# NQR, NMR, and DSC Study of $[NH_3(CH_2)_3NH_3]CdBr_4$

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The $^{79,81}Br$ nuclear quadrupole resonance(NQR) of $[NH_3(CH_2)_3NH_3]CdBr_4$ was observed. The results of the temperature dependence of NQR frequencies and differential scanning calorimetry(DSC) showed that phase transitions take place successively at 328, 363, and 495 K. The results of $^2D$ NMR of $[ND_3(CH_2)_3ND_3]CdBr_4$ showed that the cations execute the jumping reorientation about their long axes above the transition point of 328 K.

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Salts of the type $A_2MX_4$(A=cation, M=metal, X=halogen), which crystallize in the infinite two-dimensional layer perovskite structure, have attracted a great deal of attention.[1] Especially for tetrachlorocadmates, phase transitions originate in the dynamics of $NH_3^+$ groups which form hydrogen bonds to the chlorine atoms of the anion layers.[2] We have studied a number of complex salts with bromocadmate anions by $^{79,81}Br$ NQR and X-ray diffraction to get information of the influence of the cations on the condensation of bromocadmate anions.[3,4] The present NQR study of the title compound was done in the course of this study.

The compound was prepared by mixing hydrobromic acid solution of $CdBr_2$ and $NH_2(CH_2)_3NH_2$ in the ratio of the stoichiometric amount. NQR measurement was done by using a superregenerative type oscillator. DSC was carried out above 130 K with a differential scanning calorimeter DSC220 from Seiko Instruments Inc. under the following condition; sample weight ca. 10 mg, the heating rate 10 K $min^{-1}$ with flowing dry $N_2$ gas at 40 ml $min^{-1}$. The partially deuterated (full deuteration of $NH_3$ groups) compound was obtained by the recrystallization of the protonated samples from $D_2O$ solution three times. $^2D$ NMR was measured at 6.37 T($\nu_L$=41.632 MHz) using Matec pulsed spectrometer. $^2D$ NMR spectrum was obtained by a Fourier transformation of the solid echo.

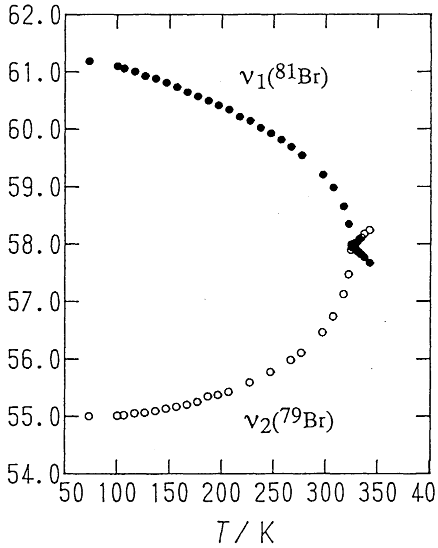

**Figure 1.** The temperature dependence of $^{79,81}Br$ NQR frequencies in $[NH_3(CH_2)_3NH_3]CdBr_4$.

**Table 1.** $^{81}Br$ NQR frequencies at several temperatures in $[NH_3(CH_2)_3NH_3]CdBr_4$ (**1**) and $[ND_3(CH_2)_3ND_3]CdBr_4$ (**2**)

| Compounds | T / K | | $\nu(^{81}Br)$/MHz | | |
|---|---|---|---|---|---|
| (**1**) | 77 | $\nu_1$ | 61.177 | $\nu_2$ | 45.934 |
| | 270 | $\nu_1$ | 59.675 | $\nu_2$ | 46.765 |
| (**2**) | 77 | $\nu_1$ | 61.162 | $\nu_2$ | 46.102 |
| | 270 | $\nu_1$ | 59.619 | $\nu_2$ | 47.047 |

