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

Koh-ichi Suzuki*, Shin’ichi Ishimaru, and Ryuichi Ikeda
Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan
* Present address: Department of Chemistry, College of Humanities and Sciences, Nihon University, Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan
Reprint requests to Dr. K. S.; Fax: +81-3-5317-9433, E-mail: suzuki_k@chs.nihon-u.ac.jp

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133Cs NMR spectra and spin-lattice relaxation times \( T_1 \) in crystalline Cs2ZnCl4 and Cs2ZnBr4 with \( \beta \)-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 \( \beta \)-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 \( \beta \)-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

\( A_2BX_4 \) compounds containing isolated tetrahedral \( BX_4^{2-} \) ions form a modification of (A) the orthorhombic \( \beta \)-K2SO4-type (Pnma, \( Z = 4 \)) or (B) the monoclinic Sr2GeS4-type (P2_1/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 \( \alpha \)-\( \beta \) transition, at a temperature \( T_{\alpha \beta} \approx 2 \)K. 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 \( \beta \)-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 \( \text{in vacuo} \) 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 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$_2$ZnCl$_4$, Cs$_2$ZnBr$_4$, Cs$_2$CdI$_4$, and Cs$_2$HgI$_4$, 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 ($\epsilon^2 Qq/\hbar$) 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 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$_2$ZnCl$_4$ and Cs$_2$ZnBr$_4$ with the $\beta$-K$_2$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$_2$CdI$_4$ and Cs$_2$HgI$_4$ with the Sr$_2$GeS$_4$ 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 $^{133}$Cs 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

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

Here, $\tilde{\sigma}$ represents the diagonalized tensor with diagonal components $\sigma_{XX}$, $\sigma_{YY}$ and $\sigma_{ZZ}$, $\tilde{\sigma}_D$, 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 $^{133}$Cs 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 $\sigma_M$ in an alkaline metal nucleus relative to the ideal ion is given by [19]

$$\sigma_M = \frac{\lambda e^2 h^2}{3 m^* c^2} \alpha_p \left\langle \frac{1}{r^3} \right\rangle_p,$$ \hspace{1cm} (2)

where $\lambda$, $e$ 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, $\alpha_p$ is a fraction of p-orbitals related to hybrid orbitals in the partial-covalent bond, $\Delta E$ is the mean energy of all excited states contributing to the probability, and $\left\langle 1/r^3 \right\rangle_p$ 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 Cs$_2$MX$_4$ crystals with the $\beta$-K$_2$SO$_4$-type structure has a lower covalency than in the other Cs ion of the $\beta$-K$_2$SO$_4$-type, and both ions in the Sr$_2$GeS$_4$-type structures.

4.2. Relations between NMR Relaxation Times and Interionic Interactions

The $^{133}$Cs 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 $\theta_D$ is the Debye temperature, the quadrupolar relaxation rate contributed from thermal lattice vibrations via the two-phonon Raman process is represented approximately as [20]

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

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

We tried to fit the experimental data by (3). Temperature dependences of $T_1$ in Cs$_2$CdI$_4$ and Cs$_2$HgI$_4$ with the Sr$_2$GeS$_4$-type structure could well be fitted with the constants $A = 3.0 \times 10^{-8}$ and $3.3 \times 10^{-8}$ s$^{-1}$K$^{-2}$ for Cs$_2$CdI$_4$ and Cs$_2$HgI$_4$, respectively, as shown in Fig. 3, but those in Cs$_2$ZnCl$_4$ and Cs$_2$ZnBr$_4$ with the $\beta$-K$_2$SO$_4$-type structure were unexplainable by a simple theoretical treatment of lattice mode with $A = 2.4 \times 10^{-8}$ s$^{-1}$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 Cs$_2$ZnCl$_4$ and Cs$_2$ZnBr$_4$; i.e., the fluctuation of the electric field gradient $\Delta e^2 Q q/h$ relating to the relaxation is increased upon cooling. A temperature depen-
Studies on Cs$_2$MX$_4$ Crystals with Sr$_2$GeS$_4$ and $\beta$-K$_2$SO$_4$ Structures

Fig. 4. Temperature dependences of $A(T)$ values in (3) obtained by substitution of $^{133}$Cs NMR $T_1$ for Cs$_2$ZnCl$_4$ ($\bullet$) and Cs$_2$ZnBr$_4$ ($\Delta$) with $\beta$-K$_2$SO$_4$ structure, and Cs$_2$CdI$_4$ ($\bigcirc$) and Cs$_2$HgI$_4$ ($\triangle$) with Sr$_2$GeS$_4$ structure. Solid lines are fitting curves assumed exponentially temperature dependent functions.

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