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1994 J. Phys.: Condens. Matter 6 137

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³⁵Cl nuclear quadrupole resonance study of anion dynamics in the paraelectric phases of Cs₂ZnCl₄ and Rb₂ZnCl₄

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Received 16 June 1993, in final form 7 September 1993

Abstract. The dynamics of the ZnCl₄ anion in two compounds, one exhibiting a structural transition to an incommensurate phase (Rb₂ZnCl₄) and another not having any structural transition at all (Cs₂ZnCl₄), are studied through ³⁵Cl NQR frequency (ν) and relaxation time (T_{1Q}) measurements as a function of temperature T in their high-temperature (paraelectric) phases. Estimates of the potential barriers hindering the reorientational motions of ZnCl₄ anions along axes parallel and perpendicular to the a axis of the crystal structure are obtained from the T_{1Q} data. These results are analysed in conjunction with a qualitative comparison of relative mean square amplitudes of such motions obtainable from frequency data, in order to investigate the differences in the dynamics and structure of the ZnCl₄ anion. There seems to be correlation between the dynamics of the anion in this phase and the possibility that the compound may exhibit a structural instability at low temperatures in this family.

1. Introduction

A large number of A₂BX₄-type compounds (A≡K, Rb, NH₄ or Cs; B ≡ Zn, Cd or Hg; X≡Cl, Br or I) have been found to have an isomorphic β -K₂SO₄ structure with space group *Pnma*. Many of them are reported to exhibit one or more phase transitions, and some of them show structurally incommensurate phases [1–5], while others do not show any phase transitions [5–7]. The structural stability of the high-temperature phase (paraelectric phase) depends on a very intricate balance of interatomic forces, and the phase transition phenomena occur when such a balance is destroyed. The general observation is that [6] the size of cation plays a major role from this point of view. If the ratio of the cation size to the unit-cell volume is above a certain value, the paraelectric phase is stabilized and no phase transition occurs [8,9]. This is because large cations are expected to hinder the torsional motions of BX₄ anions around a B–X bond parallel to the a axis of the crystal, i.e. in the direction in which the incommensurate modulation wave propagates in these compounds. In this context, two compounds, namely Rb₂ZnCl₄ and Cs₂ZnCl₄, with and without a structural phase transition, are studied with a view to obtaining details on the dynamics of the ZnCl₄ anion in the paraelectric phase. While Rb₂ZnCl₄ exhibits a paraelectric-to-incommensurate transition at 302 K and a lock-in transition to the ferroelectric phase at 192 K [10], Cs₂ZnCl₄ does not show any phase transition down to 36 K [7, 11].

NQR resonance and relaxation studies have been extensively used to study molecular dynamics in these systems (and in particular Rb₂ZnCl₄), but most of these studies were aimed at obtaining information on the dynamics in the incommensurate phase whereas the present studies are in the paraelectric phase. There are only two reports of such Br and Cl NQR frequency and quadrupolar relaxation time (T_{1Q}) studies on Cs₂ZnBr₄

[6] and $[\text{NH}_2(\text{CH}_3)_2]_2\text{ZnCl}_4$ [12], where the former shows no phase transition while the latter exhibits a paraelectric-to-ferroelectric phase transition but without an incommensurate phase. The present paper reports ^{35}Cl NQR frequency and T_{1Q} measurements for Cs_2ZnCl_4 and Rb_2ZnCl_4 . Preliminary NQR frequency measurements have been reported previously for Cs_2ZnCl_4 [13].

