

Dynamic Properties and Phase Transitions in A_2ZnBr_4 ($A = (CH_3)_4N$ and $(CH_3)_4P$) as Studied by ^{79}Br NQR and Multinuclear NMR*

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In order to understand the mechanism of ferroelastic phase transitions in A_2ZnBr_4 ($A = (CH_3)_4N$ and $(CH_3)_4P$), the temperature dependences of ^{79}Br NQR frequencies and the spin-lattice relaxation times were measured. The temperature dependences of the 1H and ^{31}P spin-lattice relaxation times were measured as well for a possible correlation between the cation dynamics and the phase transition. Although the phase transition temperatures of these two compounds differ much (~ 100 K), the correlation times for the cation reorientation at the individual transition temperatures amount to some 10^{-11} s for both compounds.

Introduction

Several complex ionic compounds with the formula A_2MX_4 ($M = Zn, Cd, Co$, and Mn , $X = Cl, Br$, and I) are known. These crystallize in the β - K_2SO_4 type structure (Pnma) and undergo successive phase transitions on cooling [1–3]. X-ray and neutron structure analyses, dielectric constant measurements, and heat capacity measurements were carried out to understand the mechanism of these successive transitions [4–6]. Among the variety of the compounds we studied Cs_2MBr_4 ($M = Cd$ and Hg) by ^{79}Br NQR and found that these undergo the normal-to-incommensurate phase transition and the incommensurate-to-commensurate transition on cooling [5]. Landau's phenomenological theory and model calculations [6] suggested that the rotational displacement of anions and the translational displacement of Cs^+ are responsible for these transitions.

$[(CH_3)_4N]_2MBr_4$ ($M = Zn, Mn$, and Co) crystallize also in the β - K_2SO_4 type structure, and each of them undergoes a ferroelastic phase transition of second order to a monoclinic $P2_1/a$ structure around 280 K. This phase transition has extensively been investigated by X-ray structural analyses [7, 8], dielectric measurements [9], NQR [10], and Landau's phenomenological theory of

structural phase transition, and has been understood as a ferridistortive structural transition associated with the rotational displacement of two inequivalent cations [11]. Recently, $[(CH_3)_4P]_2MBr_4$ ($M = Zn, Mn$, and Co) was found to assume a β - K_2SO_4 type structure and to show a first order phase transition to the monoclinic $P2_1/a$ structure around 370 K [8]. The mechanism of these transitions is considered to be almost the same as that in $[(CH_3)_4N]_2MBr_4$. However, the difference in the order of transitions as well as the large difference in the transition temperatures between $[(CH_3)_4N]_2MBr_4$ and $[(CH_3)_4P]_2MBr_4$ have not yet been understood.

In order to understand the mechanism of the phase transitions in $[(CH_3)_4N]_2MBr_4$ and $[(CH_3)_4P]_2MBr_4$ from the microscopic point of view, we measured the ^{79}Br NQR frequencies and spin-lattice relaxation times in $[(CH_3)_4N]_2ZnBr_4$ ($T_{tr} = 287$ K; second order [10]) and $[(CH_3)_4P]_2ZnBr_4$ ($T_{tr} = 368$ K; first order [12]). The temperature dependence of the 1H and ^{31}P NMR spin-lattice relaxation times (T_1) in these two compounds and the 2H NMR spectrum in $[(CH_3)_4N]_2ZnBr_4$ were also measured to examine the role of the ionic motions in the phase transition.

