$; $\text{B} = \text{Zn}, \text{Cd}, \text{Hg}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) typically exhibit a phase sequence involving an intermediate incommensurate phase (paraelectric– T_1 –incommensurate– T_c –commensurate) and the mechanism for such structural instabilities in these compounds has been a topic of considerable interest [1–3]. There are, however, a few other members of this family, like Cs_2ZnCl_4 and Cs_2ZnBr_4 , which do not exhibit any phase transition down to the lowest temperatures investigated [4, 5]. Recent studies have indicated that the size of the cation in relation to that of the anion plays a major role as regards the presence or otherwise of an instability in this family [6, 7]. The incommensurate phase is characterized by the propagation of a modulation wave (with a wave vector which is irrational with respect to the lattice periodicity) along the crystallographic a -axis in this family. It is also observed that the anion dynamics and interlayer couplings are very different in a compound exhibiting a phase transition (Rb_2ZnCl_4) from those in one which does not (Cs_2ZnCl_4) [6]. In the Rb compound, the hindrance for torsional motions of the ZnCl_4 anion around an axis parallel to the a -axis (nearly coinciding with one of the $\text{Zn}-\text{Cl}$ bonds), referred to as ‘parallel motions’, and around axes perpendicular to the a -axis (perpendicular motions), are found to be essentially the same (58 kJ mol^{-1}), while the potential barrier for parallel motions is relatively anharmonic exhibiting a double-well-type structure [6]. On the other hand in the compound with a stable paraelectric phase, Cs_2ZnCl_4 , the potential barrier for parallel motion is harmonic and high (78 kJ mol^{-1}) but the perpendicular motions seem to experience a double-well-type potential barrier with the same barrier height as in Rb_2ZnCl_4 (58 kJ mol^{-1}). Subsequent

work on $(\text{Rb}_{1-x}\text{Cs}_x)_2\text{ZnCl}_4$ led to the observation that, while the nature of the potential barrier for parallel motions is least affected by the presence of impurities, the potential for perpendicular motions seems to become anharmonic (development of a double-minimum barrier) and this anharmonicity is correlated with the dramatic improvement in the stability of the paraelectric phase [7]. The impurity cation used in such investigations is bigger than the host cation, and the corresponding compound, Cs_2ZnCl_4 has a very stable paraelectric phase. While T_i is profoundly reduced with the presence of a bigger cation as impurity, the presence of smaller cations as the impurity in Rb_2ZnCl_4 (for example K or NH_4) increases rather than decreases T_i , and even that marginally [8]. Since the rotational dynamics of the anion and the cavities available for cations within the cages formed by the anions are expected to play a dominant role in the structural stability of this family, extensive ^{35}Cl NQR measurements were carried out in the paraelectric phase of Rb_2ZnCl_4 doped with different impurity cations for a given doping concentration, in order to investigate the role of impurity cation sizes in the anion dynamics and hence the structural stability in this A_2BX_4 family.

2. Experimental details

The systems investigated are $(\text{Rb}_{1-x}\text{M}_x)_2\text{ZnCl}_4$ (for $x = 0.03$ and $\text{M} = \text{Na}, \text{K}, \text{NH}_4, \text{Rb}$ and Cs). All these were grown by slow evaporation of an aqueous solution containing the respective chlorides in stoichiometric ratios. These crystals were further purified by recrystallization and dried to remove moisture. The value of x quoted here gives the stoichiometry values of M_2ZnCl_4 used in the preparation of the samples, and the amount of impurity present was not independently verified. Dried polycrystalline samples were used for the NQR studies using a home-built pulsed NQR spectrometer. The temperature dependence of the NQR frequencies was determined by employing the Hahn spin-echo sequence whereas the quadrupolar spin-lattice relaxation rate (T_{1Q}) measurements were made by using an inversion-recovery spin-echo sequence ($\pi-\tau-\pi/2-\tau'-\pi$, with τ' fixed at $180 \mu\text{s}$). These measurements are accurate to within ± 1 kHz in frequency and to within 5% in T_{1Q} . The sample temperature was controlled to within 0.1 K, employing a gas-flow cryostat using dry air for temperatures above the room temperature and liquid nitrogen vapours for lower temperatures.