2. Experimental details

Polycrystalline A_2ZnCl_4 crystals ($\text{A} \equiv \text{Cs}$ or Rb) are grown by slow evaporation of an aqueous solution of ACl and ZnCl_2 in a 2:1 molar mixture. NQR experiments are carried out using a home-made pulsed NQR spectrometer. The temperature dependence of the NQR frequencies $\nu(T)$ are determined using a single $\frac{1}{2}\pi$ pulse for Cs_2ZnCl_4 , while for Rb_2ZnCl_4 a Hahn spin echo sequence has to be employed because of the very broad NQR lines ($T_2^* \simeq 45 \mu\text{s}$). The accuracy of these frequency measurements is ± 1 kHz. An inversion recovery sequence is employed to measure T_{1Q} in Cs_2ZnCl_4 while for Rb_2ZnCl_4 an inversion recovery spin echo sequence ($\pi - \tau - \frac{1}{2}\pi - \tau' - \pi$, τ' fixed at $180 \mu\text{s}$) is used. The accuracy in the τ_{1Q} measurements is about 5% (near the phase transition about 10%). The sample temperature is controlled to within 0.1 K, employing a gas-flow-type cryostat with liquid-nitrogen vapours for the variation in temperature from 100 K to room temperature while dry air is used above room temperature. Measurement at each temperature is carried out after waiting for about an hour so that the temperature gradient across the sample is minimized. The sample is immersed directly into liquid nitrogen for measurements at 77 K. Both T_{1Q} and ν measurements for Cs_2ZnCl_4 are made from 77 K until the lines fade out at around 420 K owing to the onset of reorientational motions of the ZnCl_4 tetrahedron. On the other hand, the data for Rb_2ZnCl_4 are collected from 302 K, the paraelectric-to-incommensurate transition temperature T_1 , until the lines fade out at high temperatures (around 380 K).

3. Results

As in the case of other compounds of this A_2BX_4 family, three ^{35}Cl NQR frequencies are observed for both compounds. These frequencies agree well (within the experimental errors) with the reported values [13, 14]. The assignment of these three frequencies is rather well established. The highest-frequency (ν_1) line is due to the chlorine atom along the a axis (say $\text{Cl}(1)$), the direction of propagation of the incommensurate modulation wave. The middle frequency ν_2 is due to the chlorine atom $\text{Cl}(2)$ lying in the mirror symmetry plane together with $\text{Cl}(1)$. The remaining two chlorine atoms in the ZnCl_4 tetrahedron $\text{Cl}(3)$ are equivalent (mirror symmetry) and these give rise to the lowest-frequency (ν_3) line. The differences between the frequencies of these three types of chlorine atom is due to the differences between the corresponding $\text{Zn}-\text{Cl}$ bond lengths. Figures 1 and 2 show the temperature (T) variation in frequencies for these two compounds, which is essentially linear. The $d\nu/dT$ -values for various lines are shown in table 1.

Figures 3 and 4 show the variation in T_{1Q} with temperature for all the three lines of Cs_2ZnCl_4 and Rb_2ZnCl_4 respectively. Both show longer T_{1Q} for ν_1 and relatively shorter and identical T_{1Q} for ν_2 and ν_3 within the error. In fact it is observed that ν_2 and ν_3 have identical experimental variations in all respects and hence one of them, say ν_3 , is referred to in the text when discussing the results for these two lines. Quadrupolar relaxation in the symmetric molecular groups is basically due to two types of mechanism; firstly librational motions

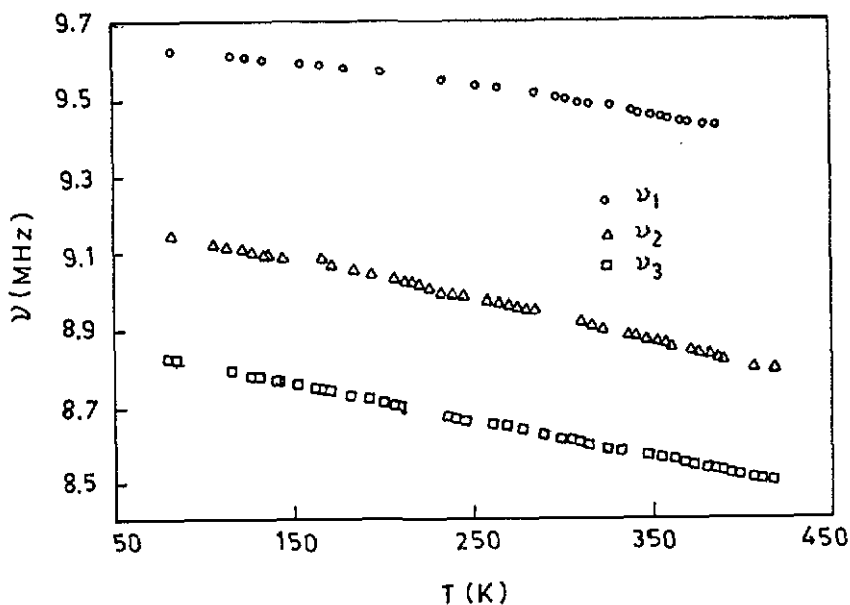


Figure 1. Temperature (T) dependence of three ^{35}Cl NQR frequencies ν_1 , ν_2 and ν_3 for Cs_2ZnCl_4 .