Experimental

$[(CH_3)_4N]_2ZnBr_4$ was prepared by slow evaporation of an aqueous solution of zinc bromide and tetramethylammonium bromide according to [10]. $[(CD_3)_4N]_2ZnBr_4$ was prepared from $ZnBr_2$ and $(CD_3)_4NBr$ which was prepared by slow evaporation of an aqueous solution of

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$(CD_3)_4NOD \cdot 5H_2O$ (Cambridge Isotope Laboratories, 98% enrichment) and HBr. $[(CH_3)_4P]_2ZnBr_4$ was prepared by slow evaporation of an aqueous solution of $(CH_3)_4PBr$ and $ZnBr_2$ at 30 °C [12]. The sample was purified by recrystallization from an aqueous solution. For $[(CH_3)_4N]_2ZnBr_4$, analysis found: H, 4.37; C 17.99; N 5.32%; Calcd.: H, 4.54; C, 18.02; N, 5.25%. For $[(CD_3)_4N]_2ZnBr_4$, analysis found: D, 8.48; C, 17.18; N, 5.09%; Calcd.: D, 8.68; C, 17.23; N, 5.03%. For $[(CH_3)_4P]_2ZnBr_4$, analysis found: H, 4.09; C, 16.94%. Calcd.: H, 4.26; C, 16.94%. The transition temperatures determined by DTA (differential thermal analysis), *i.e.* 278 K for $[(CH_3)_4N]_2ZnBr_4$ and 386 K for $[(CH_3)_4P]_2ZnBr_4$, are in good agreement with those reported in [10, 12]. There is no difference in the transition temperatures between $[(CD_3)_4N]_2ZnBr_4$ and $[(CH_3)_4N]_2ZnBr_4$. The specimens used for NQR and NMR measurements were sealed in glass ampoules of 15 mm and 12 mm diameter, respectively, with a small amount of helium gas for the heat exchange.

The ^{79}Br NQR signals were detected with an FFT pulsed spectrometer system based on a Matec Model 5100 gated modulator. The ^{79}Br spin-lattice relaxation times were measured using the $\pi/2-\tau-\pi/2$ pulse sequence with an uncertainty of about 10%. NQR frequencies were determined to within ± 1 kHz by Fourier transformation of the free induction decay signal after a single $\pi/2$ pulse. The temperature was controlled to within ± 0.1 K.

Proton spin-lattice relaxation times, T_1 , were determined by applying the saturation- $\tau-\pi/2$ pulse sequence at the Larmor frequencies of 20.4 and 40.4 MHz using a JEOL pulsed NMR spectrometer (JNM-FSE-60SS). The temperature was measured with chromel-P-constantan thermocouples to within 0.1 K. A home-built low temperature cryostat with double glass dewars was used for the measurements of the T_1 between 77 and 400 K. Above 400 K, a home-built high temperature probe with a water circulating system was used.

The ^{31}P NMR spin-lattice relaxation time, T_1 , at 81.0 MHz and the 2H NMR spectrum at 30.7 MHz were measured by a Bruker DSX-200 spectrometer. The ^{31}P spin-lattice relaxation time was measured by the $\pi/2-\tau-\pi/2$ pulse sequence, and the 2H NMR spectrum by the $(\pi/2)_x-\tau-(\pi/2)_y-2\tau$ pulse sequence (solid-echo pulse sequence). Accumulation of up to 1024 times with a recycle delay of 4 s was done for the 2H spectrum. The temperature was calibrated by measuring the temperature dependence of isotropic chemical shift value of ^{207}Pb in $Pb(NO_3)_2$ [13].

Results and Discussion

^{79}Br NQR Frequencies and the Spin-lattice Relaxation Times

The temperature dependence of the ^{79}Br NQR frequencies in $[(CH_3)_4N]_2ZnBr_4$ is shown in Figure 1. There are four resonance lines at 77 K (in the low temperature phase) in the compound as listed in Table 1, being consistent with the result of an X-ray structural analysis that the space group is $P2_1/a$ ($Z = 4$) and that there are four crystallographically inequivalent bromines in the unit cell [8, 14].

