

A Highly Disordered New Solid Phase Containing Isotropically Reorienting Cations in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ Studied by ^1H NMR and Thermal Measurements

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The ^1H spin-lattice relaxation time, linewidth, second moment of ^1H NMR absorption, differential thermal analysis, and differential scanning calorimetry of methylammonium tetrabromocadmate(II) crystals were studied. A new solid phase was found between 482 K and the melting point (493 K). The ^1H NMR measurements revealed the presence of overall reorientation of methylammonium cations in this phase. In the room temperature phase, 120° reorientational jumps of the CH_3 and NH_3^+ groups were detected.

Introduction

$(\text{CH}_3\text{NH}_3)_2\text{ZnX}_4$ -type (X = halogen) compounds containing discernible tetrahedral $(\text{ZnX}_4)^{2-}$ complex anions in crystals have recently attracted attention because of the presence of an unusual solid phase where the cations undergo translational self-diffusion as well as overall rotation [1, 2]. This phase resembles the “ionic plastic phase” found in methylammonium nitrate [3], iodide [4], perchlorate [5], and bromide [6], in which highly disordered ionic motions take place.

$(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ forms monoclinic crystals at room temperature (space group $\text{P2}_1/\text{c}$ with $a=8.1227$, $b=13.4355$, $c=11.4194$ Å, $\beta=96.194$, and $Z=4$ [7]). The room temperature phase of $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$, consisting of isolated tetrahedral CdBr_4^{2-} anions, is isomorphous with the room temperature phase of $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ [8, 9], whereas this structure is different from that of $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$, having a perovskite-type layer structure [10]. Rao et al. have found two phase transitions in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ crystals at 167 and 400 K by differential scanning calorimetry (DSC) [11]. We have now carried out measurements of the second moment (M_2) of ^1H NMR

absorption, the ^1H spin-lattice relaxation time (T_1), the linewidth parameter (T_2^*) of ^1H NMR, differential thermal analysis (DTA), and DSC, in the temperature range 80–505 K in order to further clarify the phase transitions and ionic dynamics of methylammonium cations in crystals.

Experiments

DTA and DSC were carried out with a homemade apparatus [12] and a Du Pont 9900 Thermal Analyzer, respectively. Wide-line NMR spectra were recorded at 40 MHz using a JEOL JNM-MW-40S spectrometer. Pulsed NMR spectrometers reported elsewhere [1, 13] were used for the measurements of ^1H T_1 at 8.5, 20, and 32 MHz and T_2^* at 32 MHz. A $180^\circ-\tau-90^\circ$ pulse sequence was employed for the determination of T_1 . T_2^* was determined from the shape of the free induction decay after a 90° pulse.

$(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ was prepared by mixing $\text{CH}_3\text{NH}_3\text{Br}$ and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, both dissolved in a ca. 2 mol dm $^{-3}$ hydrobromic acid. The obtained crystals were recrystallized twice from a mixed solvent of methanol-hydrobromic acid (10:1). The purified crystals were identified by taking X-ray powder patterns at room temperature and also elementary analysis. Anal. calcd. for $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$: C, 4.84%; H,

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2.42%; N, 5.65%; Cd, 22.66%. Found: C, 4.82%; H, 2.42%; N, 5.71%; Cd, 22.65%.

$(\text{CH}_3\text{ND}_3)_2\text{CdBr}_4$ was prepared from the above sample by threefold crystallization in heavy water. Since the compounds were highly hygroscopic, the purified crystals were handled in a dry bag and dried under vacuum at room temperature for 24 h and then at 60 °C for 24 h before the measurements.

Results and Discussion

DTA curves were recorded for $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ in the temperature range 80–505 K. On heating the sample, two endothermic anomalies, one large and the other very small, were found at 482 and 178 K, respectively; the sample melted at 493 K. Rao *et al.* have used DSC and reported phase transitions at 167 and 400 K, and melting at 452 K [11]. These disagreements may be due to differences in the sample manipulation. In order to clarify this, we carried out DTA for three different samples, prepared by the same method, that is, mixing $\text{CH}_3\text{NH}_3\text{Br}$ and $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, both dissolved in water, but recrystallized from three different solvents, namely, water, ca. 1 mol dm⁻³ hydrobromic acid, and methanol. These samples are named I, II, and III, in the same order. All samples were identified by X-ray diffraction and elementary analysis, which gave the same results within experimental errors. DTA of these samples yielded the same phase transition temperature (T_{tr}) at 482 K and the melting temperature (T_{m}) at 493 K. They showed, however, additional small anomalies at 167 K in sample I, at 416 K in II, and at 221 and 409 K in III. These results suggest that these additional anomalies are not intrinsic but probably due to impurities such as $(\text{CH}_3\text{NH}_3)\text{CdBr}_3$, $(\text{CH}_3\text{NH}_3)_4\text{CdBr}_6$, and etc. This presumption is supported by the ^1H NMR experiments, which gave the same results for the three samples and no evidence for phase transitions except that at 482 K. Here, we designate the two solid phases existing above and below 482 K as high- and room-temperature phases (abbreviated to HTP and RTP), respectively. A quite analogous thermal behavior has been observed in $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ [1], exhibiting a phase transition at 477 K and the melting at 552 K.