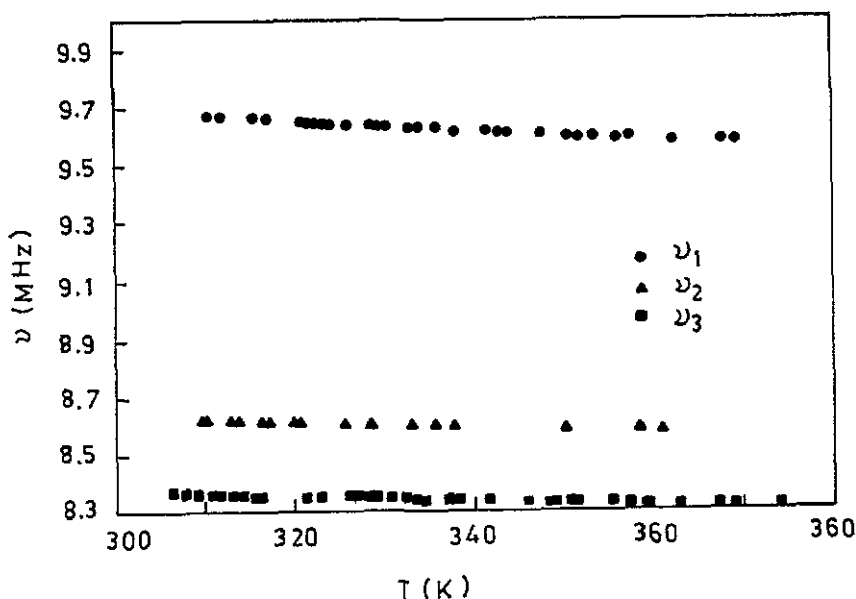


Figure 2. Temperature (T) dependence of three ^{35}Cl NQR frequencies ν_1 , ν_2 and ν_3 for Rb_2ZnCl_4 .

of the molecules within the potential wells confining them to a particular orientation and secondly sudden and infrequent reorientations of the molecules overcoming these barriers. The former mechanism, which is normally effective at relatively low temperatures, gives

