

NMR Study of Cation Motions in Ferroic $[\text{C}(\text{NH}_2)_3]_3\text{Bi}_2\text{Br}_9$

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Z. Naturforsch. **55 a**, 570–574 (2000); received March 9, 2000

The proton NMR second moment and spin-lattice relaxation time of polycrystalline $[\text{C}(\text{NH}_2)_3]_3\text{Bi}_2\text{Br}_9$ were studied in a wide-temperature range. Dynamical inequivalence of two crystallographically different guanidinium cations has been revealed. The C_3 reorientation of the two types of cations was found to be hindered by different potential barriers (25.1 kJ/mol and 34.7 kJ/mol). At higher temperatures an overall reorientation of the cations was revealed. The existence and order-disorder character of the phase transitions at 333, 350, 415, and 425 K have been confirmed.

Key words: Phase Transitions; Nuclear Magnetic Resonance.

Introduction

Molecular-ionic crystals of the formula $\text{R}_a\text{M}_b\text{X}_{a+3b}$ (where R = organic cation, M = Sb, Bi, X = Cl, Br, I) have been the subject of various experimental investigations [1 - 4]. The crystals belonging to this family containing small organic cations like monomethyl-, dimethyl- and trimethyl-ammonium revealed ferroelectric and ferroelastic properties [5]. The rich sequence of phase transitions encountered in these salts is governed by ordering processes of the alkylammonium cations. The crystals containing nearly spherical cations e. g. guanidinium: $[\text{C}(\text{NH}_2)_3]_3\text{Sb}_2\text{Cl}_9$ [6] and $[\text{C}(\text{NH}_2)_3]_3\text{SbCl}_6$ [7] do not exhibit long-range order of the ferroelectric type. The latter salt possesses pyroelectric properties in the low temperature phases (below 162 K) and is characterized by a quite large electric permittivity around the phase transition points. Very recently a new ferroic crystal with guanidinium cations, $[\text{C}(\text{NH}_2)_3]_3\text{Bi}_2\text{Br}_9$, has been discovered [8]. DSC, dilatometric, dielectric, and birefringence studies revealed a sequence of five first order phase transitions at 311, 333.5, 350, 415, and 425 K. X-ray studies have shown that the compound crystallizes in space group $\text{P2}_1/\text{m}$ in phase VI (below 311 K) and IV, while in the group Cmcm in phase III. The optical observations have revealed that the ferroelastic phase transition at 425 K takes place between a tetragonal (phase I) and an orthorhombic (phase II)

symmetry. The ferroelasticity in $[\text{C}(\text{NH}_2)_3]_3\text{Bi}_2\text{Br}_9$ is maintained down to liquid nitrogen temperature. The crystal structure consists of isolated bioctahedral $\text{Bi}_2\text{Br}_9^{-3}$ units and two types of crystallographically inequivalent guanidinium cations. The organic cations in the phase VI are ordered. Most of the phase transitions are characterized by a large entropy that points out their order-disorder nature. The mechanism of the phase transitions is postulated to be connected with reorientations both of the $[\text{Bi}_2\text{Br}_9]^{-3}$ units and $[\text{C}(\text{NH}_2)_3]^+$ cations.

To study reorientations of the guanidinium cations in the title compound, ^1H NMR studies have been undertaken in a wide range of temperature.

Molecular motions and phase transitions in guanidinium salts have been intensively studied by ^1H NMR techniques [9 - 15]. The guanidinium cation, having a planar or nearly planar structure, can form interionic hydrogen bonds with various anions. The potential barriers for the cationic reorientation around the C_3 axis detected in all the compounds studied so far were found to depend on the counter anions, their hydrogen-bonding ability and crystal packing.

Experimental

Tris-guanidinium enneabromodibismuthate (III) $[\text{C}(\text{NH}_2)_3]_3\text{Bi}_2\text{Br}_9$ was synthesized by reaction of $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ and BiBr_3 in concentrated hydro-