3. Results

Three ^{35}Cl NQR frequencies, corresponding to inequivalence among the different chlorine sites, were observed for all the compounds. The highest frequency (ν_1) is due to the chlorine atom (say Cl(1)) whose Zn-Cl bond is along the a -axis. The middle frequency (ν_2) is due to the chlorine atom Cl(2) lying in the mirror symmetry plane together with Cl(1). The remaining two chlorines, both called Cl(3), in the ZnCl_4 tetrahedron are equivalent (by mirror symmetry) and these give rise to the lowest frequency (ν_3) with double the intensity of the other two lines. Earlier observations on some of the A_2BX_4 compounds and also on the mixed systems $(\text{Rb}_{1-x}\text{Cs}_x)_2\text{ZnCl}_4$ ($x = 0.005, 0.01, 0.03$), as well as the present system have shown that the temperature variation of the frequency and the values of T_{1Q} for ν_2 and ν_3 are essentially the same [6, 7], and hence results are presented and discussed only for ν_1 and ν_3 .

The temperature variation of the NQR frequencies (ν_1 and ν_3) in a compound with the smallest impurity cation size (Na) and a compound with the biggest impurity cation size (Cs) are shown in figures 1 and 2 respectively. It is seen that $d\nu_1/dT$ is much higher than

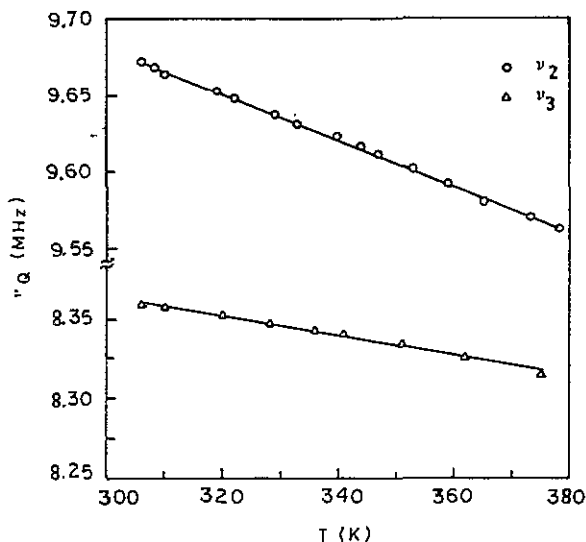


Figure 1. The temperature dependence of ^{35}Cl NQR frequencies in $(\text{Rb}_{1-x}\text{Na}_x)_2\text{ZnCl}_4$ for $x = 0.03$.

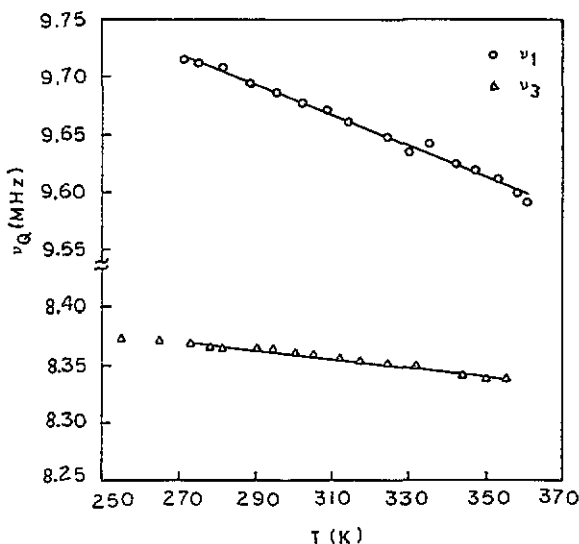


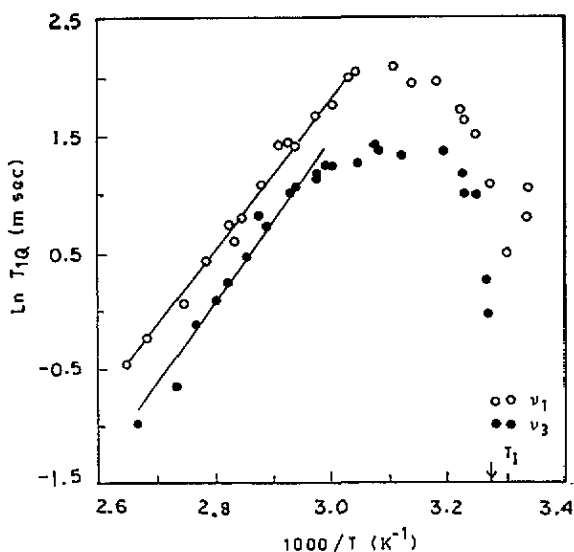
Figure 2. The temperature dependence of ^{35}Cl NQR frequencies in $(\text{Rb}_{1-x}\text{Cs}_x)_2\text{ZnCl}_4$ for $x = 0.03$.