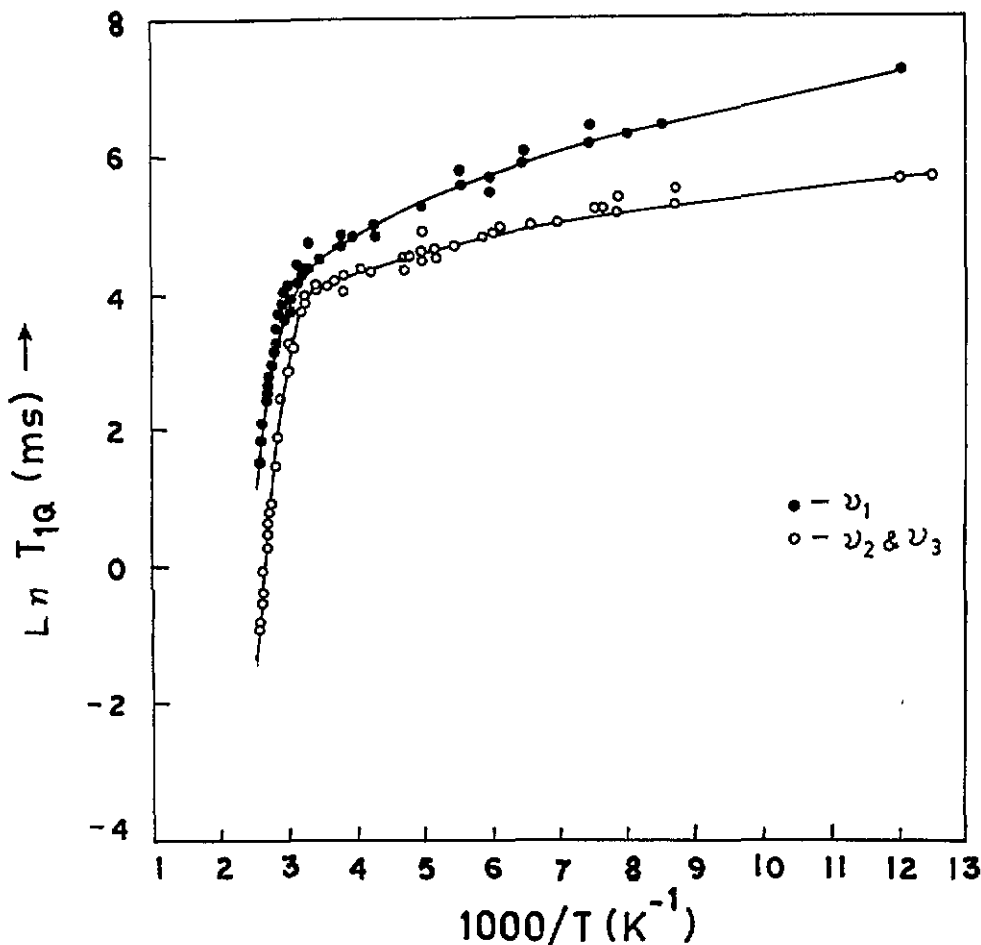


Figure 3. Variation in ^{35}Cl quadrupolar relaxation time T_{1Q} as a function of $1000/T$ for Cs_2ZnCl_4 : —, best-fit curve to equation (3) in the text.

rise to a T^m type of temperature dependence [15]. In the $\hbar\omega_t/kT \ll 1$ limit (ω_t is the frequency of torsional librations) $m = 2$, but more generally one can write

$$T_{1Q}^{-1} = aT^m \quad (1)$$

where a contains quantities such as ν_Q , ω_t and the mean lifetime of a given molecule in a torsional level. If the temperature is sufficiently high, the molecular groups will be able to undergo reorientations, overcoming the barrier, and this leads to very strong coupling between the spin systems and the lattice. T_{1Q} in this temperature region is directly related to τ_c , the correlation time associated with the motion. If these dynamics are assumed to be of an Arrhenius type, one can write [16]

$$T_{1Q}^{-1} = b \exp(-E_a/RT) \quad (2)$$

where E_a is the activation energy corresponding to this motion. In general, both these mechanisms should be mediating the quadrupolar relaxation process and in that case, on