In $[(CH_3)_4N]_2ZnBr_4$, the lower three resonance lines disappeared around 250 K on heating but the highest frequency line persisted up to the transition temperature, and no resonance line was detected in the high temperature orthorhombic phase. Perret *et al.* measured the temperature dependence of ^{79}Br NQR frequencies in $[(CH_3)_4N]_2ZnBr_4$ and reported a single resonance line in the high temperature phase [10]. Our NQR data in the low temperature phase agree well with their results in the whole temperature range of the measurements except in

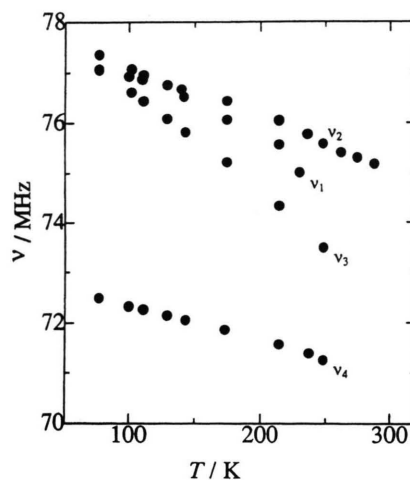


Fig. 1. Temperature dependence of ^{79}Br NQR frequencies in $[(CH_3)_4N]_2ZnBr_4$.

Table 1. ^{79}Br NQR frequencies in $[(CH_3)_4N]_2ZnBr_4$ and $[(CH_3)_4P]_2ZnBr_4$ at 77 K.

Compound	ν / MHz			
$[(CH_3)_4N]_2ZnBr_4$	77.3618	77.0692	77.0570	72.4825
$[(CH_3)_4P]_2ZnBr_4$	76.942	76.861	76.565	73.730

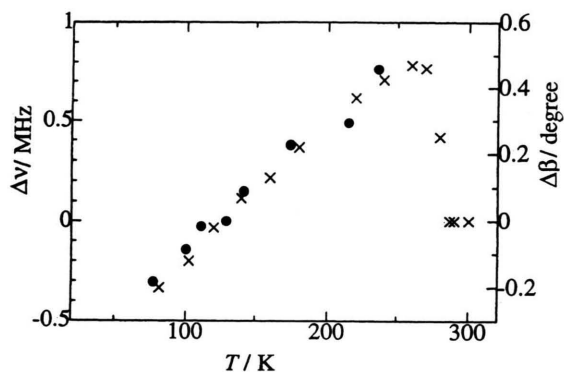


Fig. 2. Temperature dependence of the frequency difference, $\nu_1 - \nu_2$ (●) and the monoclinic angle, $\Delta\beta$ ($\beta - 90^\circ$) (X) in $[(CH_3)_4N]_2ZnBr_4$.

the close proximity of the transition point. The contradictory results for the high temperature phase can not be interpreted at the present stage: The growth of domains associated with the ferroelastic phase transition [15] may be responsible for the presence and/or absence of the NQR signals.

Figure 1 shows that the two high frequencies (ν_1 and ν_2) coincide at about 130 K. According to a recent, precise X-ray diffraction measurement [9] the monoclinic angle β in the low temperature monoclinic unit cell ($P2_1/a$) crosses 90° at ca. 125 K. Landau's phenomenological theory of structural phase transitions predicts that the transition from the high temperature $Pnma$ structure [16] to the $P2_1/a$ structure is associated with the appearance of a spontaneous strain e_5 below the transition point, T_c [17]. The strain e_5 corresponds to the order parameter of the transition and is related to the monoclinic angle β as

$$e_5 \sim \sin(\beta - 90^\circ).$$

Therefore we can regard the quantity $\Delta\beta = \beta - 90^\circ$ as an order parameter. The fact that the situation of $\beta = 90^\circ$ happens to occur at a lower temperature than T_c implies that the high temperature orthorhombic $Pnma$ structure is accidentally realized at this temperature as a consequence of the "ferridistortive" phase transition in the compound.

