

¹³³Cs NMR Spin-Lattice Relaxation Time and Chemical Shift Studies on Cs₂MX₄ Crystals with Sr₂GeS₄ and β-K₂SO₄ Structures Performing no Low Temperature Phase Transition

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¹³³Cs NMR spectra and spin-lattice relaxation times T_1 in crystalline Cs₂ZnCl₄ and Cs₂ZnBr₄ with β-K₂SO₄ structure, and Cs₂CdI₄ and Cs₂HgI₄ with Sr₂GeS₄ structure, which have no phase transition in the lower temperature regions, were measured to clarify the relation between the interionic covalency and crystal structures. Two central lines corresponding to two crystallographically inequivalent Cs sites were observed in all compounds. One of the two peaks in β-K₂SO₄-type compounds appears below 40 ppm, but another peak in those compounds and the both lines in Sr₂GeS₄-type compounds show larger shifts, 130 - 200 ppm. The temperature dependences of T_1 observed in Sr₂GeS₄-type compounds were close to the theoretical behaviour, calculated by considering contributions from normal lattice vibrations. Deviations from the calculation obtained for β-K₂SO₄-type systems are attributable to the difference in interionic interactions, i. e., partial covalency, in the crystals.

Key words: ¹³³Cs NMR; Chemical Shift; T_1 ; Partial Covalency.

1. Introduction

A₂BX₄ compounds containing isolated tetrahedral BX₄²⁻ ions form a modification of (A) the orthorhombic β-K₂SO₄-type (Pnma, $Z=4$) or (B) the monoclinic Sr₂GeS₄-type (P2₁/m, $Z=2$) structure. Many of the (A) compounds undergo phase transitions to incommensurate (IC) phases at low temperatures [1], but all (B) compounds have no IC phase. Some of (B) compounds transform to (A), called α-β transition, at a temperature $T_{\alpha-\beta}$ [2 - 4]. Below $T_{\alpha-\beta}$, (B) is more stable than (A), but often (A) can exist as a metastable state [5].

Recently, we reported ¹³³Cs NMR results on Cs₂CdBr₄, Cs₂HgBr₄ [6], Cs₂CdI₄ [7], and Cs₂HgCl₄ [8], which form modification (A) with phase transitions, and discussed the lattice dynamics in IC phases and the mechanism of phase transitions caused by differences in interionic interactions. To clarify the relations between interionic interactions and crystal

structures, we measured ¹³³Cs NMR spectra and spin-lattice relaxation times T_1 of β-K₂SO₄-type Cs₂ZnCl₄ [9] and Cs₂ZnBr₄ [10], and Sr₂GeS₄-type Cs₂CdI₄ [3] and Cs₂HgI₄ [4]. All perform no phase transitions below room temperature. These compounds were suitable to investigate lattice motions because we can exclude influences from phase transitions.

2. Experimental

Crystals of Cs₂ZnCl₄, Cs₂ZnBr₄, and Cs₂HgI₄ were grown by cooling a molten mixture containing stoichiometric amounts of corresponding CsX and MX₂ (purity of 99.9% for all). Cs₂CdI₄ crystals of modification (B) were obtained by slow evaporation of an aqueous solution containing stoichiometric amounts of CsI and CdI₂. The obtained fine crystals were dried *in vacuo* and then sealed in glass tubes with nitrogen gas for differential thermal analysis (DTA) and NMR measurements. DTA was carried out to

confirm the absence of phase transitions in the the range 100 - 360 K. The sample temperature was determined within ± 0.2 K by using a chromel-constantan thermocouple. ^{133}Cs NMR spectra and spin-lattice relaxation times T_1 were measured with a Bruker MSL-300 NMR system at a Larmor frequency of 39.4 MHz in the ranges 211 - 364 K, 173 - 373 K, 220 - 360 K and 214 - 359 K for Cs_2ZnCl_4 , Cs_2ZnBr_4 , Cs_2CdI_4 , and Cs_2HgI_4 , respectively. Chemical shifts of observed lines were recorded relative to a saturated CsCl aqueous solution. The sample temperature was controlled within ± 1 K with a VT-1000 temperature controller and determined by a copper-constantan thermocouple with the same accuracy. The uncertainty in the T_1 measurement was estimated to be within 5%.

