^{13}C CP/MAS NMR Study of the Layered Compounds $[C_6H_5CH_2CH_2NH_3]_2[CH_3NH_3]_{n-1}Pb_nI_{3n+1}$ ($n = 1, 2$)

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^{13}C CP/MAS NMR spectra were measured on the layered compounds $[C_6H_5CH_2CH_2NH_3]_2[CH_3NH_3]_{n-1}Pb_nI_{3n+1}$ ($n = 1, 2$). The linewidth of the resonance peak corresponding to the phenyl carbons changed with temperature. The maximum broadening took place at 363 K for both compounds. The activation energy E_a for the reorientation of the phenyl group was determined to be 25 kJ mol^{-1} for $n = 1$ and 26 kJ mol^{-1} for $n = 2$. The frequency factor τ_0 was evaluated from the linewidth at 363 K. The value of the second moment, estimated from the maximum linewidth, was interpreted by assuming a 180° flip of the phenyl group around its two-fold axis. The similarity of the activation energies for the reorientation of the phenyl group suggested that the local structure and the molecular motion of the organic cations is little affected by the difference in the sub-structure of the inorganic layer in those compounds.

Key words: ^{13}C CP/MAS NMR, Molecular motion, Layered compounds, Activation parameters, Local structure.

1. Introduction

Recently, layered compounds,

$$[C_6H_5CH_2CH_2NH_3]_2[CH_3NH_3]_{n-1}Pb_nI_{3n+1} \quad (n = 1, 2)$$

have been synthesized to establish their behavior as two-dimensional semiconductors and to construct a natural multi-quantum well system [1]. These compounds have a two-dimensional layered perovskite-type structure in which, if $n = 1$, the inorganic semiconductor layers, consisting of PbI_4^{2-}, are sandwiched between organic insulating spacers consisting of phenethylammonium ion, $C_6H_5CH_2CH_2$-NH_3^+. In the natural multi-quantum well system, the former act as "wells" and the latter as "barriers".

The structure of both compounds has been determined by X-ray diffraction using single crystals [1]. The space group of $[C_6H_5CH_2CH_2NH_3]_2PbI_4$ (hereafter abbreviated as Ph-PbI_4) is monoclinic $C2/m$ with the lattice parameters $a = 3.2508$ nm, $b = 0.6131$ nm, $c = 0.6185$ nm, and $\beta = 93.80°$ at ca. 200 K. The inorganic perovskite-like PbI_4^{2-} layer (monolayer) is built up of corner-sharing PbI_6 octahedra twisted by ca. 13.6° from the tetragonal positions. The space groups of $[C_6H_5CH_2CH_2NH_3]_2[CH_3NH_3]Pb_2I_7$ (hereafter abbreviated as Ph-Me-Pb_2I_7) is triclinic $P\bar{1}$ with the lattice parameters $a = 0.8794$ nm, $b = 0.8792$ nm, $c = 2.2766$ nm, $\alpha = 94.02°$, $\beta = 97.02°$, and $\gamma = 90.18°$ at room temperature. The inorganic perovskite-like $[CH_3NH_3]Pb_2I_7^{2-}$ layer (bilayer) is built up of methylammonium ions and corner-sharing PbI_6 octahedra twisted by ca. 12.1° from the tetragonal position. The phenethylammonium ions are lying between the inorganic layers, the phenyl groups facing each other. Disorder of the organic cations has also been reported [1]. In Ph-PbI_4, the organic cations are disordered across mirror planes, whereas in Ph-Me-Pb_2I_7 they are very poorly located by disorder and/or large thermal motion.

In these compounds the optical and the electronic properties, originating from the natural multi-quantum well structure, have been examined in detail by means of optical absorption, reflectance, photo-current, and photoluminescence spectra [2, 3]. However, the structural disorder and the molecular motion of the organic cations have not been studied yet, although considerable disorder of the organic cations has been observed. It is expected that the anisotropy of the intermolecular interaction in the two-dimensional systems may bring about some interesting phe-

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nomena such as phase transition and glass formation of the organic cations.