$d\nu_3/dT$ for all of the compounds (table 1). Interestingly the values of these parameters are almost the same as those observed for the pure Rb_2ZnCl_4 for all impurity cations of smaller size (i.e. Na, K and NH_4). On the other hand, for the compound with a heavier impurity cation (Cs), the rate of variation in NQR frequency with temperature for the ν_1 -site has decreased from about 2 kHz K^{-1} to 1.3 kHz K^{-1} while such values for the ν_3 -site seem to be unaffected (typically around 0.6 kHz K^{-1}).

Figures 3 and 4 show the variation in T_{1Q} with temperature for ν_1 - and ν_3 -lines for two compounds (with Na or Cs as the impurity). In all of the compounds, T_{1Q} for ν_1 is

Table 1. Dynamic parameters in the $(\text{Rb}_{1-x}\text{M}_x)_2\text{ZnCl}_4$ system for $\text{M} = \text{Na}, \text{K}, \text{NH}_4, \text{Rb}$ and Cs .

M	R (Å)	x	$d\nu/dT$ (± 0.05 kHz K^{-1})		E_a (± 2 kJ mol^{-1})		T_1 (K)
			ν_1	ν_3	ν_1	ν_3	
Na	0.97	0.03	-1.5	-0.6	58	58	305
K	1.33	0.03	-1.5	-0.7	59	56	305
NH_4	1.43	0.03	-1.5	-0.6	59	59	303
Rb	1.47	0.03	-2.0	-0.7	58	59	302
Cs	1.67	0.03	-1.3	-0.5	39	58	277

**Figure 3.** The temperature dependence of the quadrupolar spin-lattice relaxation time T_{1Q} in $(\text{Rb}_{1-x}\text{Na}_x)_2\text{ZnCl}_4$ for $x = 0.03$.

longer than that for ν_3 . T_{1Q} -values for both ν_1 and ν_3 show a cusp-like minimum at T_1 and start to increase with increase in the temperature, reaching a maximum value at around 330 K. Above this temperature, T_{1Q} exhibits an Arrhenius type of behaviour. Quadrupolar relaxation in these symmetric molecular groups in this temperature range (above 330 K) is primarily due to sudden and infrequent reorientations of the molecules overcoming their hindering potential barriers, and this leads, in the case of quadrupolar interaction, to a strong coupling between the spin system and the lattice. In such a case, the relaxation rate can be expressed as [9]

$$T_{1Q}^{-1} = b \exp[-E_a/RT] \quad (1)$$

where E_a is the activation energy corresponding to this motion, R is the universal gas constant and b is the proportionality constant. Table 1 summarizes the values of E_a for different lines as a function of impurity cation radii. Interestingly, E_a calculated at the ν_1 -site with Cs as the impurity is lower than that for other impurity cations (table 1 and figure 5). On the other hand, E_a measured at the ν_3 -site is rather insensitive to the size of the impurity cation.

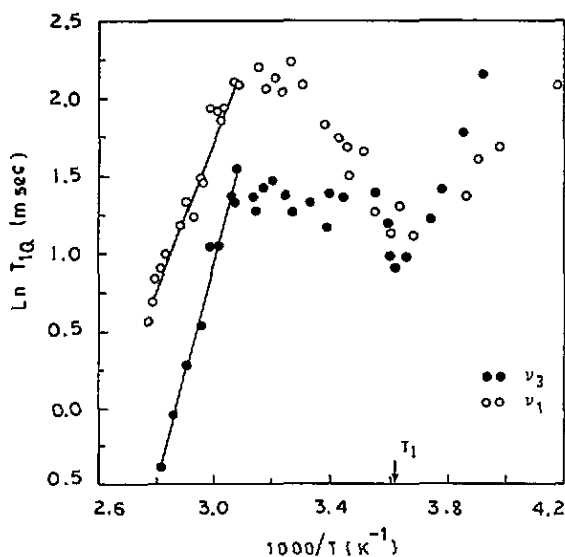


Figure 4. The temperature dependence of the quadrupolar spin-lattice relaxation time T_{1Q} in $(Rb_{1-x}Cs_x)_2ZnCl_4$ for $x = 0.03$.