3. Results

No thermal anomaly was detected by DTA measurement between 100 and 360 K for all compounds studied.

Quadrupolar perturbed ^{133}Cs NMR spectra are shown in Figure 1. The width of the 90° pulse tuned for the measurement of all powdered samples was close to that of a saturated CsCl aqueous solution used as standard. This suggests that a single quantum transition in ^{133}Cs NMR was excited in all observations, i. e., ^{133}Cs nuclei have small quadrupole coupling constants (e^2Qq/h) compared with the Zeeman interaction in all compounds. The observed line-shapes were explained by the superposition of two 1st order perturbed spectra. This is consistent with the reported crystal structure containing crystallographically in-

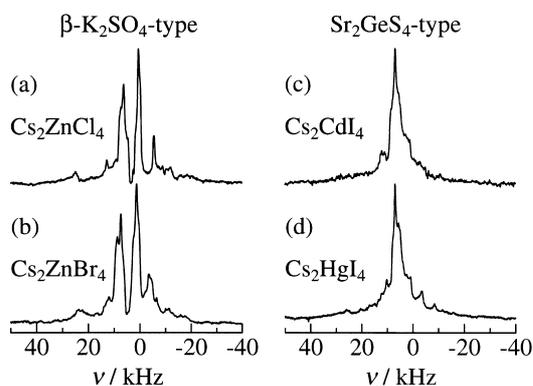


Fig. 1. Quadrupolar perturbed ^{133}Cs NMR spectra at 39.4 MHz at room temperature in Cs_2ZnCl_4 (a) and Cs_2ZnBr_4 (b) with $\beta\text{-K}_2\text{SO}_4$ structure, and Cs_2CdI_4 (c) and Cs_2HgI_4 (d) with Sr_2GeS_4 structure.

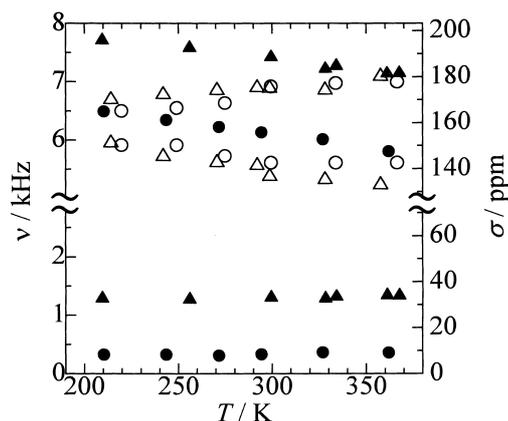


Fig. 2. Temperature dependences of central peak frequencies ν and their chemical shifts σ in ^{133}Cs NMR spectra for Cs_2ZnCl_4 (●) and Cs_2ZnBr_4 (▲) with $\beta\text{-K}_2\text{SO}_4$ structure, and Cs_2CdI_4 (○) and Cs_2HgI_4 (△) with Sr_2GeS_4 structure.

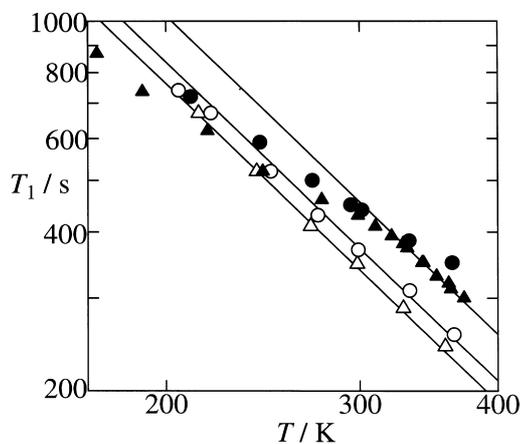


Fig. 3. Temperature dependences of ^{133}Cs NMR T_1 in Cs_2ZnCl_4 (●) and Cs_2ZnBr_4 (▲) with $\beta\text{-K}_2\text{SO}_4$ structure, and Cs_2CdI_4 (○) and Cs_2HgI_4 (△) with Sr_2GeS_4 structure. Solid lines are theoretical curves calculated by using (3).