The entropy changes ΔS_{tr} (482 K) and ΔS_{f} (493 K) determined by DSC were 20 and 34 J K⁻¹ mol⁻¹, respectively. These values are almost the same as the corresponding entropy changes, ΔS_{tr} (20 J K⁻¹ mol⁻¹, 477 K) and ΔS_{f} (36 J K⁻¹ mol⁻¹, 552 K), determined

for $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ [1]. Since the present complex and the tetrachlorozincate(II) are isomorphous at room temperature [7–9], one can expect similar ionic motions in the HTP of $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ and $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$, where cationic self-diffusion and overall reorientation take place quite frequently [1].

The temperature variation of M_2 is shown in Figure 1. An M_2 of 8.3 G² observed at 112 K indicates that the CH_3 and NH_3^+ groups in a cation reorient by 120° about its C–N bond axis (abbreviated C₃ reorientation) more frequently than 10⁵ Hz [14–16]. With increasing temperature, M_2 decreased gradually and reached 4.5 G² at 473 K. At T_{tr} of 482 K, M_2 decreased suddenly to 0.5 G². This small M_2 implies the onset of overall reorientation of the cation in the HTP [3, 17].

The temperature dependences of ^1H T_1 for $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ and $(\text{CH}_3\text{ND}_3)_2\text{CdBr}_4$ in the range 90–300 K are shown in Figure 2. The protonated and deuterated salts yielded a T_1 minimum of 22 and 39 ms, respectively, both at ca. 106 K. These T_1 minima can be attributed to the C₃ reorientation of the cations by referring to the foregoing results of M_2 . These minimum values are, however, about twice as large as the calculated or observed ones of 9–10 and 14–15 ms of the same motion of the CH_3NH_3^+ and CH_3ND_3^+ cations, respectively, in crystals [4, 16, 18, 19]. This implies that there exist two kinds of cations in the crystal, in agreement with the crystal structure of the RTP [7], each T_1 minimum observed being attributable to one of these cations. The activation energies evaluated from the gradient of the log T_1 vs. T^{-1} curve on the high temperature side of the minimum are (9.6 ± 0.3) and (8.9 ± 0.6) kJ mol⁻¹ for the cationic C₃ reorientations in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ and $(\text{CH}_3\text{ND}_3)_2\text{CdBr}_4$, respectively.

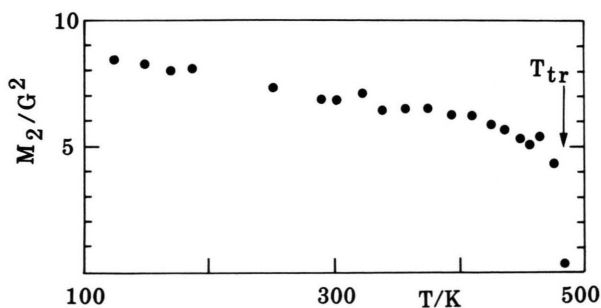


Fig. 1. The temperature dependence of the ^1H NMR second moment (M_2) observed for $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$. The phase transition temperature (T_{tr}) determined by DTA is indicated by an arrow.

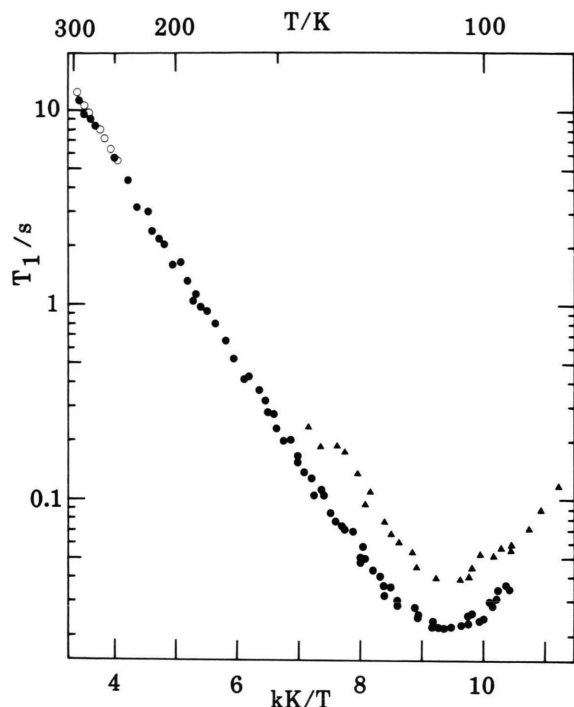


Fig. 2. The temperature dependence of the ^1H spin-lattice relaxation time (T_1) below room temperature observed in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ at 20 (●) and 32 MHz (○) and $(\text{CH}_3\text{ND}_3)_2\text{CdBr}_4$ at 20 MHz (▲).

