NQR and NMR Studies of Phase Transitions in $R_2Pb[Cu(NO_2)_6]$ ($R = K$, Rb, Tl, Cs, and NH_4)*

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^{39}K, ^{87,85}Rb, ^{133}Cs, ^{205}Tl, and ^{1,2}H NMR spin-lattice relaxation times T_1 and ^{14}N NQR spin-lattice relaxation times T_{1Q} were determined for $R_2Pb[Cu(NO_2)_6]$ ($R = K$, Rb, Tl, Cs, and NH_4). T_1 of ^{39}K and ^{87}Rb showed very short values in the incommensurate phase as compared with those in the other phases. When the commensurate-incommensurate phase transition point is approached from below, ^{14}N T_{1Q} of the $R = K$, Rb, Tl, and NH_4 compounds showed rapid decrease. On the other hand, that of the $R = Cs$ compound began to decrease first after passing beyond the corresponding transition point. The difference of the T_{1Q} behavior may be ascribed to the difference of the condensed phonon mode in the incommensurate phase.

Introduction

$R_2Pb[Cu(NO_2)_6]$ ($R = K$, Rb, Tl, Cs, and NH_4) are known to show successive phase transitions caused by the cooperative Jahn-Teller effect and to have an incommensurate intermediate-temperature phase [1–5]. In the compounds with $R = K$, Rb, and Tl, two phase transitions are observed [1, 2]. As the temperature is lowered, these compounds transform from the cubic highest temperature phase I into the incommensurate intermediate-temperature phase II, where the modulation of the local Jahn-Teller distortion of $[Cu(NO_2)_6]^{4-}$ octahedra is expressed by the wave vector $[\xi\xi 0]$, and further into the low-temperature phase III. In phase III, $[Cu(NO_2)_6]^{4-}$ octahedra form an antiferrodistortive order structure, where two crystallographically nonequivalent $[Cu(NO_2)_6]^{4-}$ octahedra are elongated along [100] and [010]. Besides the three phases described above, the $R = NH_4$ compound has the lowest-temperature phase IV [5]. In the phase IV, $[Cu(NO_2)_6]^{4-}$ octahedra form a ferrodistortive order structure, where all $[Cu(NO_2)_6]^{4-}$ octahedra are elongated along the same direction. As for the $R = Cs$ compound, several intermediate-temperature phases (II, II′, and II″) exist, phase II′ being incommensurate [3, 4]. The modulation of the local Jahn-Teller distortion of $[Cu(NO_2)_6]^{4-}$ octahedra in phase II′ is expressed by the wave vector $[1/2\ 1/2\ \zeta]$. In order to obtain information about the dynamics of phase transitions, ^{39}K, ^{87,85}Rb, ^{133}Cs, ^{205}Tl, and ^{1,2}H NMR spin-lattice relaxation times T_1 and the ^{14}N NQR spin-lattice relaxation time T_{1Q} were measured.

Experimental

A home-made pulsed NQR spectrometer was employed for the T_{1Q} measurements [6, 7], using the $180° - \tau - 90°$ pulse sequence. T_1 was measured by use of a home-made pulsed NMR spectrometer. For ^{39}K T_1 measurements, the $180° - \tau - 90° - \tau_e - 180°$ pulse sequence was used, where the spacing time τ was varied and τ_e was set constant. The $180° - \tau - 90°$ pulse sequence was used for the T_1 measurements of the other nuclei. The error of the T_1 and T_{1Q} measurements was estimated to be ca. $\pm 10\%$. The sample temperature was controlled within ± 0.5 K by employing a temperature controller Ohkura EC-61 equipped with a copper-constantan thermocouple.

Results and Discussion

NMR Spin-Lattice Relaxation

Figure 1 shows the temperature dependences of ^{133}Cs and ^{205}Tl T_1 of the $R = Cs$ and Tl compounds. T_1 of both compounds were almost temperature inde-

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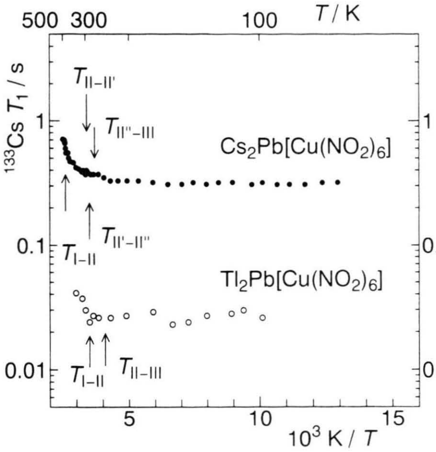