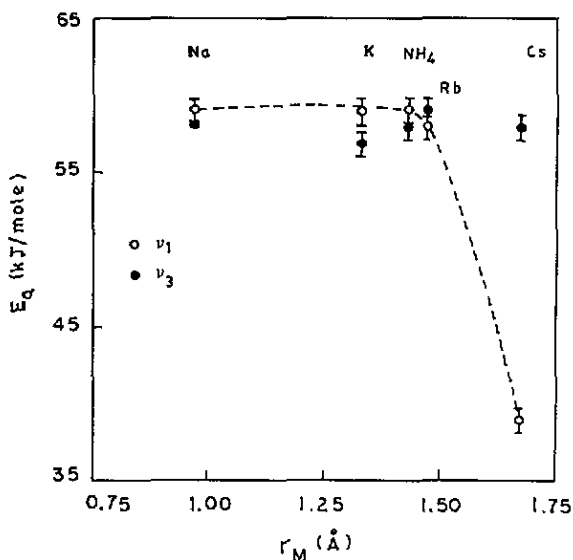


Figure 5. The variation of E_Q with different impurity cation sizes in the system $(Rb_{1-x}M_x)_2ZnCl_4$ for $x = 0.03$.

The variation of T_1 with impurity cation size measured from the cusp in the T_{1Q} -data is given in figure 6. It is seen that the presence of smaller impurity cations only marginally increases T_1 , while T_1 has decreased by almost 25 K for a heavier impurity cation (Cs).

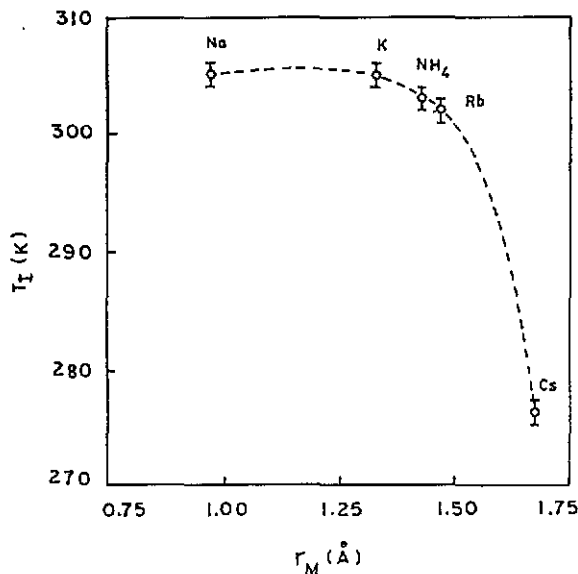


Figure 6. The variation of T_{IQ} with different impurity cation sizes in the system $(Rb_{1-x}M_x)_2ZnCl_4$ for $x = 0.03$.

4. Discussion

The size of the cation in relation to the anion is known to have a profound influence on the stability of the paraelectric phase in the A_2BX_4 family. For example, while K_2ZnCl_4 exhibits an order-disorder-type transition from its paraelectric to its incommensurate phase at 553 K, $(NH_4)_2ZnCl_4$ exhibits a similar transition at 406 K. A compound with a slightly bigger cation size, Rb_2ZnCl_4 , undergoes a phase transition from its paraelectric to its incommensurate phase at 302 K, while the one with the biggest cation size (for a given anion), Cs_2ZnCl_4 , does not exhibit any instability down to 36 K. From the lattice dynamics studies on this family [3], it is surmised that the potential barrier for anion torsional dynamics in a direction parallel to the crystallographic a -axis (the direction of propagation of the incommensurate modulation wave), referred to as 'parallel motions', becomes increasingly harmonic with increasing cation size leading to a more displacive type of transition (from K to Cs). NQR studies also indicate such a decrease in anharmonicity for parallel motions for Rb and Cs [6], but, in contrast to lattice dynamics studies, NQR studies also indicated that perpendicular motions become more anharmonic in Cs compounds than in Rb compounds. In fact NQR studies on the $(Rb_{1-x}Cs_x)_2ZnCl_4$ system show that as the potential structure for perpendicular motions becomes more and more anharmonic (as the Cs impurity concentration increases, the paraelectric phase becomes more and more stable as is evident from the decrease in T_I), indicating that perpendicular motions do indeed have a major role to play in the structural stability of the A_2BX_4 family [7].