The instantaneous appearance of the $Pnma$ structure at ~ 125 K implies that a mirror appears in the ac -plane of the unit cell and makes two bromine atoms (Br(3) and Br(4) the notation in [14]) equivalent. Since ν_1 and ν_2 corresponds to the order parameter of the transition. Figure 2 shows that $\Delta\nu$ and $\Delta\beta$ are proportional to each other, validating the above assumption that the NQR fre-

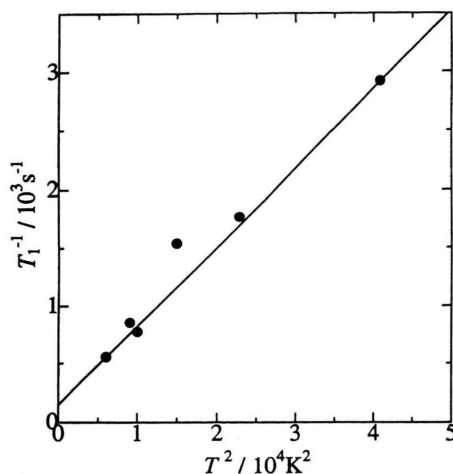


Fig. 3. Temperature dependence of the ^{79}Br NQR spin-lattice relaxation time in $[(CH_3)_4N]_2ZnBr_4$.

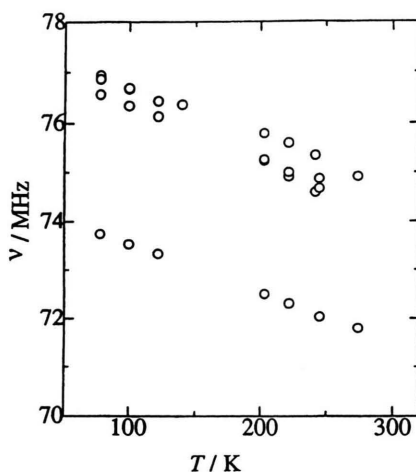


Fig. 4. Temperature dependence of ^{79}Br NQR frequencies in $[(CH_3)_4P]_2ZnBr_4$.

quency difference behaves as an order parameter. Figure 3 is the plot of the ^{79}Br NQR spin-lattice relaxation rate T_1^{-1} and T^2 in $[(CH_3)_4N]_2ZnBr_4$. The fact that a linear relation holds between T_1^{-1} and T^2 suggests that the relaxation is governed by a small-angle libration of $[ZnBr_4]^{2-}$ [18]. No evidence of the reorientation of the anion and/or any critical phenomenon associated with the phase transition was detected.

Figure 4 shows the temperature dependence of the NQR frequencies in $[(CH_3)_4P]_2ZnBr_4$. Four resonance lines were observed in the low-temperature monoclinic phase. These lines disappeared around 120 K on heating

but reappeared above 200 K. On further heating, two lines disappeared around 250 K and the other two lines disappeared around 280 K, *i.e.* far below the transition temperature (386 K). It is impossible to derive any information from the NQR frequency data about the phase transition at the present stage. Although it was difficult to measure the spin-lattice relaxation times in $[(CH_3)_4P]_2ZnBr_4$ because of the very poor NQR signal, rough estimation of T_1 gave no evidence of the reorientation of the anion.

1H Spin-lattice Relaxation Time

In order to examine any possible correlation between cationic motions and the phase transition, and to shed light on the origin of the large difference of transition temperatures in between $[(CH_3)_4N]_2ZnBr_4$ and $[(CH_3)_4P]_2ZnBr_4$, the 1H spin-lattice relaxation times T_1 in these two compounds were measured. Figure 5 shows the temperature dependence of T_1 in $[(CH_3)_4N]_2ZnBr_4$; T_1 has two minima, as in the case of many compounds containing $[(CH_3)_4N]^+$ group. It is generally considered that at low temperatures methyl group reorientation is excited and then the overall reorientation of the $[(CH_3)_4N]^+$ group is excited at a higher temperature, giving rise to

