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Structural instability and anion dynamics in the system $(Rb_{1-x}Cs_x)_2ZnCl_4$—a ^{35}Cl nuclear quadrupole resonance study

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Abstract. The dynamics of the $ZnCl_4$ anion in the paraelectric phases of $(Rb_{1-x}Cs_x)_2ZnCl_4$ with $x = 0.005$, 0.01, 0.03 and 0.05 are investigated through ^{35}Cl nuclear quadrupole frequency ν and spin-lattice relaxation time (T_{1Q}) studies. The data, collected as a function of temperature for different lines in these compounds, are analysed to obtain the hindering potential barrier heights and the relative mean square amplitudes for librational motions parallel and perpendicular to the a-axis of the crystal structure. A comparison of these results shows that the presence of impurity affects only perpendicular motions and the corresponding potential becomes anharmonic, probably developing a double-well structure, as the concentration of impurity increases. As the paraelectric–incommensurate transition temperature is suppressed by the presence of impurity, the above results suggest that the perpendicular motions have an important role to play in stabilizing the paraelectric phase in this system.

1. Introduction

The structural stability of the compounds belonging to the A_2BX_4 family ($A \equiv K$, NH_4, $N(CH_3)_4$, Rb, Cs; $B \equiv Zn$, Cd, Hg and $X \equiv Cl$, Br, I), and the mechanism for the paraelectric to incommensurate phase transition observed in the majority of them, have been topics of considerable interest in the recent literature [1–7]. These transitions are presumed to be of order–disorder type involving the dynamics of the BX_4 anion [1]. Some of these systems however are stable and do not exhibit any structural transition [7–9]. An empirical analysis based on experimental data [8] shows that all those compounds for which the ratio of cation size to the unit cell volume is above a certain value do not exhibit structural instabilities, supposedly due to the increase in the hindrance to the dynamics of the BX_4 anion due to the large cations, leading to the stabilization of the paraelectric phase [1].

Recent ^{35}Cl nuclear quadrupole resonance (NQR) frequency (ν) and spin-lattice relaxation time (T_{1Q}) studies in the paraelectric phases of two compounds belonging to this family [2], viz. Rb_2ZnCl_4 (with the phase sequence paraelectric $\xleftrightarrow{302\ K}$ incommensurate $\xleftrightarrow{192\ K}$ commensurate [10]), and Cs_2ZnCl_4 (with no structural transition [9, 11]), clearly show the difference between the dynamics of the same anions in these two compounds. In the former compound, the hindrance for the reorientations around an axis parallel to the a-axis, hereafter referred to as 'parallel motions' (the direction along which the incommensurate modulation wave propagates in these compounds), and around the two axes perpendicular to the a-axis (perpendicular motions) are found to be essentially the same, but the potential
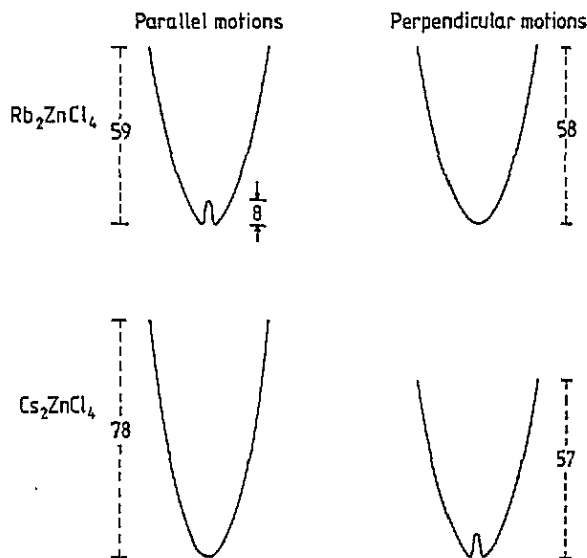
Figure 1. Potential wells for the motions parallel and perpendicular to the a-axis for Rb_2ZnCl_4 and Cs_2ZnCl_4. The barrier heights are in kJ mol^{-1}.

for the parallel motion is highly anharmonic, exhibiting a double-well structure as shown in figure 1. On the other hand, in the second compound with a stable paraelectric phase, viz. Cs_2ZnCl_4, the potential for the parallel motion is harmonic but perpendicular motions seems to experience a double-well potential (figure 1). Reexamination of the earlier NQR results (^{35}Cl and ^{87}Br) for several other compounds with this structure indicate that this feature seems to be a distinguishing factor for the dynamics of the anions with respect to their structural stabilities with temperature.