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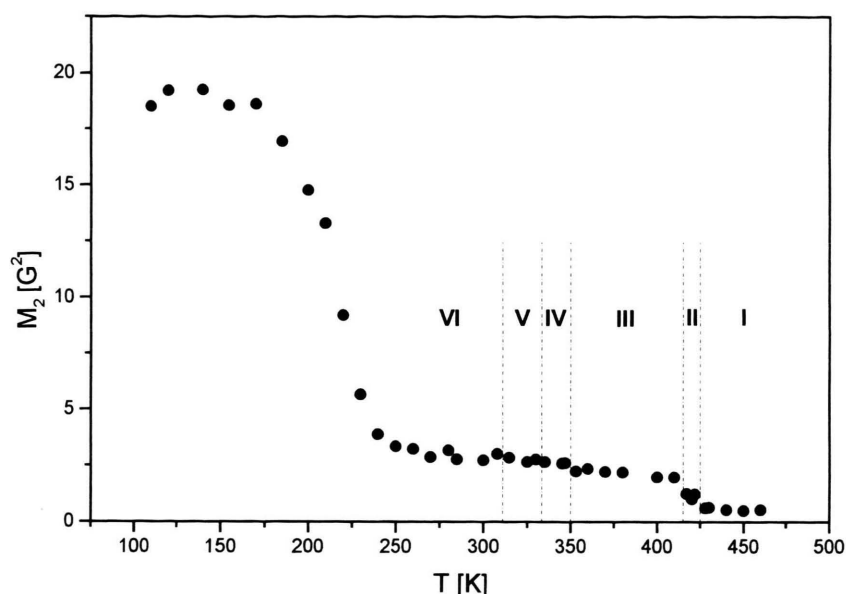


Fig. 1. The temperature dependence of the NMR second moment.

bromic acid. The stoichiometry was confirmed by elemental analysis. The synthesized compound was ground to a powder, dried, evacuated, and sealed in glass ampoules.

Measurements of the proton NMR second moments M_2 were carried out over a wide range of temperature using a home-made wide-line spectrometer operating at 28 MHz. The second moment was calculated by numerical integration of the spectra and corrected for the finite modulation field. The proton spin-lattice relaxation time T_1 was measured with a 60 MHz pulse spectrometer by a saturation recovery method, while the relaxation time $T_{1\rho}$ in a rotating field of 18.5 G by a spin-locking method. The temperature of the sample was controlled to an accuracy of 1 K.

Results

The temperature dependence of the proton second moment M_2 is shown in Figure 1. The M_2 value of about 19 G^2 registered at the lowest temperatures studied starts to decrease at ca. 175 K to 3 G^2 . The latter value, reached at 250 K, is maintained constant up to 333 K where it starts to decrease monotonically to 2 G^2 attained at ca. 380 K. Then, at 415 K, there is a jump to 1 G^2 and at 425 K the second moment diminishes to 0.5 G^2 , the constant value observed in phase I.

Figure 2 shows the temperature dependence of the spin-lattice relaxation time T_1 . Upon increasing the

temperature, T_1 decreases up to 333 K, and above 350 K it starts to increase rapidly. On passing through the phase transition temperatures 333 K and 350 K two discontinuities appear in the T_1 plot. Supercooling the phases III and IV, two T_1 minima are revealed: one of 67 ms at 345 K and another, apparent one of 85 ms at 323 K. A jump of T_1 is observed at 333 K.

The temperature dependence of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$, presented in Fig. 3, shows an asymmetric minimum of 0.26 ms at ca. 240 K and a slightly outlined shallow minimum of 0.8 ms at 205 K.

Discussion

The significant decrease of the experimental second moment observed in the lowest temperature phase (VI) evidently indicates the occurrence of cation motion, greatly reducing the dipolar interactions in the crystal. The activation energy of the motion, estimated from the Waugh-Fiedin formula [16], is about 26 kJ/mol. An identification of the motional process responsible for the NMR line narrowing is accomplished by a comparison of the observed value of the second moment plateau with those predicted theoretically for the assumed model of reorientation. The value of 19 G^2 observed below 175 K corresponds well to the second moment calculated for the rigid cationic sublattice of the crystal 18.2 G^2 . The latter value has been obtained by using Van Vleck's

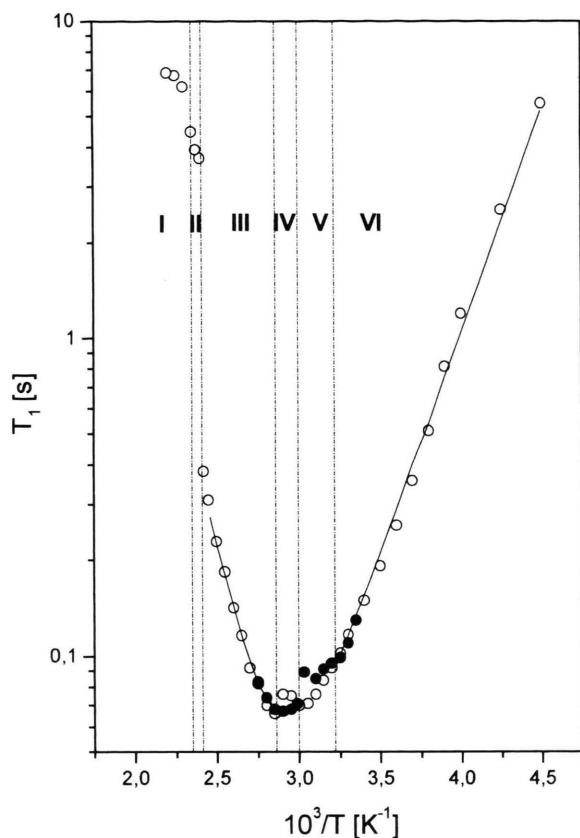


Fig. 2. The temperature dependence of the NMR spin-lattice relaxation time T_1 (○: on heating, ●: on supercooling). The solid lines are theoretical fits.