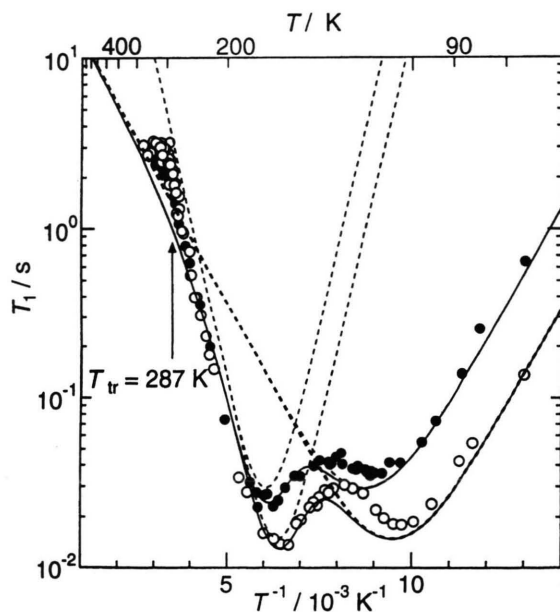


Fig. 5. Temperature dependence of the 1H spin-lattice relaxation time in $[(CH_3)_4N]_2ZnBr_4$ at the Larmor frequencies of 40.4 MHz (●) and 20.4 MHz (○). The solid lines denote calculated T_1 's using (1). The activation parameters are listed in Table 2.

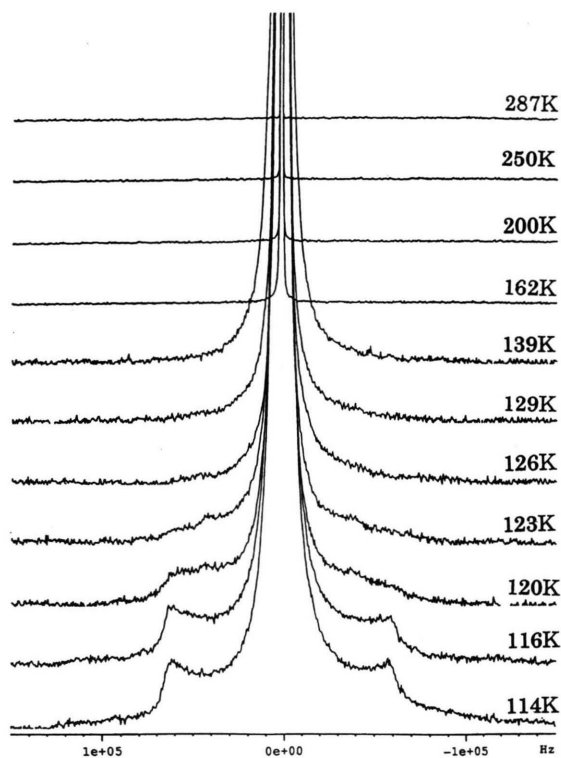


Fig. 6. Temperature dependence of the 2H NMR spectrum in $[(CD_3)_4N]_2ZnBr_4$ at the Larmor frequency of 30.7 MHz.

successive two minima in T_1 [19]. However, a 2H NMR work suggested that this is not always the case and that we should be careful for the assignment of the two minima in T_1 [20].

In $[(CH_3)_4N]_2ZnBr_4$, the depths of the two minima of T_1 are nearly equal. It is difficult to distinguish two motional modes only from the T_1 data. In order to specify the motional mode which brings about each of the two T_1 minima, the temperature dependence of the 2H NMR spectrum in $[(CD_3)_4N]_2ZnBr_4$ was measured between 114 and 287 K (Figure 6). A sharp resonance line with the half-width of 700 Hz was observed at room temperature, indicating that a fast isotropic reorientation of all cations takes place. On cooling, a broad component appeared below 120 K. The line shape of this component can be fitted to a theoretical line shape with $e^2Qq/h = 160$ kHz and $\eta = 0.06$. The value of the quadrupole coupling constant is nearly the same as the rigid lattice value in $(CD_3)_4NCl$, $(CD_3)_4NI$ and $[(CD_3)_4N]_2ZnCl_4$ [20]. However, there still exists a sharp peak even at 114 K. The X-ray structure analysis [7] states that there are two crystallographically inequivalent cations in the