Fig. 1. Temperature dependences of ^{133}Cs and ^{205}Tl T_1 observed for $Cs_2Pb[Cu(NO_2)_6]$ and $Tl_2Pb[Cu(NO_2)_6]$. (●: ^{133}Cs (33.5 MHz), ○: ^{205}Tl (32 MHz))

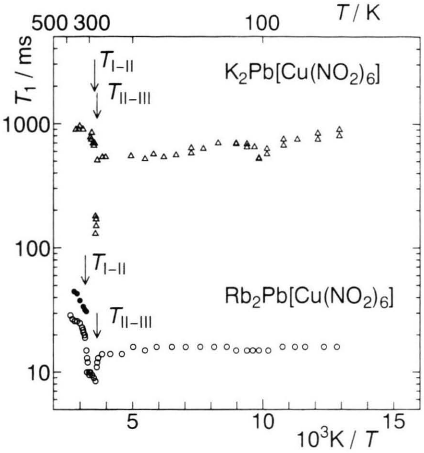

Fig. 2. Temperature dependences of ^{39}K and ^{85,87}Rb T_1 observed for $K_2Pb[Cu(NO_2)_6]$ and $Rb_2Pb[Cu(NO_2)_6]$. (△: ^{39}K (12.7 MHz), ○: ^{87}Rb (88.7 MHz), ●: ^{85}Rb (26.2 MHz))

pendent in phase III and increased with increasing temperature in the phases I and II. These temperature dependences of T_1 can be explained by assuming that the relaxation of the nuclei is dominated by the magnetic dipolar interaction between the resonant nuclei and the paramagnetic Cu^{2+} ions [8–11]. Since $\omega \tau_e \ll 1$ usually holds, where ω is NMR angular frequency and τ_e is the electron spin correlation time, T_1^{-1} is proportional to τ_e. Temperature-independency of T_1 at low temperatures suggests that τ_e is determined by a temperature-independent characteristic time for spin flip caused by the exchange interaction between electrons. The temperature dependences of T_1 at high temperatures suggest that τ_e is determined by the temperature-dependent electron spin-lattice relaxation time T_{1e}, which is considered to be dominated by the rate of thermal jumps between different Jahn-Teller distortions of $[Cu(NO_2)_6]^{4-}$.

Figure 2 shows the temperature dependences of ^{39}K, ^{87,85}Rb T_1 of the R = K and Rb compounds. NMR spectra of ^{85}Rb could only be detected in phase I. In analogy to the R = Cs and Tl compounds, T_1 of both compounds was almost temperature independent in phase III and increased with increasing temperature in phase I. In phase II of the R = K and Rb compounds, however, T_1 of ^{39}K and ^{87}Rb was very short as compared to the other phases. For the NMR relaxations of ^{39}K and ^{87}Rb, which have rather large quadrupole moments the nuclear quadrupole relaxation may be effective in the incommensurate phase II, though the magnetic dipolar relaxation due to Cu^{2+} ions can be considered to be dominant in the phases I and III.

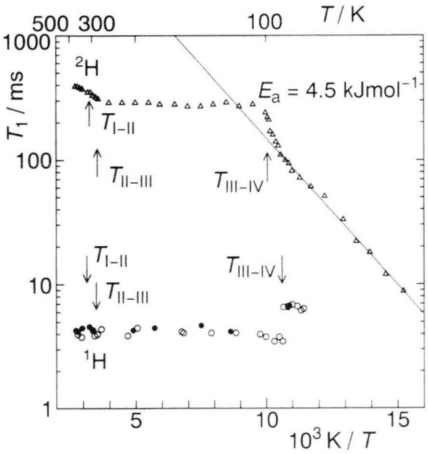

Fig. 3. Temperature dependences of ^{1,2}H T_1 observed for $(NH_4)_2Pb[Cu(NO_2)_6]$. (△: ^{2}H (41.6 MHz), ●: ^{1}H (32 MHz), ○: ^{1}H (20 MHz))

The temperature dependences of ^{1,2}H T_1 of the $R = NH_4$ compound are shown in Figure 3. ^{1}H T_1 was constant (ca. 6 ms) in phase IV and ca. 4 ms in the phases I, II and III. These results are considered to indicate the fluctuations of the magnetic dipolar interaction between the proton and electron which dominate T_1 are caused by the exchange interaction between electron spins. ^{2}H T_1 increased with increasing temperatures in the phases I and II, and was almost temperature-independent in phase III. Since these temperature dependences of T_1 are similar to those of the R = Cs and Tl compounds, the ^2H T_1 of the $R = NH_4$ compound is assumed to be determined by the magnetic interactions between the resonant nuclei and the paramagnetic Cu^{2+} ions in the phases I, II, and III. In phase IV, ^2H T_1 decreased with decreasing temperatures. ^2H T_1 is assumed to be determined by the fluctuations of the quadrupole interactions caused by the reorientation of NH_4^+ ions in phase IV. The activation energy for the reorientation of the ammonium ions $E_a = 4.5$ kJ mol^{-1} was obtained from the gradient of the log T_1 vs. T^{-1} plot in phase IV. This value is reasonable, since $E_a = 3$ kJ mol^{-1} has been reported for non-deuterated $(NH_4)_2Pb[Cu(NO_2)_6]$ [12].