formula [17] and crystal data given in [8], assuming a normalised geometry of the amino groups [18]. By considering magnetic dipolar interactions among the ^1H , ^{14}N , ^{79}Br , and ^{81}Br spins, the intramolecular part of the second moment was found to be 16.8 G^2 and the intermolecular part 1.4 G^2 . The calculation performed for the two crystallographically inequivalent cations did not show any significant difference in the calculated values. A reorientation of the guanidinium cation about its C_3 axis reduces the second moment to 4.5 G^2 , a value evidently higher than the plateau value of 3 G^2 observed in our experiment above 260 K . Therefore it is concluded that, apart from C_3 reorientation of all the cations occurring, there must be another motional mechanism which causes further diminishing of the second moment. This is probably a flipping motion of an NH_2 group reducing the second moment by about 1.5 G^2 , as was found in other guanidinium salts [12 - 14]. A monotonic decrease of the second

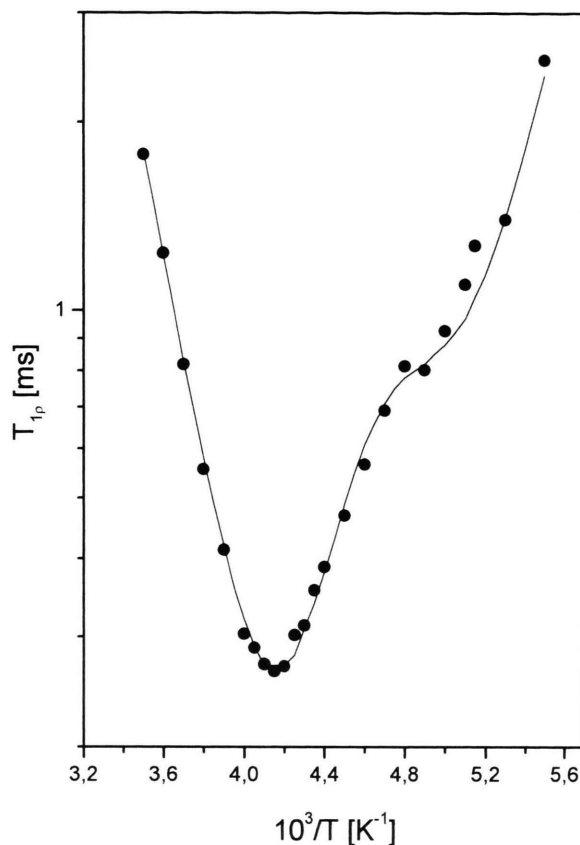


Fig. 3. The temperature dependence of the spin-lattice relaxation time T_{1p} . The solid line is a theoretical fit.

moment observed above the phase transition at 333 K may reflect an oscillation of the whole cation or its amino groups, slightly modulating the dipolar spin interactions. A jump of the second moment at 415 K confirms the existence of the phase transition $\text{III} \rightarrow \text{II}$. The value of 1 G^2 above the transition can be interpreted in terms of overall reorientation of one of the crystallographically independent cations. Overall reorientation of all the cations is observed in phase I, leading to a second moment of 0.5 G^2 . Thus it proves that in the high temperature phases II and I the dynamical inequivalence of the two crystallographically independent cations and their great disorder have appeared.

By referring to the above discussion of the second moment, the temperature dependence of the spin-lattice relaxation time T_1 can be analysed using the BPP theory [19]. The relaxation rate T_1^{-1} for the motional averaging of the magnetic interactions can be expressed as

$$T_1^{-1} = \frac{2}{3} \gamma^2 \Delta M_2 \left[\frac{\tau}{1 + \omega^2 \tau^2} + \frac{4\tau}{1 + 4\omega^2 \tau^2} \right]. \quad (1)$$

Here γ is the magnetogyric ratio of ^1H nuclei, ω the Larmor frequency, and ΔM_2 the second moment reduction by the motion considered. The correlation time τ can be related to the activation energy E_a through the Arrhenius relation

$$\tau = \tau_0 \exp(E_a/kT). \quad (2)$$

The relaxation time $T_{1\rho}$ in the rotating frame is described by the expression

$$T_{1\rho}^{-1} = \frac{2}{3} \gamma^2 \Delta M_2 \left[\frac{5\tau}{2(1 + \omega^2 \tau^2)} + \frac{\tau}{1 + 4\omega^2 \tau^2} + \frac{3\tau}{2(1 + 4\omega_1^2 \tau^2)} \right], \quad (3)$$

where ω_1 is the frequency in the spin-locking field.