The temperature variation of the NQR frequency in this type of system arises because of the averaging of the electric field gradient due to torsional motions of the molecules, primarily in a direction perpendicular to the direction of the maximum component of the field gradient (the quantizing direction). As the parallel motions do not displace Cl(1), only perpendicular motions are effective in averaging the NQR frequencies arising from the chlorine along the Zn-Cl(1) bond which gives rise to the highest NQR frequency ν_1 ,

and hence the spectral parameters (ν/T and E_a) corresponding to ν_1 contain information about the perpendicular motions. On the other hand, although Cl(2) and Cl(3) are affected by both parallel and perpendicular motions, the influence of perpendicular motions can be considered negligible—as the corresponding axes of motion are very close to the plane containing Cl(2) and Cl(3)—in comparison to such effects arising from parallel motions. Hence, the spectral parameters corresponding to ν_2 and ν_3 will essentially give information about the parallel motions.

From Bayer's theory for the temperature variation in NQR frequency,

$$\nu(T) = \nu_0 \left[1 - \frac{3}{2} \langle \theta^2 \rangle \right] \quad (2)$$

where ν_0 is the resonance frequency at absolute zero temperature and $\langle \theta^2 \rangle$ is the mean square amplitude of torsional motions given by

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

Here ν_i and I_i are the frequency and moment of inertia associated with the i th normal mode, respectively, and α_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 [10, 11]. From equation (2), one can obtain estimates of the mean square amplitude for torsional motions knowing the rate of variation of the NQR frequencies with temperature. Although a deviation from linearity is expected at very low temperatures, such effects can be ignored for comparison of relative differences among inequivalent sites. Thus, qualitatively, the rate of variation of the NQR frequency with temperature is large for motions with large mean square amplitudes. On the other hand, an estimate of the barrier heights encountered for such motions can be obtained from relaxation studies (as a function of temperature) in the appropriate temperature region where the reorientational motions are effective in causing the spin relaxation.

Such an analysis of the data indicates contrasting differences between compounds with a smaller impurity cation and one with the biggest impurity cation size (Cs) (table 1). In the former (Na, K, NH_4) neither the mean square amplitude nor the activation energies (corresponding to both the parallel and perpendicular motions) are affected by the presence of such impurities. Thus the potential barrier predicted from earlier studies for the parallel and perpendicular motions of anions in the pure compound (Rb_2ZnCl_4) seems unaffected by the presence of smaller cation impurities [6]. On the other hand, the presence of a heavier cation impurity (Cs) results in a substantial reduction in the height of the potential barrier for perpendicular motions. Curiously, the barrier height for parallel motions remains unaffected by the presence of larger impurities (table 1). While one would expect the mean square amplitude of librational motions to increase with reducing barrier height, the contrasting observation of a reduction in such amplitudes suggests that the shape of the barrier should be becoming anharmonic. It has been argued earlier, on the basis of studies of the barrier heights and mean square amplitudes of several pure and doped compounds [6, 7], that such anharmonicity could indicate the development of a double-minimum barrier for perpendicular motions in this compound. These observations show that: (i) neither the shape nor the height of the hindering potential barrier corresponding to the parallel motions is sensitive to the presence of impurity; and (ii) the perpendicular motions develop a double-well structure when the impurity cation is heavier than the host cation. Thus the reduction in T_1 by almost 25 K with the Cs impurity (figure 6) seems to be well correlated with the development of anharmonicity in the potential barrier for perpendicular motions. On the other hand, the very marginal increase in T_1 with smaller impurity cations seems to indicate no significant change in the potential barriers for either motion in these doped systems. Recent NQR studies in the incommensurate phase of

Rb₂ZnCl₄ doped with impurities also revealed a dramatic influence of a heavier cation (Cs) on the dynamics of the incommensurate phase compared to such effects arising from smaller impurity cations [12, 8].

5. Conclusions

The presence of a heavier cation impurity in the A₂BX₄ system considerably improves the stability of the paraelectric phase and also makes the potential barrier for perpendicular motions anharmonic. On the other hand, smaller cation impurities increase T₁ only marginally and the anion dynamics seems to be rather insensitive to the presence of such impurities. Smaller cations perhaps find greater freedom of movement within the cavities formed by the anions, and there are, then, no new changes in steric hindrances arising due to this impurity cation in the anion dynamics, leading to no appreciable change in the molecular environment of the anions compared to that in the pure compound. On the other hand, the presence of a heavier cation may be directly affecting the coupling of the anions, leading to dramatic changes in the structural stability of the A₂BX₄ family.

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