The ^{13}C CP(cross polarization)/MAS NMR spectrum can give dynamic and structural information independently of the carbon in the organic molecules. Especially, measurement of the line-broadening in ^{13}C CP/MAS NMR spectra can yield an activation energy E_a and a frequency factor τ_0 for the molecular motion. This procedure has been applied by Rothwell and Waugh to determine the activation parameters of hexamethylbenzene, hexamethylethane and adamantane, undergoing rapid molecular reorientation [4].

In the present study, we have measured the temperature dependence of ^{13}C CP/MAS NMR spectra of phenethylammonium ions in Ph-PbI_4 and Ph-Me-Pb_2I_7, have derived E_a and τ_0 from the temperature dependence of the linewidths and have discussed the mode of the molecular motion and the local structure of the organic cations.

2. Experimental

Ph-PbI_4 and Ph-Me-Pb_2I_7 were synthesized according to [5, 6]. The precursors phenethylammonium iodide ($C_6H_5CH_2CH_2NH_3I$) and methylammonium iodide (CH_3NH_3I) were prepared by neutralization of phenethylamine ($C_6H_5CH_2CH_2NH_2$) and methylamine (CH_3NH_2), respectively, with hydroiodic acid (HI) in aqueous solution. The excess HI and H_2O, as well as the impurity of iodine, were removed by drying the compounds *in vacuo* at ca. 60 °C for several days. Acetonitrile solutions containing $C_6H_5CH_2CH_2NH_3I$, CH_3NH_3I and PbI_2 with stoichiometric ratios were heated at 60 °C under N_2 atmosphere. The solvent was removed by flowing N_2 gas until the crystallization of the desired substances (Ph-PbI_4 or Ph-Me-Pb_2I_7) started. The precipitate was filtered and dried at ca. 40 °C under reduced pressure. Analysis for Ph-PbI_4 found: H, 2.54; C, 20.78; N, 2.91; I, 51.96%, Calcd.: H, 2.52; C, 20.03; N, 2.92; I, 52.59% and for Ph-Me-Pb_2I_7 found: H, 1.94; C, 13.54; N, 2.64; I, 56.01%, Calcd.: H, 1.92; C, 12.93; N, 2.66; I, 55.94%.

^{13}C CP/MAS NMR spectra were measured with a Bruker MSL-400 spectrometer operating at a Larmor frequency of 100.613 MHz for carbon-13. A sample spinning rate of ca. 6 kHz was employed by use of a ZrO_2 sample rotor, the dimension of which is ϕ 4 mm × 18 mm. The spectra were recorded at temperatures from 295 to 368 K under ^1H irradiation with a decoupling field $\nu_1 = 57$ kHz. The temperature was controlled by heating the bearing gas within ± 2 K using a Bruker VT-1000 unit. As external standard of the chemical shift hexamethylbenzene was used, in which the chemical shift for the methyl carbon is known to be 17.17 ppm downfield from tetramethylsilane (TMS) [7].

3. Results and Discussion

Peak Assignment of the ^{13}C CP/MAS NMR Spectra of Ph-PbI_4 and Ph-Me-Pb_2I_7

Figure 1 shows the ^{13}C CP/MAS NMR spectra of Ph-PbI_4 and Ph-Me-Pb_2I_7 at room temperature. In Ph-PbI_4 it consists of five peaks, three in the region of 120 to 140 ppm with relative intensity ratios 1:4:1 and two in the region of 30 to 50 ppm with the ratio 1:1. In Ph-Me-Pb_2I_7, the spectrum has an additional peak at 30.5 ppm. The experimental chemical shifts, measured from TMS, and their assignment to the carbon atoms of the phenethylammonium ion, together with the literature values for phenethylamine (PEA) in $CDCl_3$ and phenethylammonium chloride (PEA · HCl) in D_2O [8], are listed in Table 1. The additional peak observed in Ph-Me-Pb_2I_7 is considered to originate from the methyl group in $\underline{C}H_3NH_3^+$ located in the inorganic layers.

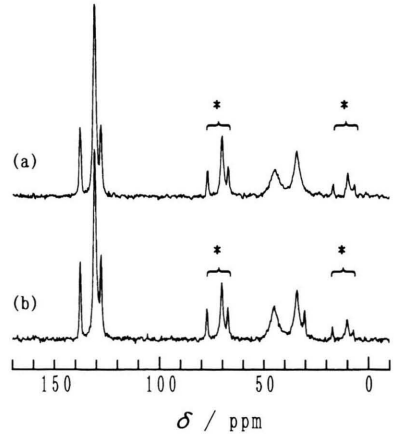
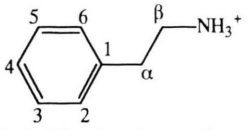


Fig. 1. ^{13}C CP/MAS NMR spectra of Ph-PbI_4 (a) and Ph-Me-Pb_2I_7 (b) at room temperature. The peaks with asterisks are spinning sidebands.