$^{81}Br$ NQR frequencies at 77 and 270 K are listed in Table 1. The temperature dependence of $^{79,81}Br$ NQR frequencies in $[NH_3(CH_2)_3NH_3]CdBr_4$ is shown in Figure 1. The gradient of the curve of NQR frequencies vs. temperature changed suddenly at 327 K. DSC measurement was carried out up to the melting point, 554 K. Three peaks were observed as listed in Table 2. The transition point of the peak I is 328 K which is in good agreement with the deflection point of 327 K in the NQR frequency vs. temperature curve. The observed DSC curves suggested the second-order character of the peak I and the first-order of the other two transitions. The large entropy change of the peak I implies an order-disorder character of the transition. The temperature dependence of the quadrupole splittings of $^2D$ NMR spectra in the partially deuterated sample (cations: $[ND_3(CH_2)_3ND_3]^{2+}$) is shown in Figure 2. The quadrupole splittings were 132 kHz at 87 K and 44 kHz at 219 K, which correspond to the values for the static $ND_3^+$ groups and the rotational $ND_3^+$ groups about their three-fold axes, respectively.[5,6] The intensity of the quadrupole-splitting component decreased with increasing temperature, but it could be observed at temperatures up to the transition point of 323 K determined for the partially deuterated compound. The spectra above the transition point had no quadrupole-splitting component, which suggests that the averaging process for the quadrupole splitting takes place. This process is the jumping reorientation of whole 1,3-propanediammonium ions about their long axes among 3 or 4 orientations, because the observed transition entropy of 10.5 J $K^{-1}$ $mol^{-1}$ is nearly equal to

**Table 2.** The transition points $T_{tr}$, transition enthalpies $\Delta H_{tr}$, and transition entropies $\Delta S_{tr}$ in $[NH_3(CH_2)_3NH_3]CdBr_4$

| Peaks | $T_{tr}$ / K | $\Delta H_{tr}$ /(kJ $mol^{-1}$) | $\Delta S_{tr}$ / (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|
| I | 328 | 3.3 | 10.5 |
| II | 363 | 0.71 | 2.0 |
| III | 495 | 0.76 | 1.5 |

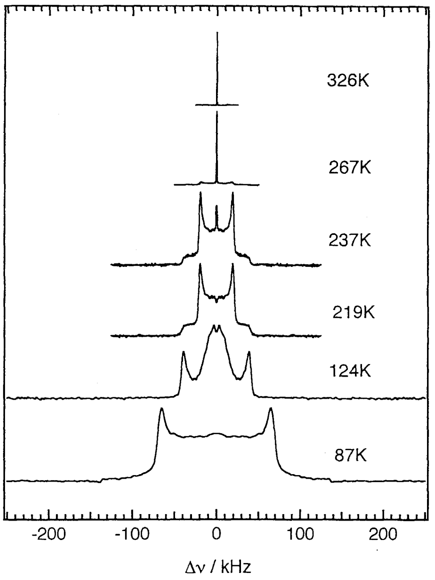

**Figure 2.** ${}^2$D NMR spectra in $[ND_3(CH_2)_3ND_3]CdBr_4$.

$R\ln 3=9.13$ or $R\ln 4=11.5$ J $K^{-1}$ $mol^{-1}$. This motion gives rise to the dynamically disordered cations in the crystal above 328 K, which results in the phase transition.

The preliminary result of the X-ray structure determination at 293 K shows that the space group is *Pnma* with $a$=7.721, $b$=19.054, $c$=7.898 Å, and $Z$=4, and that the crystal has the layer perovskite structure with two crystallographically different Br atoms, one of which is a terminal one and another a bridging one. In the case of $[NH_3(CH_2)_3NH_3]MnCl_4$ in the *Pnma* phase(phase III),[7] isomorphous with the room temperature phase of the title compound, the low-frequency line of two ${}^{35}$Cl NQR lines was assigned to the terminal chlorine atom and the high-frequency line to the bridging chlorine atom.[8] If we adopt the same assignment in the title compound, the following facts are successfully explained: If the low-frequency NQR line is assigned to the terminal bromine atom, the positive temperature dependence for the low-frequency line might be due to the breaking of hydrogen bonds with increasing temperature, as known in many cases.[9] Secondly the frequency shift by the deuteration was much more apparent for the low-frequency line, $\nu_2$ which shows a positive shift by about 300 kHz at 270 K, while the shift in $\nu_1$ was only ca. 50 kHz, as shown in Table 1.

## References and Notes

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