compound. The above 2H spectrum below 114 K suggests that one of these inequivalent cations undergoes fast reorientation, while another cation remains stationary. Therefore, the two T_1 minima with equal depth should be attributed to the overall reorientation of two inequivalent cations. In order to analyze the 1H relaxation time in Fig. 5 we adopt Woessner's theory for the dipolar relaxation in a system in which the methyl reorientation and the overall reorientation are excited simultaneously but independently [21]:

$$(T_1)^{-1} = \frac{1}{2} \{A_a g(\omega_H, \tau_{c2a}) + B_a g(\omega_H, \tau_{ca})\} + \frac{1}{2} \{A_b g(\omega_H, \tau_{c2b}) + B_b g(\omega_H, \tau_{cb})\}, \quad (1)$$

where

$$\tau_{c2a}^{-1} = \tau_{ca}^{-1} + \tau_{c1a}^{-1} \quad (2a)$$

and

$$\tau_{c2b}^{-1} = \tau_{cb}^{-1} + \tau_{c1b}^{-1}. \quad (2b)$$

a and *b* distinguish two inequivalent sites. *A* and *B* denote the dipolar coupling constants for the methyl group reorientation and the overall reorientation. τ_c and τ_{c1} are the correlation times for the overall and the methyl group reorientations. Each correlation time is assumed to obey the Arrhenius equation

$$\tau_c = \tau_0 \exp(E_a/RT). \quad (3)$$

It is almost impossible to separate the contributions of the methyl group reorientation and overall reorientation to T_1^{-1} at each site, because there appears only one minimum in the T_1 curve for each site. Therefore, we assume that $\tau_{ca} = \tau_{c1a}$ and $\tau_{cb} = \tau_{c1b}$ and take *A* and *B* in (1) as adjustable parameters. The best fit of (1) to the experimental T_1 was obtained using the activation parameters

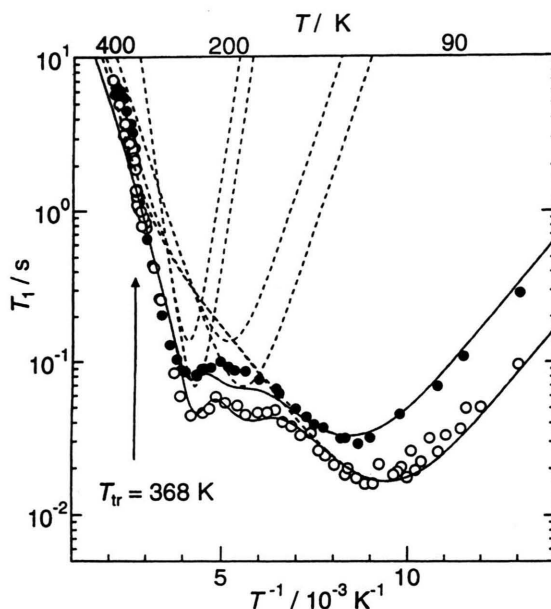


Fig. 7. Temperature dependence of the 1H spin-lattice relaxation time in $[(CH_3)_4P]_2ZnBr_4$ at the Larmor frequencies of 40.4 MHz (●) and 20.4 MHz (○). The solid lines represent calculated T_1 's using (1). The activation parameters are listed in Table 2.

listed in Table 2. The results of the calculation are shown in Figure 5. The values of the coupling constants *A* and *B* thus determined agree well with the theoretical values calculated from the geometry of $N(CH_3)_4$ group.

T_1 shows no jump at the transition temperature, but instead the slope varies significantly at the transition point, being characteristic of the second order transition. The activation energy of the overall reorientation in the high temperature phase is 3.0 kJ mol^{-1} , which is considerably smaller than 18.0 kJ mol^{-1} in the low temperature phase.