When T_{1e} is dominated by the rate of the thermal jump between different Jahn-Teller distortions of $[Cu(NO_2)_6]^{4-}$, T_{1e} can be written as

$$T_{1e} \propto \exp(\Delta/kT), \tag{1}$$

where Δ is the activation energy for jumping between the valleys corresponding to different Jahn-Teller distortion of $[Cu(NO_2)_6]^{4-}$ [9, 11].

For the compounds in which the relation of $T_1^{-1} \propto \tau_e \sim T_{1e}$ can be expected to hold in phase I, Δ estimated from the gradient of the log T_1 vs. T^{-1} plots is shown in Table 1. These values are reasonable compared with those reported for some octahedral copper complexes [9, 11, 13].

NQR Spin-Lattice Relaxation

Though ^{14}N NQR spectra of the R = K, Rb, Tl, and NH_4 compounds could be observed only in the low-temperature commensurate phase or phases, those of the R = Cs compound could be observed even in the intermediate-temperature phases. In the phase III of the all compounds, two sets of ν_+ and ν_- lines were observed, which were assigned to nitrogen atoms on the elongated N–Cu–N axes of two crystallographically nonequivalent complex anions [14, 15]. In phase IV of the $R = NH_4$ compound, a pair of ν_+ and ν_- lines was detected [14]. Here ν_+ and ν_- are written by use of the nuclear quadrupole coupling constant eQq/h and asymmetry parameter η as

$$\nu_+ = (eQq/h)(3 + \eta)/4, \tag{2}$$

$$\nu_- = (eQq/h)(3 - \eta)/4. \tag{3}$$

Table 1. The activation energy Δ for jumping between different configurations of Jahn-Teller distortion estimated from NMR T_1 measurements in the phase I of $R_2Pb[Cu(NO_2)_6]$ (R = K, Rb, Tl, Cs, and NH_4).

Compounds	Δ/cm^{-1}	Resonant nuclei
$K_2Pb[Cu(NO_2)_6]$	290	^{39}K
$Rb_2Pb[Cu(NO_2)_6]$	430	^{87}Rb
$Tl_2Pb[Cu(NO_2)_6]$	600	^{205}Tl
$Cs_2Pb[Cu(NO_2)_6]$	420	^{133}Cs
$(NH_4)_2Pb[Cu(NO_2)_6]$	170	^2H

Figures 4 and 5 show the temperature dependence of T_{1Q} of the R = K compound and the R = Rb, Tl compounds, respectively. A difference of T_{1Q} among the different resonance lines was not observed. At low temperatures, T_{1Q} of the R = K, Rb, and Tl compounds increased gradually with increasing temperature. These temperature dependences of T_{1Q} cannot be explained by the fluctuation of the electric field gradient which is caused by the lattice vibrations [16]. The relaxation of the ^{14}N NQR are supposed to be dominated by the magnetic interactions between nitrogens and paramagnetic Cu^{2+} ions at low temperatures [9–11]. T_{1Q} of the R = K, Rb, and Tl compounds decreased very rapidly when the transition point from the phase III to II is approached from below. These rapid decreases of T_{1Q} suggests the existence of a slow vibrational mode which affects the relaxation of NQR.

Figure 6 shows the temperature dependence of T_{1Q} of the $R = NH_4$ compound. In phase IV, T_{1Q} was almost temperature independent and can be considered to be determined by the magnetic relaxation caused by Cu^{2+}. In analogy with the results of the R = K, Rb, and Tl compounds, T_{1Q} of the $R = NH_4$ compound decreased very rapidly when the transition points from phase III to II is approached from below. Further, T_{1Q} of the $R = NH_4$ compound decreased rapidly when the transition point from phase III to IV is approached from above. The slow vibrational mode can be considered to be exist not only near the transition point from phase III to II but also near that from phase III to IV.