This paper is concerned with ^{35}Cl NQR studies in Rb_2ZnCl_4 doped with small amounts of Cs_2ZnCl_4. The aim is to investigate further the correlation between the dynamics of the $ZnCl_4$ anion and the structural stability as evidenced by the change in the paraelectric to incommensurate transition temperature (T_1) with the concentration of impurity.

2. Experimental details

$(Rb_{1-x}Cs_x)_2ZnCl_4$ compounds with four concentrations ($x = 0.005, 0.01, 0.03$ and 0.05) are grown by slow evaporation of an aqueous solution of RbCl, CsCl and $ZnCl_2$ mixture in stoichiometric ratio. The values of x quoted here and subsequently in this paper are the stoichiometries of Cs_2ZnCl_4 used in the preparation of the samples and the exact amount x that is present in the compounds thus prepared is not independently verified. Dried polycrystalline samples are used for the NQR studies made on a home built pulsed NQR spectrometer. The temperature dependence of NQR frequencies is determined employing the Hahn spin echo sequence whereas the T_{1Q} measurements are made using an inversion recovery spin echo sequence (π–τ–$\pi/2$–τ'–π, with τ' fixed at 180 μs). These measurements are accurate to within ± 1 kHz in frequency and to within 5% in relaxation time. The sample temperature is controlled to within 0.1 K, employing a gas flow type cryostat using dry air for temperatures above the room temperature and liquid nitrogen vapour for lower temperatures. The measurement at each temperature is taken after allowing sufficient time for the sample to reach equilibrium at a given temperature, to minimize errors due to thermal gradients.
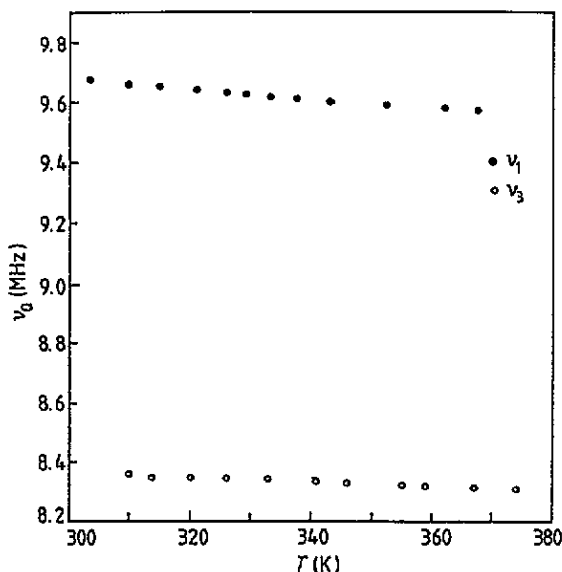
Figure 2. Temperature (T) dependence of two ^{35}Cl NQR frequencies (ν_1 and ν_3) in Rb_2ZnCl_4.

3. Results

As in the case of other compounds of this family, three ^{35}Cl NQR frequencies are observed for the pure as well as for the doped compounds. These frequencies for pure compound agree very well (within the experimental error) with the reported values [12]. The assignment of these frequencies, arising from the three inequivalent chlorines, due to differing Zn–Cl bond lengths, is rather well established. The highest-frequency (ν_1) line is due to the chlorine atom along the a-axis (say Cl(1)). 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 in the ZnCl$_4$ tetrahedron Cl(3) are equivalent (mirror symmetry) and these give rise to the lowest frequency (ν_3) line. Figures 2 and 3 show the temperature (T) variation of frequencies ν_1 and ν_3 for the pure compound and one with $x = 0.03$, respectively, and these variations are essentially linear. The dν/dT values for various lines for different impurity concentrations are shown in table 1.