In the low-temperature phase VI a significant, linear decrease of T_1 certainly indicates the onset of C_3 reorientation of the guanidinium cations, greatly modulating dipole-dipole interactions. However the full interpretation of the data obtained upon heating the sample was not possible as an expected T_1 minimum was obscured by the existing phase transitions at 333 and 350 K. On supercooling the sample from phase III two minima were revealed, separated by a jump of T_1 at 333 K. The shift of the discontinuity of T_1 from 350 K on heating to 333 K on supercooling the sample is consistent with the hysteresis observed in the DSC experiment [8], reflecting the phase transition $\text{III} \rightarrow \text{IV}$ at the lower temperature. Since the calorimetric study has revealed the hystereses of the other phase transitions too, there is a question whether the apparent T_1 minimum observed at 323 K upon supercooling does not come from the next shifted phase transition $\text{IV} \rightarrow \text{V}$. Thus, as the T_1 minimum at 323 K is not quite reliable, we have performed a calculation and fitting of the spin-lattice relaxation time T_1 for the phase III (supercooled) and phase VI. The fitting procedure yielded the values: $E_a = 41.0$ kJ/mol, $\tau_0 = 1.0 \cdot 10^{-15}$ s, $\Delta M_2 = 8.3$ G² for the phase III and $E_a = 25.1$ kJ/mol for the phase VI. These fitted values may indicate a dynamical inequivalence of the crystallographically inequivalent guanidinium cations. The value of ΔM_2 obtained for the supercooled phase III does not certainly reflect the C_3 reorientation of all the guanidinium cations for which the expected value

should be around 13 G², leading to $T_{1\text{min}} \cong 40$ ms. Since the molecular unit contains three guanidinium cations we can thus assume that two of them are dynamically different from the third one. The value of 8.3 G², fitted to the data of the supercooled phase III, corresponds well to the C_3 reorientation performed by the two guanidinium cations, with the activation energy of 41 kJ/mol, very often revealed for such a motion in the guanidinium salts [11, 12, 15]. The C_3 reorientation of the third cation is probably activated in the phase VI hindered by the lower potential barrier of 25.1 kJ/mol, the value corresponding well to that obtained from the second moment experiment.

The dynamical inequivalence of the guanidinium cations is confirmed by the $T_{1\rho}$ experiment. A fitting of the theoretical values to the experimental $T_{1\rho}$ plot has evidenced the existence of two motions activated in the phase VI. These motions are certainly the C_3 reorientations of all the guanidinium cations since the sum of the fitted ΔM_2 values, equal to 12.5 G², corresponds – in the accuracy limit – to the theoretically obtained value for such motion (13 G²). The two motions arise gradually, since two $T_{1\rho}$ minima of different depths are observed in the experiment. The higher minimum reflects the onset of the C_3 reorientation of one guanidinium cation, and the lower the onset of two other cations. The fitted parameters derived for the two motions are as follows: $E_a(1) = 25.1$ kJ/mol, $\tau_0(1) = 2.7 \cdot 10^{-13}$ s and $E_a(2) = 34.7$ kJ/mol, $\tau_0(2) = 3.3 \cdot 10^{-14}$ s.

The activation energies, especially that of 25.1 kJ/mol obtained for the reorientation of one guanidinium cation, are relatively low when compared with those of other salts. This results from the rather weak hydrogen bonds $\text{N-H}\cdots\text{Br}$ and small dipolar proton-proton interactions among the nearest cations in the crystal lattice. The overall reorientation of the guanidinium cations observed in the wide-line experiment has been rather rarely observed in the guanidinium salts, reflecting the great mobility of the cation in this compound. It proves that the cations, being separated by the large bioctahedral anionic units, are loosely packed in the crystal. May be the great dynamical freedom of the cations is a reason for the interesting physical properties of the compound [8]. It is also worth noting that our NMR studies performed for the polycrystalline sample evidently confirmed the existence of the phase transitions at 333, 350, 415, and 425 K. The jumps of T_1 and/or M_2 at these temperatures have shown that the dynamics of

the guanidinium cations significantly changes at the phase transitions, pointing out their important role in the mechanism of the transitions.

Conclusions

The proton NMR study has confirmed the existence of phase transitions at 333, 350, 415, and 425 K and revealed a dynamical inequivalence of two crystallographically independent guanidinium cations. A C_3

reorientation hindered by the potential barriers of 25.1 kJ/mol for one cation and 34.7 kJ/mol for two others has been discovered. Upon increasing the temperature the dynamical freedom of the cations increases leading to the successive overall reorientation of the cations in the phases II and I.

Acknowledgements

The present work was supported by the Scientific Research Committee under Grant No 2PO3B 137 15.

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