Figure 7 shows the temperature dependence of T_{1Q} of the R = Cs compound. The temperature dependence of T_{1Q} at low temperatures is similar to that of the R = K, Rb, and Tl compounds and T_{1Q} is evidently dominated by magnetic relaxation due to Cu^{2+}. In contrast to the R = K, Rb, Tl, and NH_4 compounds,

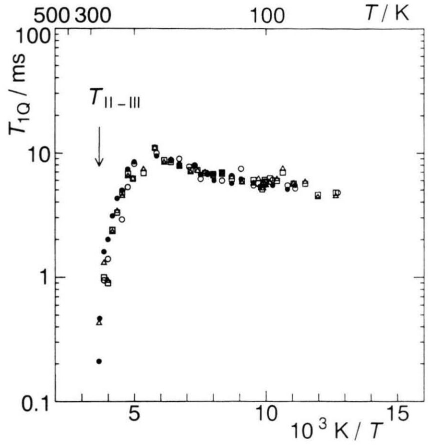

Fig. 4. Temperature dependences of ^{14}N T_{1Q} observed for $K_2Pb[Cu(NO_2)_6]$. T_{1Q} are indicated by ●, ○, △, and □ from high-frequency side of the four resonance lines, respectively.

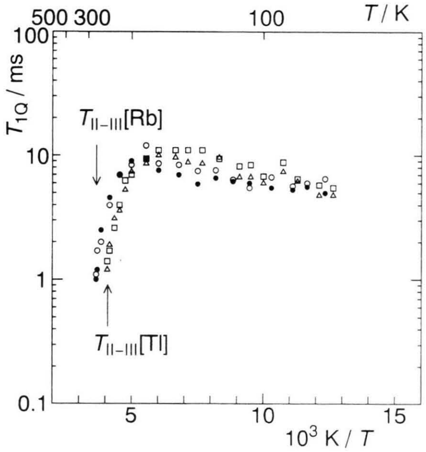

Fig. 5. Temperature dependences of ^{14}N T_{1Q} observed for $Rb_2Pb[Cu(NO_2)_6]$ and $Tl_2Pb[Cu(NO_2)_6]$. T_{1Q} are indicated by ●, ○, △, and □ for the high- and low-frequency lines of ν_- of $Rb_2Pb[Cu(NO_2)_6]$ and $Tl_2Pb[Cu(NO_2)_6]$, respectively.

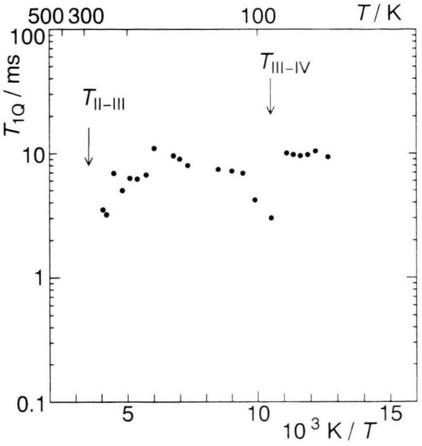

Fig. 6. Temperature dependences of ^{14}N T_{1Q} observed for the lowest-frequency line of $(NH_4)_2Pb[Cu(NO_2)_6]$.

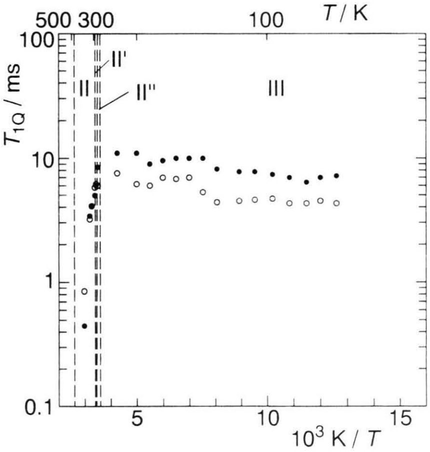

Fig. 7. Temperature dependences of ^{14}N T_{1Q} observed for $Cs_2Pb[Cu(NO_2)_6]$. T_{1Q} are indicated by ● and ○ for the high- and low-frequency lines of ν_-, respectively.

T_{1Q} of the R = Cs compound began to decrease very rapidly with increasing temperature after transition to the incommensurate phase II'. It is known that the phonon mode which condenses in the incommensurate phase of the R = K, Rb, and Tl compounds [1, 2] is expressed by the wave vector $[\xi\ \xi\ 0]$, while that of the R = Cs compound [3, 4] by the wave vector $[1/2\ 1/2\ \zeta]$. The difference of the T_{1Q} behavior between the R = Cs and the other compounds near the commensurate-incommensurate phase transition point may be ascribed to the difference of the condensed phonon mode in the incommensurate phase.

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