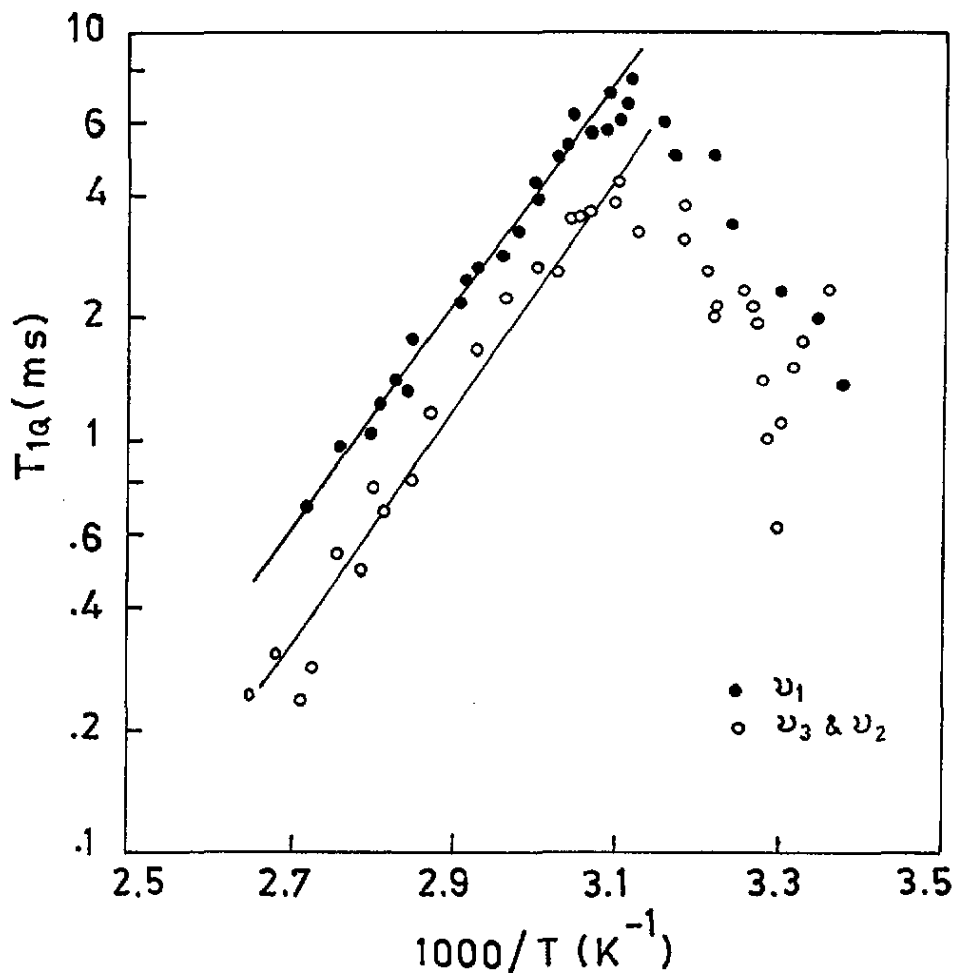


Figure 4. Variation in ^{35}Cl quadrupolar relaxation time T_{1Q} as a function of $1000/T$ in Rb_2ZnCl_4 : —, best-fit curve to equation (2) in the text.

Table 1. Dynamic parameters for Cs_2ZnCl_4 and Rb_2ZnCl_4 .

Compound	$d\nu/dT$ (kHz K^{-1})		E_a (kJ mol^{-1})		m	
	ν_1	ν_3	ν_1	ν_3	ν_1	ν_3
Rb_2ZnCl_4	-2	-0.7	58	59	—	—
Cs_2ZnCl_4	-0.7	-1	57	78	2.1	1.2

combination of equations (1) and (2), T_{1Q} can be written as [17]

$$T_{1Q}^{-1} = aT^m + b \exp(-E_a/RT). \quad (3)$$

The T_{1Q} -values for ν_1 and ν_3 of Cs_2ZnCl_4 show a T^m type of behaviour below 300 K and start to decrease suddenly at high temperatures (approximately 350 K and 340 K for ν_1 and ν_3 , respectively). This shows that both types of mechanism discussed above are

mediating the T_{1Q} process in Cs_2ZnCl_4 for the temperature region studied. Hence the data are fitted to equation (3), using non-linear curve-fitting techniques, and the values of m and E_a thus obtained for different lines are presented in table 1.

On the other hand, T_{1Q} for Rb_2ZnCl_4 shows a cusp-like dip characteristic of a conventional structural phase transition at T_1 and starts to increase with increase in temperature, reaching a maximum value at around 330 K. From this temperature onwards, T_{1Q} starts to exhibit Arrhenius behaviour without a T^m region. Hence these data above 330 K are fitted to equation (2), and the E_a -values thus obtained for different lines are listed in table 1.

4. Discussion

The influence of the size of the cation on the dynamics of the BX_4 anion, *vis-à-vis* the possibility of a phase transition, is a point of much discussion in the literature. It is believed that, as the cation size increases without a matching increase in the unit-cell size, the anion dynamics will become more hindered, stabilizing the high-temperature phase. Hence only systems for which the ratio of the cation size to unit-cell size is below a certain value are expected to exhibit structural instabilities, leading to a phase transition at lower temperatures [6, 8, 9]. The type of dynamics that is involved here is the librational motions of the ZnCl_4 anion about the Zn-Cl(1) bond, which is almost parallel to the a axis of the crystal structure. The anions also undergo such motions about two orthogonal axes perpendicular to the a axis, but these motions are believed to be relatively small in amplitude and considered to be unimportant [8, 9].

The motions about the a axis (parallel motions) do not contribute to the temperature variation in ν_1 , and its T_{1Q} , and so ν_1 provides information about only the motions perpendicular to the a axis (perpendicular motions). On the other hand, both the motions (parallel and perpendicular) cause displacement of Cl(2) and Cl(3) (thereby leading to similar behaviour of ν_2 and ν_3), with the effect of parallel motion, however, being predominant. Accordingly, ν_2 and ν_3 essentially reflect the effects of librations about the a axis. The temperature dependences of NQR frequencies, in principle, contain information about these motions in terms of mean square amplitudes of these torsional oscillations, or their average frequency, etc, but analysis of the data involving more than one such motion is not straightforward based on existing models [18, 19] and is known often to lead to ambiguous results, particularly in the absence of other relevant molecular parameters needed for such analysis. At a qualitative level, however, the rate of variation in NQR frequency with temperature is large for motions with large mean square amplitudes [20–22]. Thus the NQR frequency and relaxation data can be used to infer the relative mean square amplitudes of the librational motions about different axes and the corresponding barrier heights.