Table 1. Dynamic parameters in $(Rb_{1-x}Cs_x)_2ZnCl_4$ for different values of x.

x	T_1 (K)	dν/dT (kHz K^{-1})		E_a (kJ mol^{-1})	
		ν_1	ν_3	ν_1	ν_3
0.00	302	−2.0	−0.7	58	59
0.005	298	−1.8	−0.6	56	57
0.01	294	−1.7	−0.6	48	59
0.03	277	−1.3	−0.5	39	58
0.05	259	−1.1	−0.5	21	60
1.00	—	−0.7	−1.0	57	78

Figures 4 and 5 show the variation in T_{1Q} with temperature for all the three lines of two compounds (($Rb_{1-x}Cs_x)_2ZnCl_4$, $x = 0$ and 0.03, respectively). In all these compounds, T_{1Q} for ν_1 is relatively longer, while shorter and identical T_{1Q} are observed for ν_2 and ν_3 within the experimental error. Since ν_2 and ν_3 have identical experimental variations in all respects,
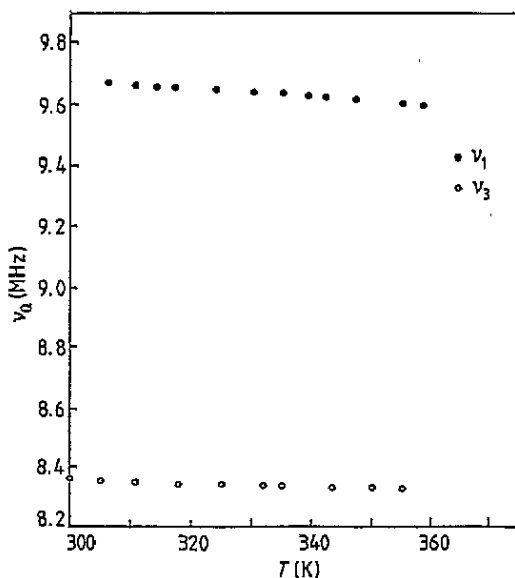
Figure 3. Temperature (T) dependence of two ^{35}Cl NQR frequencies (ν_1 and ν_3) in $(Rb_{1-x}Cs_x)_2ZnCl_4$ for $x = 0.03$.

only one of them (say ν_3) is referred to in the text for a discussion of the results for these two lines. Quadrupolar relaxation in these symmetric molecular groups (in the investigated temperature range) is primarily due to sudden and infrequent reorientations of the molecules overcoming their potential barriers, and this leads, in the case of a quadrupolar interaction, to a strong coupling between the spin system and the lattice. T_{1Q} is then directly related to τ_c, the correlation time associated with the motion, and with an Arrhenius type thermal excitation, one has [13]

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

where E_a is the activation energy corresponding to this motion, R is the universal gas constant and b is a proportionality constant.

$T_{1Q}(T)$ values for all the compounds show a cusp like minimum characteristic of a conventional structural phase transition at T_1 and start to increase with increase in temperature, reaching a maximum value at around 330 K. Above this temperature, T_{1Q} starts to exhibit an Arrhenius behaviour and it is in this temperature interval that the above strong coupling to the lattice is most effective; these data consequently report on the details of parameters of this model, in particular the activation energies, E_a. Table 1 summarizes the values of E_a for different lines as a function of x.