Table 2. The activation parameters of cationic motions in $[(CH_3)_4N]_2ZnBr_4$ and $[(CH_3)_4P]_2ZnBr_4$.

Mode of motion	Coupling constant/ s^{-1} (calc.)	$E_a/\text{kJ mol}^{-1}$	τ_0/s
$[(CH_3)_4N]_2ZnBr_4$			
site 1			
Internal rotation of CH_3 group	8.05×10^9 (8.05×10^9)	7.5	1.2×10^{-12}
Overall reorientation of $(CH_3)_4N^+$	4.61×10^9 (4.61×10^9)	7.5	1.2×10^{-12}
site 2			
Internal rotation of CH_3 group	8.05×10^9 (8.05×10^9)	18.0	6.0×10^{-15}
Overall reorientation of $(CH_3)_4N^+$	4.61×10^9 (4.61×10^9)	18.0	6.0×10^{-15}
$[(CH_3)_4P]_2ZnBr_4$			
Internal rotation of CH_3 group	5.5×10^9 (8.05×10^9)	5.7	7.5×10^{-12}
Overall reorientation of $(CH_3)_4P^+$	2.6×10^9 (3.57×10^9)	32	3.0×10^{-16}
Overall reorientation of $(CH_3)_4P^+$	2.6×10^9 (3.57×10^9)	14	4.0×10^{-13}

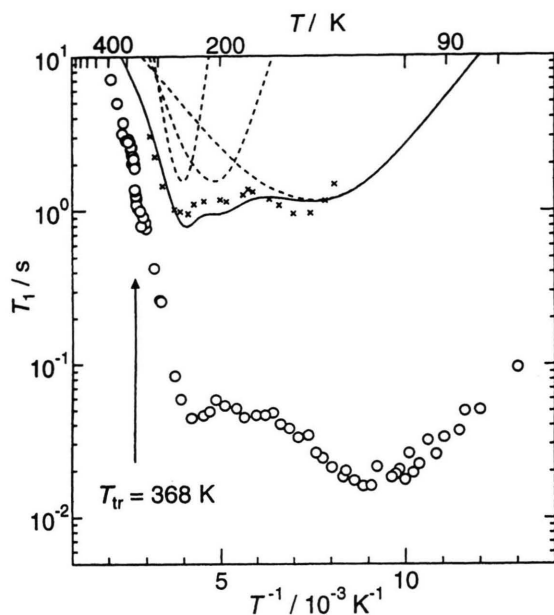


Fig. 8. Temperature dependence of the ^{31}P spin-lattice relaxation time in $[(\text{CH}_3)_4\text{P}]_2\text{ZnBr}_4$ at the Larmor frequency of 81.0 MHz (X). ^1H T_1 at 20.4 MHz is also reproduced ($\circ$).

Figure 7 shows the temperature dependence of the T_1 of ^1H in $[(\text{CH}_3)_4\text{P}]_2\text{ZnBr}_4$. T_1 assumes a deep minimum at 110 K and shallow minima at 170 K and 230 K. We examined the behavior of T_1 in each of various models for combined rotations of methyl groups and two inequivalent cations [19]. Although detailed structural data of $[(\text{CH}_3)_4\text{P}]_2\text{ZnBr}_4$ are not available, we confirmed the existence of two crystallographically inequivalent cations by measuring the ^{31}P MAS (magic angle spinning) NMR spectrum at 81 MHz; the MAS spectrum consists of two superposed peaks within the total half-width of 1.2 ppm, implying the existence of two different cations. The line-shape did not show any significant change in the low temperature phase between 309 and 345 K. We then found that the experimental T_1 of ^1H can be reproduced by the model of a rotational process in which all methyl groups undergo rotation with similar rates, and the two inequivalent cations undergo reorientation with unequal rates. Equation (1) can be applied to the case when assuming that $\tau_{ca} \neq \tau_{cb}$, and $\tau_{c1a} = \tau_{c1b}$. The best fit of (1) to the experimental T_1 curves is obtained, as shown in Fig. 7, using the activation parameters listed in Table 2. The values of the coupling constants, A and B , determined in the simulation agree well with the values calculated from the geometry of the $(\text{CH}_3)_4\text{P}$ group. In order to confirm the validity of the above model, the temperature dependence