equivalent two Cs ions [11 - 15]. Temperature dependences of the peak position of central lines observed in ^{133}Cs NMR are shown in Figure 2. In Cs_2ZnCl_4 and Cs_2ZnBr_4 with the $\beta\text{-K}_2\text{SO}_4$ structure, we observed two kinds of central lines at room temperature, one has a small chemical shift of ca. 10 and 30 ppm and the other has a large shift ca. 150 and 190 ppm. In Cs_2CdI_4 and Cs_2HgI_4 with the Sr_2GeS_4 structure, observed two lines gave large chemical shifts in a range of 140 - 180 ppm at room temperature.

The magnetization recovery in ^{133}Cs nuclei observed after saturation pulses could be reproduced by

a single exponential curve in the whole temperature range studied, and a unique T_1 value could be determined. Temperature dependences of ¹³³Cs NMR T_1 are shown in Figure 3. T_1 increased with decreasing temperature.

4. Discussion

4.1. Relations between NMR Chemical Shifts and Interionic Interactions

The NMR shielding tensor was formulated by Ramsey in the first approximation [16] as

$$\tilde{\sigma} = \tilde{\sigma}_D + \tilde{\sigma}_P. \quad (1)$$

Here, $\tilde{\sigma}$ represents the diagonalized tensor with diagonal components σ_{XX} , σ_{YY} and σ_{ZZ} . $\tilde{\sigma}_D$, called the diamagnetic term, is related only to the electron density around the nucleus in question. The paramagnetic term $\tilde{\sigma}_P$, is related to the local field induced by electron transfer from the ground to excited states. Taking into account relative chemical shift values from that of the reference sample, it was shown that the paramagnetic term in the heavy atoms is by about two orders of magnitude larger than the diamagnetic one [17]. In the following interpretation of ¹³³Cs NMR chemical shifts we only consider the paramagnetic terms. Moreover, we use the isotropic shielding constant $\sigma = (\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})/3$ as an approximation because isotropic shielding can be assumed in alkali metal ions in first order approximation. Since it was reported that the chemical shift is influenced by the degree of partial covalency in interionic bonds [18, 19], we take into account the covalency in this study. When the covalency of the chemical bond is small enough to approximate a cation in the bonding as an isolated system, the isotropic shielding constant σ_M in an alkaline metal nucleus relative to the ideal ion is given by [19]

$$\sigma_M = \lambda \frac{2e^2\hbar^2}{3m^2c^2} a_p^2 \frac{1}{\Delta E} \left\langle \frac{1}{r^3} \right\rangle_p, \quad (2)$$

where λ , e and m are the total bond covalency in Cs-X bonds (conversely, $(1 - \lambda)$ is the bond ionicity), the charge and the static mass of an electron, respectively, a_p is a fraction of p-orbitals related to hybrid orbitals in the partial-covalent bond, ΔE is the mean energy of all excited states contributing to the probability, and $\langle 1/r^3 \rangle_p$ is the mean $1/r^3$ value of a valence p-electron

causing partial covalency in a Cs-X ionic bond. In the case of heavy atoms such as Cs, d-orbital electrons also contribute to the chemical shift which can be analogously expressed [19]. This shift is, accordingly, getting larger with the increase of the total degree of covalency. Thus, we can see from Fig. 2 that one of the two crystallographically nonequivalent Cs ions in Cs₂MX₄ crystals with the β-K₂SO₄-type structure has a lower covalency than in the other Cs ion of the β-K₂SO₄-type, and both ions in the Sr₂GeS₄-type structures.