4. Discussion

The librational motions of the $ZnCl_4$ anion around different axes cause the averaging of NQR frequencies leading to their temperature dependence [14, 15], which in principle, can be analysed to obtain information about the torsional frequencies or mean square amplitudes of these motions. However, such an analysis of the data involving more than one motion has been generally found not to be possible in practice, essentially due to the demand on the
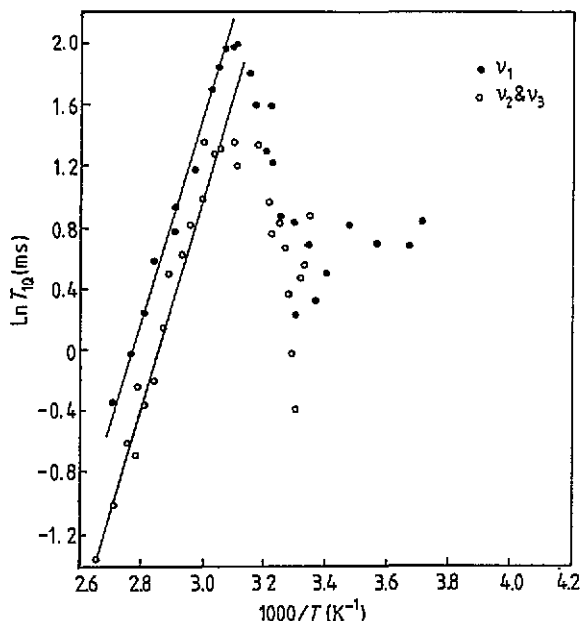
Figure 4. Variation in logarithm of ^{35}Cl quadrupolar relaxation time (T_{1Q}) as a function of $1000/T$ in Rb_2ZnCl_4. The solid line is the best-fit curve to equation (1) in the text.
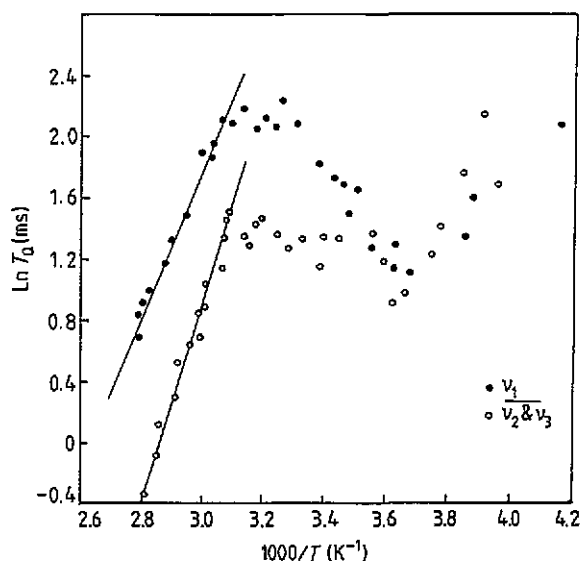

Figure 5. Variation in logarithm of ^{35}Cl quadrupolar relaxation time (T_{1Q}) as a function of $1000/T$ in $(Rb_{1-x}Cs_x)_2ZnCl_4$ for $x = 0.03$. The solid line is the best-fit curve to equation (1) in the text.

knowledge of certain temperature dependent parameters (necessitated by the temperature dependent solid state effects), and often one analyses the experimental data with one dominant motion only [18]. At a qualitative level, however, it is transparent that the rate of variation of NQR frequency with temperature can be correlated to the mean square

amplitude of librations in the usual high-temperature approximation [16–18]. On the other hand, at high enough temperatures, the molecules may gain sufficient energy to overcome the potential barriers and undergo sudden but infrequent reorientations, bringing about dramatic changes in relaxation parameters [13]. Thus, while temperature variation in NQR frequencies have information about the mean square amplitudes of the torsional motions, corresponding T_{1Q} variations reflect a measure of the hindrance due to these potential barriers.

While considering the effect of librational motions on the different NQR lines, a clear distinction can be made regarding the role of parallel and perpendicular motions. The NQR spectral parameters (ν and T_{1Q}) for the high-frequency line (corresponding to Cl(1)) are affected exclusively by perpendicular motions, while the other two resonance lines are in principle sensitive to both types of motion, but with parallel motions being more predominant [18]. Thus, while ν_1 can be used to obtain information about perpendicular motions, ν_2 and ν_3 provide information about the parallel motions.