Table 1 indicates an increase in the relative hindrance to the motion about a axis in Cs_2ZnCl_4 due to larger cations. Further, the E_a -values corresponding to the perpendicular motions are essentially the same for both the compounds, suggesting that the size of the cation does not influence these barriers, but the mean square amplitudes of these motions, as inferred from the frequency data, do not vary accordingly. Normally one associates smaller mean square amplitudes with higher barriers, at a given temperature and for comparable molecular environments, but the variation in ν_3 is higher for Cs_2ZnCl_4 than for Rb_2ZnCl_4 whereas the corresponding E_a is smaller in the latter case. It is also expected that anions in Rb_2ZnCl_4 should have larger amplitude librations about the a axis, than those in Cs_2ZnCl_4 [9]. This discrepancy seems to be due to the anharmonic nature of the potential for the

parallel motion in Rb_2ZnCl_4 . It is known that these anions experience a double-well type of potential (with the minima separated by about 7°) for parallel motions, and such effects are known to be very weak in Cs_2ZnCl_4 (figure 5) [9, 23]. In such a case, the average amplitude of the librational motions in Rb_2ZnCl_4 could be small, as seen by NQR probes, relative to the case of the harmonic potential and the present observation is consistent with this picture. Such anharmonic effects are essentially absent for parallel motions in the case of Cs_2ZnCl_4 , leading to relatively large mean square amplitudes as indicated by the temperature variation in the NQR frequency of the corresponding line, even with a higher barrier. This model also explains consistently the data for Rb_2ZnCl_4 , wherein the activation energies for all motions are equal (within the experimental errors) but the NQR lines do exhibit widely different rates of variations with temperature. It may also be noted that conclusions from this scenario differ from the belief that the parallel motions (which are associated with the mechanism for phase instabilities at lower temperatures) have higher mean square amplitudes.

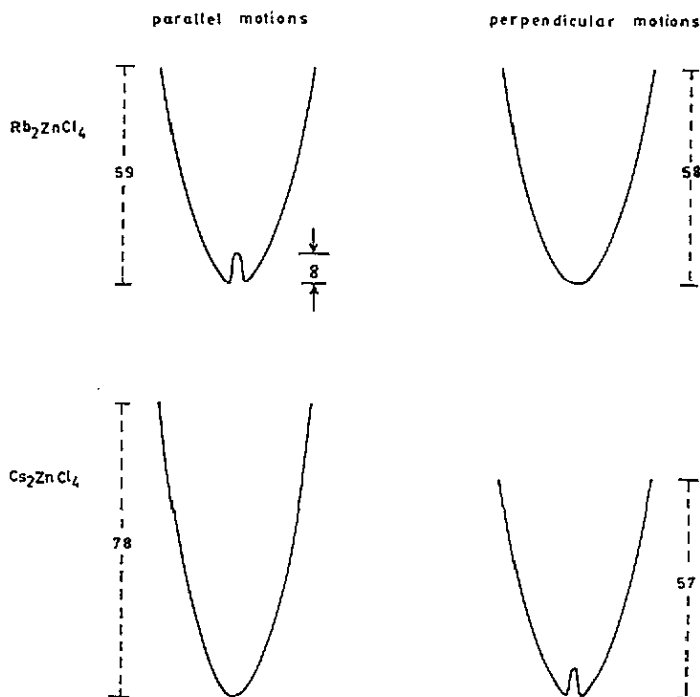


Figure 5. Proposed shapes of potential wells for the motion parallel and perpendicular to the a axis in Rb_2ZnCl_4 and Cs_2ZnCl_4 . The barrier heights are in kilojoules per mole. The barrier shape for the perpendicular motion in the latter compound is shown to be similar to that of parallel motion in the former compound because of the similarities in the corresponding data as explained in the text.

Low mean square amplitudes for librational motions are in principle possible for different types of anharmonicity in the corresponding potentials [24, 25]. For example quartic potentials could lead to a reduction in mean square amplitudes [24]. Further it has been shown earlier [25] that a double-well potential for the torsional motions could lead to an increase in the torsional frequency. This results in a decrease in the mean square amplitude of these motions, and in fact the observed low rate of variation in ν_z compared with $\nu_{x,y}$ with