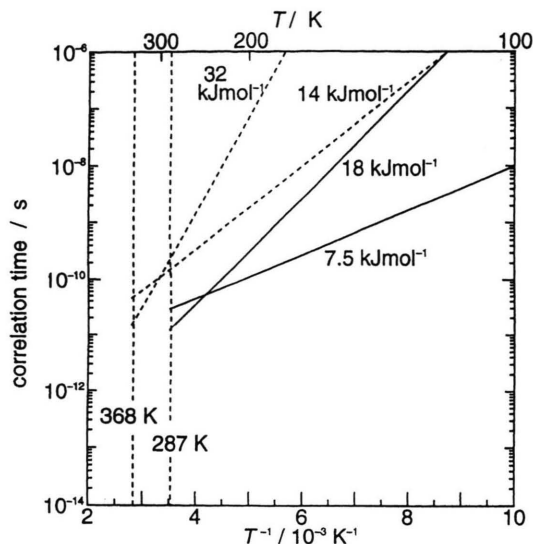


Fig. 9. Temperature dependence of the correlation times of overall reorientation in $[(\text{CH}_3)_4\text{N}]_2\text{ZnBr}_4$ (solid lines) and in $[(\text{CH}_3)_4\text{P}]_2\text{ZnBr}_4$ (broken lines). The perpendicular broken lines indicate the transition temperatures in both compounds.

of the ^{31}P spin-lattice relaxation time was measured (Figure 8). Three minima were observed in T_1 between 120 and 300 K. The lowest minimum is due to the methyl group reorientation, and the other two shallow minima are brought about by the overall reorientation of the two inequivalent cations. In calculating the contribution of the overall reorientation to the relaxation rate the theoretical formula for the heteronuclear dipolar interaction is applied [22]. The calculated T_1 , using the activation parameters derived from the ^1H T_1 data, reproduces the experimental result well.

T_1 of ^1H shows a small jump together with a change of the slope at the transition temperature (386 K), being characteristic of a first-order transition (Figure 7). The activation energy of overall reorientation of the cation in the high temperature phase is 2.0 kJ mol^{-1} , being considerably smaller than 14 and 32 kJ mol^{-1} in the low temperature phase.

Figure 9 shows the temperature dependence of the correlation times for the overall reorientation of the cations of both compounds. Although the activation energies for the two inequivalent cations in the two compounds are largely different, all correlation times lie inside a narrow range, $10^{-10} - 10^{-11} \text{ s}$ at the transition temperatures. The tendency that the rotational phase transition takes place when the correlation time for the molecular overall rota-

tion reaches 10^{-11} s has been recognized in many plastic crystals [23, 24]. The fact that the phase transition occurs when the rate of the overall reorientation of the cation reaches 10^{-11} Hz in each of the present two compounds suggests strongly that the motion of the large cations plays an important role in the “ferridistortive” transition, where it is thought that the shear strain plays the principal role.

In conclusion, it was found that the correlation times for the overall reorientation of the cations must exceed

10^{-10} s to trigger the ferroelastic phase transitions in $[(CH_3)_4N]_2ZnBr_4$ and $[(CH_3)_4P]_2ZnBr_4$. This finding can explain the large shift of the transition temperature on substituting P for N in $[(CH_3)_4N]_2ZnBr_4$ in a qualitative manner. It was also found that the difference in the NQR frequency, *i.e.* $(\nu_1 - \nu_2)$ behaves as order parameter of the transition in $[(CH_3)_4N]_2ZnBr_4$. There is no evidence for any large amplitude anionic motion through the transition region in both compounds.

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