It is known [1] that the librational motion about the a-axis in Rb_2ZnCl_4 experiences a double-well type of structure as shown in figure 1. This has been further verified by the recent NQR studies [2], as this resulted in reduced mean square amplitudes for the parallel motions and thus to much smaller $d\nu/dT$ for ν_3 compared to that for ν_1 (even though both motions experience essentially the same barrier heights, as shown in table 1 [2]). Cs_2ZnCl_4, on the other hand, shows a higher hindering barrier for parallel motion, relative to perpendicular motion, but, interestingly, exhibits comparatively low $d\nu_1/dT$. The higher E_a for parallel motion can be readily visualized as due to the presence of a bigger cation. Now, the perpendicular motions with less hindrance are normally expected to exhibit librational motions with comparatively larger mean square amplitudes, leading to relatively higher values for $d\nu_1/dT$, whereas such is not the experimental observation. This discrepancy was explained [2] as due to a possible anharmonicity for the perpendicular motion in Cs_2ZnCl_4. The similarities between E_a and $d\nu/dT$ of ν_3 in Rb_2ZnCl_4 and those of ν_1 in Cs_2ZnCl_4 suggest that this anharmonicity for the perpendicular motion in Cs_2ZnCl_4 is perhaps similar to that of parallel motion in Rb_2ZnCl_4, i.e., a double-well structure.

Now, from the variation of the $d\nu/dT$ and E_a for different resonance lines in the $(Rb_{1-x}Cs_x)_2ZnCl_4$ system as a function of x (figure 6), it can be seen that the Cs impurity in Rb_2ZnCl_4 has no discernible effect either on the activation energy or on the mean square amplitudes of the parallel motions of the anions (table 1), even though, interestingly, the T_1 value is sensitive to the impurity concentration (figure 7). This indicates that the parallel motions are insensitive to changes in environment brought about by impurity substitution, while such substitutions do affect the phase transition in terms of lowering the T_i—a rather curious result in the light of the current belief [1]. On the other hand, both the mean square amplitudes and the barrier heights of the perpendicular motion show a dramatic and systematic variation with respect to impurity concentration, and this observation is equally interesting from the view of our present understanding of the role of these dynamic processes. The decrease in E_a with x seems to be due to the increase in the distance between $ZnCl_4$ tetrahedra along the a-axis. However, this variation of E_a, in the harmonic approximation, should lead to a consequent increase in the mean square amplitudes, but this conclusion is not borne out by the experimental data on $d\nu_1/dT$. Keeping in view the earlier observations on the anharmonic nature of the potential for perpendicular motions in Cs_2ZnCl_4 [2], the present data for both E_a and $d\nu_1/dT$ require, for consistent interpretation, the assumption that perhaps there is some anharmonicity associated with the perpendicular motions in this impurity substituted system, and that the addition of Cs impurity in Rb_2ZnCl_4 is leading to a double-well-type structure even for the perpendicular motions in this doped system.

From an earlier study [2] based on the difference in the values of ν_1, ν_2 and ν_3 in
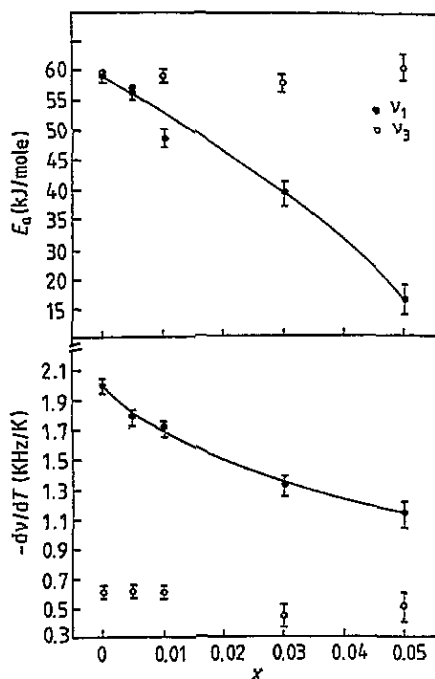
Figure 6. Variation in $d\nu/dT$ and E_a for ν_1 and ν_3 with impurity concentration (x) in $(Rb_{1-x}Cs_x)_2ZnCl_4$.
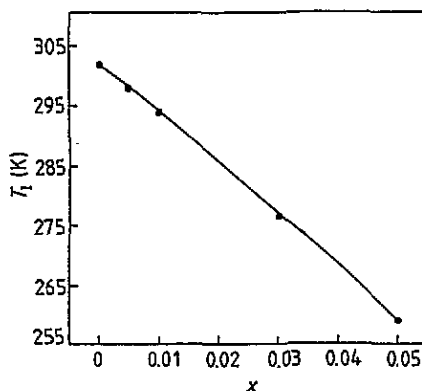
Figure 7. Variation in paraelectric to incommensurate transition temperature (T_I) with impurity concentration (x) in $(Rb_{1-x}Cs_x)_2ZnCl_4$.