Table 1. ^{13}C chemical shifts determined from ^{13}C CP/MAS NMR spectra and literature.



Substance	Chemical shift values in ppm from TMS						
	C_1	C_2, C_6	C_3, C_5	C_4	C_α	C_β	CH_3
Ph-PbI_4	137.6	130.7		127.7	34.1	44.5	
Ph-Me-Pb_2I_7	137.7	130.8		127.8	34.1	45.0	30.5
PEA[a]	139.99	129.05	128.75	126.44	39.84	43.24	
PEA · HCl[b]	139.50	131.67	131.85	130.15	35.35	43.24	

[a] Solvent: $CDCl_3$ [8]; [b] Solvent: D_2O [8].

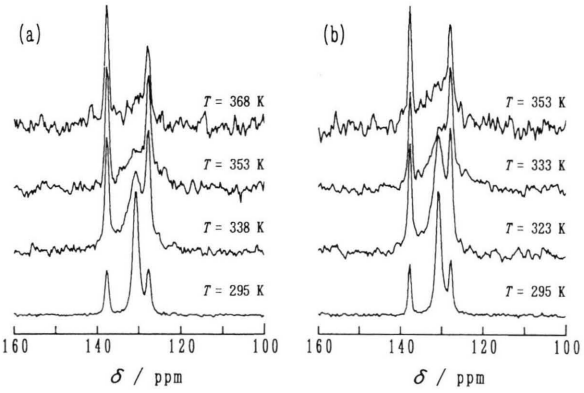


Fig. 2. Temperature dependence of ^{13}C CP/MAS NMR spectra corresponding to the peaks of the phenyl carbons: (a) Ph-PbI_4, (b) Ph-Me-Pb_2I_7.

Temperature Dependence of the Linewidths of the Phenyl Carbons in ^{13}C CP/MAS NMR Spectra

Figure 2 shows the temperature dependence of the ^{13}C CP/MAS NMR signals from the carbon atoms of the phenyl group in Ph-PbI_4 and Ph-Me-Pb_2I_7. The linewidths of the peaks from $C_2(C_6)$ and $C_3(C_5)$ broaden drastically on heating. In both substances, the linewidth broadens from $1 \sim 2$ ppm at 295 K to about 10 ppm at 368 K. However, the linewidths of the peaks from C_1 and C_4 appear to dependent little on temperature, maintaining $1 \sim 2$ ppm over the whole temperature range. This suggests that the phenyl group reorientates around a two-fold axis passing through the C_1 and the C_4 carbons, with the order of ^1H decoupling frequency.

Generally, molecular motion in solids can cause linebroadening by providing relaxation pathways for the transverse ^{13}C magnetization. When ^{13}C is coupled by a *stochastically* and *isotropically* modulated dipole-dipole interaction to ^1H under rf irradiation, the ^{13}C spin-spin relaxation rate $1/T_2$ is given by [4, 9]

$$\frac{1}{T_2} = \frac{\gamma_H^2 \gamma_C^2 \hbar^2}{5 r_{CH}^6} \left[\frac{\tau_c}{1 + \omega_1^2 \tau_c^2} \right], \tag{1}$$

where γ_C and γ_H are the gyromagnetic ratios of ^{13}C and ^1H, respectively, r_{CH} is the internuclear distance between ^{13}C and ^1H, ω_1 ($\equiv 2\pi\nu_1$) the strength of the rf irradiation (^1H decoupling) field, and τ_c the correlation time for the stochastic modulation of the $^{13}C-^1H$ dipolar interaction. The prefactor on the right hand side of (1) is equal to the $^{13}C-^1H$ Van Vleck second moment M_2 expressed in rad^2/sec^2. The NMR linewidth $\Delta\nu$, which is expressed in Hz, is proportional to $1/T_2$. When the line shape of the ^{13}C CP/MAS NMR spectra is approximated by a Lorentzian curve, the relation $\Delta\nu = 1/\pi T_2$ is satisfied [9].