4.2. Relations between NMR Relaxation Times and Interionic Interactions

The ¹³³Cs NMR T_1 , which increased with temperature decrease, can be explained by the fluctuation of the quadrupole interaction due to normal lattice vibrations because of the absence of phase transitions in all four compounds. Since the frequencies of lattice vibrations are much higher than the NMR Larmor frequency $\nu_L = \omega_L/2\pi$, it can be assumed that the two-phonon Raman process is much more effective than the one-phonon direct process. In the high-temperature limit, i. e., $T \geq \theta_D$ where θ_D is the Debye temperature, the quadrupolar relaxation rate contributed from thermal lattice vibrations via the two-phonon Raman process is represented approximately as [20]

$$T_1^{-1} = AT^2. \quad (3)$$

The constant A is determined by the amplitude of the quadrupole coupling fluctuation $\Delta e^2 Qq/h$ caused by lattice vibrations [20].

We tried to fit the experimental data by (3). Temperature dependences of T_1 in Cs₂CdI₄ and Cs₂HgI₄ with the Sr₂GeS₄-type structure could well be fitted with the constants $A = 3.0 \times 10^{-8}$ and $3.3 \times 10^{-8} \text{ s}^{-1} \text{ K}^{-2}$ for Cs₂CdI₄ and Cs₂HgI₄, respectively, as shown in Fig. 3, but those in Cs₂ZnCl₄ and Cs₂ZnBr₄ with the β-K₂SO₄-type structure were unexplainable by a simple theoretical treatment of lattice mode with $A = 2.4 \times 10^{-8} \text{ s}^{-1} \text{ K}^{-2}$. The deviations in the calculation from experimental data were getting large with decreasing temperature. This result suggests that A is not a constant but a function of temperature in Cs₂ZnCl₄ and Cs₂ZnBr₄, i. e., the fluctuation of the electric field gradient $\Delta e^2 Qq/h$ relating to the relaxation is increased upon cooling. A temperature depen-

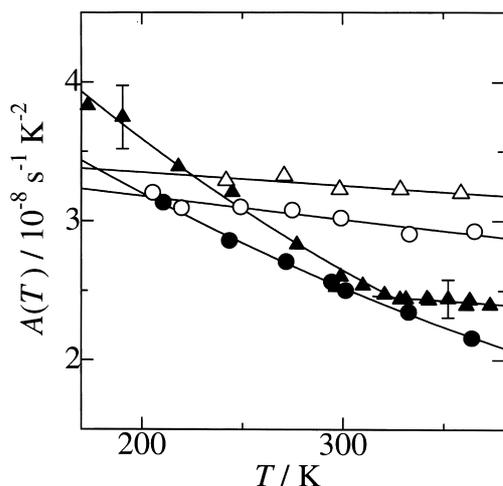


Fig. 4. Temperature dependences of $A(T)$ values in (3) obtained by substitution of ^{133}Cs NMR T_1 for Cs_2ZnCl_4 (●) and Cs_2ZnBr_4 (▲) with $\beta\text{-K}_2\text{SO}_4$ structure, and Cs_2CdI_4 (○) and Cs_2HgI_4 (△) with Sr_2GeS_4 structure. Solid lines are fitting curves assumed exponentially temperature dependent functions.

dent A given by the relation $A(T) = T_1^{-1}T^{-2}$ derived from (3) was plotted in Figure 4. The value of the $A(T)$'s for Cs_2ZnCl_4 and Cs_2ZnBr_4 increased exponentially with increasing temperature. This anomaly in $\beta\text{-K}_2\text{SO}_4$ -type compounds can be understood by considering the change of the covalency λ related to the interionic distance, and it may cause the anharmonicity of lattice vibrations. This temperature variation of the covalency may be related to the anomalously small ^{133}Cs chemical shift in one of the two lines observed in $\beta\text{-K}_2\text{SO}_4$ -type crystals. This difference of the potential harmonicity in the $\beta\text{-K}_2\text{SO}_4$ -type from that in Sr_2GeS_4 -type crystals derived from crystal structures seems to be one of the reasons for the appearance of IC phase only in Cs_2MX_4 compounds with the $\beta\text{-K}_2\text{SO}_4$ -type structure.

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