Rb and Cs compounds, it is concluded that the $ZnCl_4$ anion is axially compressed in the former compound (as ν_1 is comparatively high, indicating a shorter Zn–Cl bond length) whereas the anion in the other compound is laterally compressed (as ν_2 and ν_3 are relatively larger in Cs_2ZnCl_4). In this context, figure 8 shows that ν_2 and ν_3 in $(Rb_{1-x}Cs_x)_2ZnCl_4$ are unaffected, at any given temperature, by the presence of impurity whereas ν_1 decreases with increase in x. Thus it seems that the addition of Cs impurity in the Rb compound reduces axial stress on the $ZnCl_4$ tetrahedron, while leaving the lateral stress unchanged. This agrees with the physically consistent picture of increased distance between anions along the a-axis with the substitution of a larger impurity (cation). Further, the observed variation of E_a and $d\nu_1/dT$ with impurity concentration confirms this conclusion.

5. Conclusion

The reorientational motions of the $ZnCl_4$ anion about axes perpendicular to the direction of propagation of the incommensurate modulation wave (a-axis) seem to have an important role to play at the paraelectric–incommensurate transition in the $(Rb_{1-x}Cs_x)_2ZnCl_4$ system. Addition of Cs impurity to Rb_2ZnCl_4 reduces the phase transition temperature (T_I), affecting only the perpendicular motions of the anions, and changing the proximity between them along the a-axis of the crystal structure. It is found that the parallel motions of the $ZnCl_4$ anion, which are qualitatively different in the Rb and Cs compounds, are unaffected by the presence of impurity even though the phase transition temperature is suppressed by 45 K over the concentration range investigated. On the other hand, the perpendicular motions seem to develop a double-well-type potential as impurity concentration is increased, very
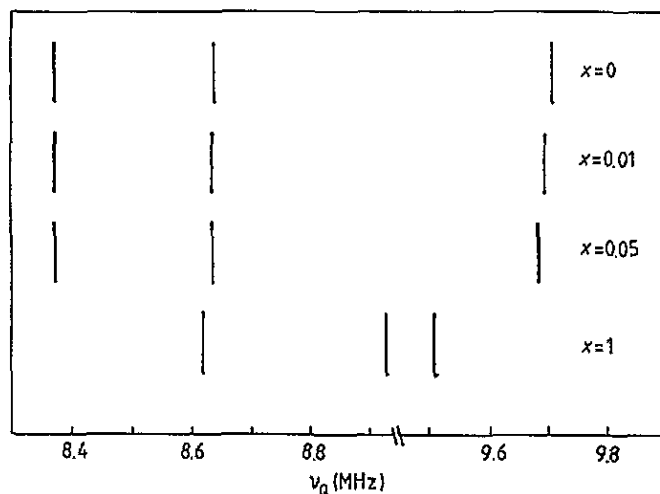
Figure 8. NQR splitings at 290 K in $(Rb_{1-x}Cs_x)_2ZnCl_4$ for various impurity concentrations (x).

similar to the potential observed for pure Cs compound (which does not have a phase transition). Consolidating these ideas, it is observed that the presence of this anharmonicity for perpendicular motions seems to be a stabilizing factor for the paraelectric phase, while parallel motions seem unimportant from this point of view. Such a statement seems to be in disagreement with current notions on the role of anion motion in mediating this transition.

Acknowledgments

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