Assuming an Arrhenius activation process for the correlation time τ_c,

$$\tau_c = \tau_0 \exp(E_a/RT), \tag{2}$$

a plot of $\log(1/\pi T_2)$, vs. the $1/T$, gives a Λ-shaped curve; its slope on the both sides of the maximum of $1/T_2$ gives the activation energies, and the value of $1/T_2$ maximum is used to determine the M_2 value. The analysis of the M_2 values obtained by the model calculation on the basis of the details of molecular structure leads to the mode of molecular motion contributing to the linebroadening. Furthermore, τ_0 can be determined from the knowledge of ω_1 and the temperature T' at which the maximum broadening takes place,

$$\tau_0 = \omega_1^{-1} \exp(-E_a/RT') \tag{3}$$

which follows from (2) under the condition $\omega_1 \tau_c = 1$.

In order to discuss the molecular reorientation quantitatively, the temperature dependence of the linewidth $\Delta\nu$ is inferred by a least squares curve fitting procedure assuming Lorentzian shape. Figure 3 shows $\Delta\nu$ vs. $1/T$ for the two substances, yielding according to (1) and (2) the activation energy of the molecular motion modulating the $^{13}C-^1H$ dipolar interaction. In Ph PbI_4 and Ph-Me-Pb_2I_7, the activation energies for the reorientation of the phenyl group are evaluated to be 25 kJ mol^{-1} and 26 kJ mol^{-1}, respectively. Furthermore, the peak appears to be most

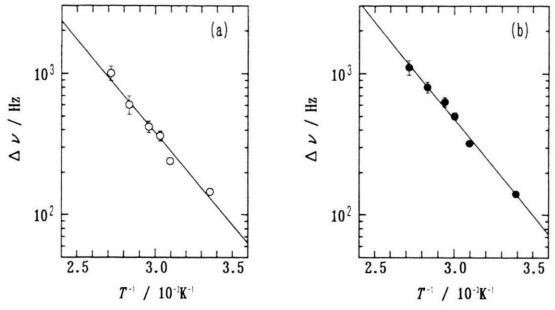


Fig. 3. Temperature dependence of the linewidth, $\Delta\nu$, in Ph-PbI_4 (a) and Ph-Me-Pb_2I_7 (b). The solid line represents the least squares curve fitted with an exponential function.

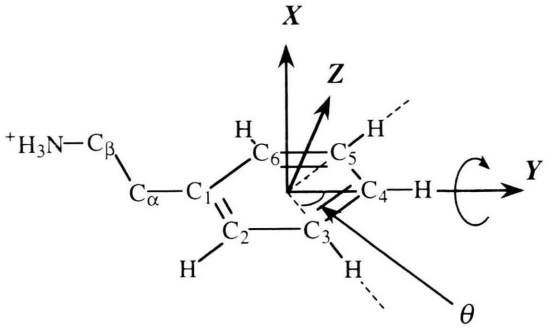


Fig. 4. The phenyl group in phenethylammonium ion illustrating the C-H bond vector and a Cartesian coordinate system where X is perpendicular to the plane of the ring, Y is parallel to the C_1-C_4 axis (the two-fold axis), and Z lies perpendicular to those directions. The phenyl group reorientates with a rigid angle of θ between the C_3 (C_5)-H vector and the Y axis (for C_2 (C_6)-H vector, the angle is $180-\theta$). The typical value of θ is 60° for the phenyl group.

broadend at 368 K, although the linewidth is evaluated to be about 1000 Hz by the least square's curve fitting. This temperature may be considered to be the temperature T' at which the maximum broadening takes place. Thus, we estimate τ_0 to be 8×10^{-10} s and 6×10^{-10} s for Ph-PbI_4 and Ph-Me-Pb_2I_7, respectively, using (3) with ν_1 ($\omega_1/2\pi$) = 57 kHz, E_a and T' = 368 K.