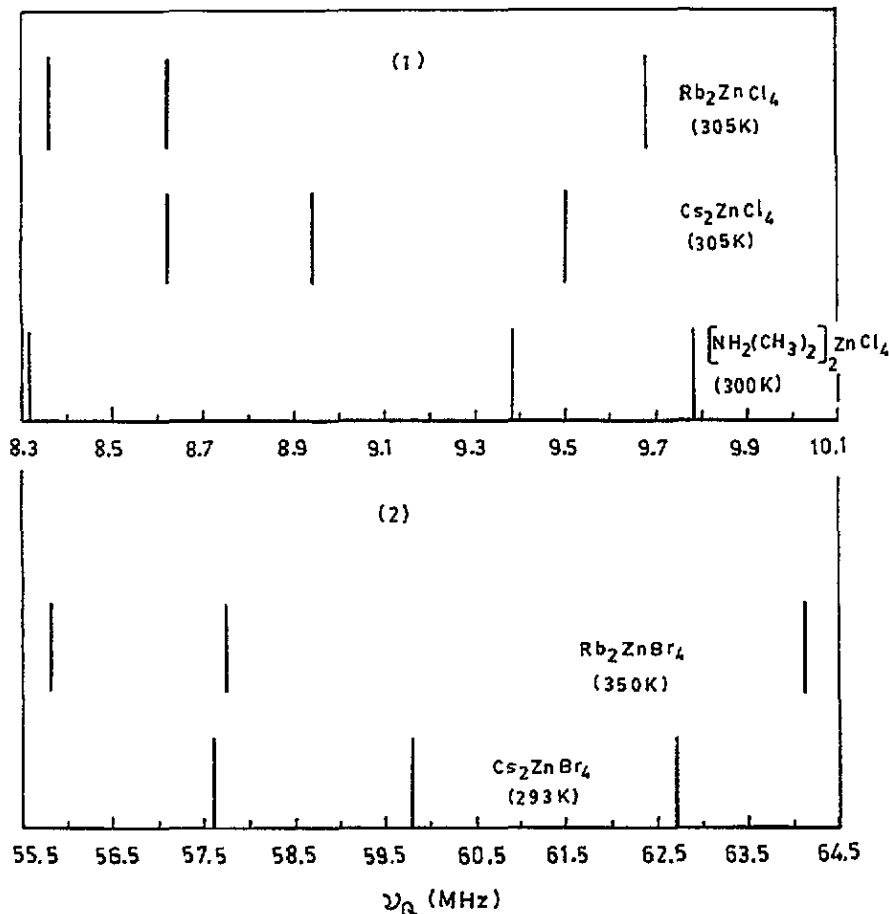


Figure 6. ^{35}Cl NQR frequencies for five A_2BX_4 compounds.

temperature in the tetragonal phase of K_2PtBr_6 [25] should be because of the double-well structure. As it is already known that the parallel motion in Rb_2ZnCl_4 has a double-well structure, correlating the observed low $d\nu_3/dT$ to this anharmonicity is, perhaps, justified.

From the $d\nu/dT$ -values of both the compounds for ν_1 , it can be seen that the perpendicular motions in the Rb compound possess relatively larger mean square amplitudes, even though the barrier heights for such motions are the same in both, as revealed by the relaxation data. Further, in the Cs system, the perpendicular motion has a much lower E_a , relative to the parallel motion, but its $d\nu/dT$ is also smaller. These two observations suggest the presence of anharmonicity of potential surfaces for the perpendicular motions in this compound. Similarity of the barrier heights and $d\nu/dT$ -values of the motion in the Cs system about the perpendicular direction, with the corresponding values for parallel motion in the Rb system, suggest that perhaps the anharmonicity for such motions in the Cs compound is related to the possible presence of a double-minimum barrier as experienced by the anions for their perpendicular torsional motions (figure 5).

A comparison of the dynamics of BX_4 tetrahedron in other A_2BX_4 compounds shows an interesting trend. Table 2 presents $d\nu/dT$ and activation energy data for several