^1H T_1 at 8.5, 20, and 32 MHz and ^1H T_2^* at 32 MHz observed for $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ are shown in Figure 3. T_1 showed a frequency dependence above 350 and a broad maximum around 400 K. The frequency dependent T_1 above 350 K is probably due to the onset of a new cationic motion in accordance with the M_2 decrease observed in the same temperature range. A precession about the C–N bond is a possible

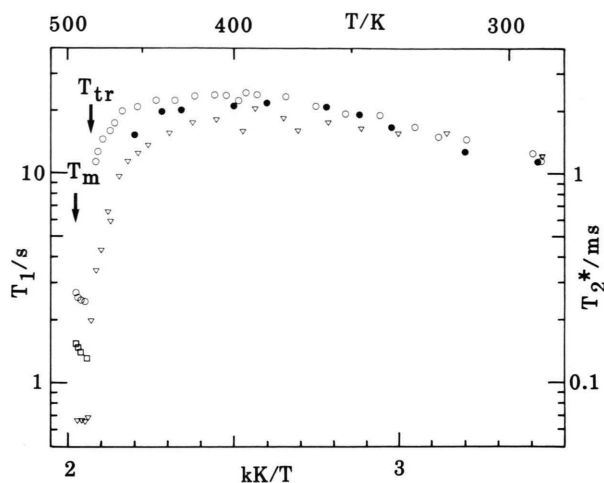


Fig. 3. The temperature dependence of ^1H T_1 observed in $(\text{CH}_3\text{NH}_3)_2\text{CdBr}_4$ at 8.5 (▽), 20 (●), and 32 MHz (○) and ^1H T_2^* at 32 MHz (□).

motional mode for this new motion. On further heating, T_1 decreased suddenly and T_2^* increased from ca. 30 to 140 μs at T_{tr} of 482 K. In the HTP T_1 was frequency dependent, and T_2^* and T_1 observed at 32 MHz increased with temperature, whereas T_1 at 8.5 MHz was almost temperature independent. These relaxation data cannot be assigned to only a single relaxation mechanism, but the cationic overall reorientation seems to contribute mainly to these relaxation processes.

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- [1] H. Ishida, T. Iwachido, N. Hayama, R. Ikeda, M. Terashima, and D. Nakamura, *Z. Naturforsch.* **44a**, 741 (1989).
- [2] H. Ishida, K. Takagi, T. Iwachido, M. Terashima, D. Nakamura, and R. Ikeda, *Z. Naturforsch.*, in press.
- [3] H. Ishida, R. Ikeda, and D. Nakamura, *J. Chem. Soc. Faraday Trans. 2*, **81**, 963 (1985).
- [4] H. Ishida, R. Ikeda, and D. Nakamura, *Bull. Chem. Soc. Japan* **59**, 915 (1986).
- [5] H. Ishida, R. Ikeda, and D. Nakamura, *Bull. Chem. Soc. Japan* **60**, 467 (1987), and references therein.
- [6] M. Tansho, D. Nakamura, and R. Ikeda, *Z. Naturforsch.* **44a**, 738 (1989).
- [7] D. Altermatt, H. Arend, A. Niggli, and W. Petter, *Mat. Res. Bull.* **14**, 1391 (1979).
- [8] B. Morosin and K. Emerson, *Acta Cryst.* **B 32**, 294 (1976).
- [9] J. M. Pérez-Mato, J. L. Mañes, J. Fernández, J. Zúñiga, M. J. Tello, C. Socías, and M. A. Arriandiaga, *phys. stat. sol. (a)* **68**, 29 (1981).
- [10] G. Chapuis, R. Kind, and H. Arend, *phys. stat. sol. (a)* **36**, 285 (1976), and references therein.
- [11] C. N. R. Rao, S. Ganguly, H. R. Swamy, and I. A. Oxtan, *J. Chem. Soc. Faraday Trans. 2*, **77**, 1825 (1981).
- [12] Y. Kume, R. Ikeda, and D. Nakamura, *J. Magn. Reson.* **33**, 331 (1979).
- [13] L. S. Prabhuram, R. Ikeda, and D. Nakamura, *Ber. Bunsenges. Phys. Chem.* **85**, 1142 (1981).
- [14] J. Tsau and D. F. R. Gilson, *Can. J. Chem.* **48**, 717 (1970).
- [15] E. R. Andrew and P. C. Canepa, *J. Magn. Reson.* **7**, 429 (1972).
- [16] H. Ishida, R. Ikeda, and D. Nakamura, *J. Phys. Chem.* **86**, 1003 (1982).
- [17] Y. Furukawa, H. Kiriya, and R. Ikeda, *Bull. Chem. Soc. Japan* **54**, 103 (1981).
- [18] S. Albert and J. A. Ripmeester, *J. Chem. Phys.* **58**, 541 (1973).
- [19] H. Ishida, R. Ikeda, and D. Nakamura, *Bull. Chem. Soc. Japan* **54**, 3116 (1982).