Next, we will discuss the motion of the phenyl group in phenethylammonium ion through a second moment M_2 analysis. Experimentally, M_2(exp.) is given by the maximum value of $\Delta\nu$ using the relation $1/T_{2\,(\min)} = M_2(\text{exp.})\,\omega_1^{-1}/2$, which is derived from (1) as $\omega_1\,\tau_c = 1$. Assuming $\Delta\nu \approx 1000$ Hz at T = 368 K to be the maximum value, in a similar manner as τ_0 estimated above, M_2(exp.) is evaluated to be 2.3×10^9 rad^2/s^2. If the phenyl group undergoes the reorientation *isotropically*, the experimental value will agree with the theoretical value M_2(rigid) calculated for the rigid lattice. For the unlike two spin systems, M_2(rigid) can be calculated by the prefactor on the right hand side of (1) and is calculated to be 4.5×10^9 rad^2/s^2 with the typical value of the C–H distance in the phenyl group, r_{CH} = 0.108 nm. This is twice the experimental value. The discrepancy in the second moment between the experimental and the theoretical values suggests that the phenyl group undergoes the reorientation *anisotropically*. When the molecule undergoes anisotropic motion, M_2 reduces by a factor F depending on the mode of the molecular motion [10]. The second moment, reduced by the anisotropic motion, is represented by $\Delta M_2 = [1-F]\,M_2$(rigid). ΔM_2 contributes to the linebroadening in ^{13}C CP/MAS NMR spectra. Thus, the prefactor on the right hand side of (1) must be replaced by ΔM_2, as anisotropic motion is taking place. Assuming that the phenyl group reorientates around the two-fold axis with 180° flip angle, as described in Fig. 4, the reduction factor F is represented by

$$F = 1 - \tfrac{3}{4}\sin^2 2\theta\,, \tag{4}$$

where θ is the angle between the rotation axis and the ^{13}C–^{1}H vector [10]. In the phenyl group, a typical value of θ is 60° as shown in Figure 4. Considering the reduction factor ΔM_2 is 2.5×10^9 rad^2/s^2, which is in good agreement with the experimental value M_2(exp.) $= 2.3 \times 10^9$ rad^2/s^2. This consideration leads to the conclusion that the phenyl group flips by 180°.

Local Structure of the Phenethylammonium Ion in Ph-PbI_4 and Ph-Me-Pb_2I_7

On the basis of the activation energies evaluated above, we discuss the local structure of the phenethylammonium ion in Ph-PbI_4 and Ph-Me-Pb_2I_7. The values of E_a are 25 kJ mol^{-1} and 26 kJ mol^{-1} for Ph-PbI_4 and Ph-Me-Pb_2I_7, respectively. Approximately, the activation energy will reflect the intermolecular interaction. That is, the similar values in E_a mean that the phenethylammonium ions interact with each other in both substances in a similar manner. Furthermore, this aspect will bring about the similar environments surrounding an organic cation. For instance, the thickness of the organic layer and the molar volume occupied by the organic cation are esti-

mated by using the lattice constants to be 0.944 nm and 1.08×10^{-4} m^3 mol^{-1} for Ph-PbI_4, and 0.898 nm and 1.05×10^{-4} m^3 mol^{-1} for Ph-Me-Pb_2I_7, respectively. These values also suggest the above aspect. One can conclude that the structure in the organic layer is little affected by the difference of the structure of the inorganic layer in those compounds.

The E_a values observed in our substances are lower than in other compounds, in which the phenyl group undergoes reorientation around the two-fold axis. For example, an activation energy of 40 kJ mol^{-1} has been reported for azo- and azoxybenzene soluted in poly-(methylmethacrylate) (PMMA), as determined by means of ^2H NMR [11]. In the tyrosine side chain of crystalline enkephalin, an activation energy of 42 kJ mol^{-1} has been reported [12]. In these materials it is assumed that the phenyl group reorientates relatively easily around its twofold-axis because the phenyl group is located in a synthetic polymer with low crystallinity and/or a natural pentapeptide with structural disorder and has a large free volume around it. Our activation energies are about one half of these. This indicates that the disorder in the organic cations is considerably larger than in the two materials. That is, the disorder will cause stacking faults of the phenyl rings and loose packing of the organic cations, and therefore the free volume around the organic cation becomes large.

Detailed information on the thermal expansion and compressibility for these compounds as well as the pressure dependence of E_a and lattice parameters is necessary for a further discussion of the relation between the free volume and E_a.

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