compounds, some of them having an incommensurate transition, one showing a simple structural transition and the rest showing no transition at all. The $d\nu/dT$ -values presented in table 2 are the values that we calculated from the ν versus T plots presented in the papers referenced in the table. T_{1Q} data at high temperatures are not available in many cases and hence the corresponding barrier heights could not be quoted. It should be noted that the perpendicular motions are always associated with larger mean square amplitudes relative to their parallel counterparts, for all compounds showing a phase transition, into either an incommensurate phase or a commensurate phase (simple structural phase transition). This trend is reversed in systems which do not exhibit any phase transition at all. The activation energies for both types of motion in $[\text{NH}_2(\text{CH}_3)]_2\text{ZnCl}_4$ (which exhibits a simple structural phase transition) are the same as in Rb_2ZnCl_4 . An indication that emerges from this comparison is that the $d\nu/dT$ -values for ν_1 and ν_3 seem to distinguish between the compounds that have or do not have potential for structural instabilities as the temperature is lowered. Some of our recent results on Rb_2ZnCl_4 compounds doped with impurities seem to indicate that the anharmonic nature of the potential governing the perpendicular motions may have a role to play in stabilizing the high-temperature phase [28]. Thus the above discussion suggests that there seems to be a qualitative difference in the dynamic environments experienced by the anions in A_2BX_4 -type compounds, directly reflecting the ability of the corresponding compound to be thermodynamically stable with respect to the variation in temperature. In this context, similar investigations on the high-temperature phase in other systems exhibiting phase transitions could perhaps prove to be rewarding in understanding this correlation

Table 2. Comparison of activation energies and $d\nu/dT$ -values for certain A_2BX_4 compounds.

Compound	$d\nu/dT$ (kHz K ⁻¹)		E_a (kJ mol ⁻¹)		T_1 (K)	Reference
	ν_1	ν_3	ν_1	ν_3		
Rb_2ZnCl_4	-2	-0.7	58	59	302	
Cs_2ZnCl_4	-0.7	-1	57	78	—	
Rb_2ZnBr_4	-15	-4.6			347	[26]
Cs_2ZnBr_4	-2.9	-5.7			—	[6, 27]
Cs_2CdBr_4	-10	-6			252	[27]
Cs_2HgBr_4	-21	-12			243	[27]
$[\text{NH}_2(\text{CH}_3)_2]\text{ZnCl}_4$	-2.5	-0.5	110	110	257	[12]

A close look at the NQR frequencies of these compounds reveals another interesting point. Figure 6(a) shows the NQR frequencies, at room temperature, in three compounds having the same ZnCl_4 anion. A striking feature of these frequencies is that the splitting between the three lines in Rb_2ZnCl_4 and $[\text{NH}_2(\text{CH}_3)]_2\text{ZnCl}_4$, both exhibiting phase transitions, is much greater than that in Cs_2ZnCl_4 , which does not have a phase transition. Further it can be seen from figure 6(a) that the ν_1 -values for Rb_2ZnCl_4 and $[\text{NH}_2(\text{CH}_3)]_2\text{ZnCl}_4$ are higher than ν_1 for Cs_2ZnCl_4 , whereas ν_2 and ν_3 for Rb_2ZnCl_4 are lower than those for Cs_2ZnCl_4 . This indicates that the $\text{Zn}-\text{Cl}(1)$ bond length in the first two compounds is shorter than the same bond length in Cs_2ZnCl_4 and the $\text{Zn}-\text{Cl}(2)$ and $\text{Zn}-\text{Cl}(3)$ bonds are longer in Rb_2ZnCl_4 . The $\text{Zn}-\text{Cl}(2)$ bond is shorter in $[\text{NH}_2(\text{CH}_3)]_2\text{ZnCl}_4$ which exhibits a simple paraelectric-to-ferroelectric phase transition. A similar behaviour can be seen with the ZnBr_4 anion in Rb_2ZnBr_4 [26], exhibiting an incommensurate phase transition, and CsZnBr_4 [6], not having a phase transition as shown in figure 6(b).

5. Conclusions

There are qualitative differences in both the dynamics and the structure of the BX_4 anion in A_2BX_4 systems, between two categories: those which do not exhibit any structural instability with temperature, and those which do. In the former case, the librations of the BX_4 anion perpendicular to a axis seem to experience a double-well type of potential whereas the parallel motions experience relatively higher potential barriers. Further, these ions seem to have been compressed from the perpendicular directions, reflecting the larger cation sizes in such compounds. On the other hand, these ions in the latter case experience similar double-well potentials, but this time for parallel motions, and the hindrances for both types of motion in this type of compound are about the same. Further the distortion of the anion seems to be axial, indicating perhaps the increased proximity between different anions in the direction of the a axis arising from the smaller cation size in these systems.

Acknowledgments

The financial assistance to one of the authors (RKS) by the Department of Atomic Energy, Government of India, and by the Council of Scientific and Industrial Research, India, in different stages of this work is gratefully acknowledged.

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