NMR Study of Cation Motion in Guanidinium Iodoplumbates

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Z. Naturforsch. **52 a,** 783–788 (1997); received October 6, 1997

Proton NMR second moments and spin-lattice relaxation times of polycrystalline $C(NH_2)_3PbI_3$ and $[C(NH_2)_3]_2PbI_4$ were studied in a wide temperature range. The order-disorder character of the existing solid-solid phase transitions was confirmed and for tetraiodoplumbate a new phase transition at 170 K was discovered. For both compounds a dynamical inequivalence and unusual high mobility of the guanidinium cations were revealed. For the reorientations discovered (NH_2 group flipping, C_3 in-plane reorientation and a tumbling) the activation parameters were determined.

Key words: NMR, Molecular Motions, Phase Transitions.

Introduction

Crystals of the general formulas AMX_3 and A_2MX_4 where A is a molecular cation, M a divalent metal and X a halogen, have been the subject of extensive studies for many years [1]. The interest in these compounds arises mainly from the variety of phase transitions they undergo, but not only. It has been reported that layered tetraiodoplumbates from the A_2MX_4 family exhibit specific electronic properties [2, 3]. In these crystal structures the inorganic semiconducting PbI_4 layers are sandwiched between the organic layers. Such an arrangement leads to the so-called natural-quantum-wells providing the possibility for model studies of size-related quantum effects. A tendency to formation of the low-dimensional structures is characteristic of both AMX_3 and A_2MX_4 crystals, however, the type of anionic sublattice depends on many factors, among others, on the kind of molecular cation [4]. Recently, two new iodoplumbates, $C(NH_2)_3PbI_3$ and $[C(NH_2)_3]_2PbI_4$ containing guanidinium cations were synthesized [5]. Both compounds undergo structural phase transitions.

Calorimetric studies of $C(NH_2)_3PbI_3$ [5] revealed two first-order phase transitions at 255 and 432 K. The transition entropies indicate their order-disorder character. The crystals in phase I, existing above 432 K, exhibit metastable behaviour. The crystal structure of phase II has been recently determined by X-rays [6]. In this phase the crystal has orthorhombic symmetry of $KCdCl_3$ type [7], space group Pnma. The Pb^{2+} ions are octahedrally coordinated and the PbI_6 octahedra are arranged in double chains with chain axis parallel to the *b*-axis. The inorganic chains are separated by guanidinium cations.

The crystals of $[C(NH_2)_3]_2PbI_4$ undergo a continuous phase transition at 307 K. Calorimetric studies suggest disordering of the high-temperature phase [5]. A very recent X-ray investigation [8] has showed that the room temperature phase has monoclinic symmetry, space group Pc, while the high-temperature phase has orthorhombic symmetry, space group $Pmc2_1$. In both phases the anionic sublattice consists of puckered sheets of linked PbI_6 octahedra with the layer planes perpendicular to the *b*-axis. The guanidinium cations are located in two different cavities.

The above results of the calorimetric and structural studies induced us to undertake NMR investigations of both iodoplumbates: guanidinium triiodoplumbate, $C(NH_2)_3PbI_3$, and bis-guanidinium tetraiodoplumbate, $[C(NH_2)_3]_2PbI_4$, (hereafter denoted as $GuPbI_3$ and Gu_2PbI_4 respectively). It was interesting to examine reorientations of the guanidinium cation in all phases of the compounds and provide an insight into the mechanism of the phase transitions. For this purpose measurements of the proton NMR second moments and spin-lattice relaxation times were performed in a wide range of temperature.

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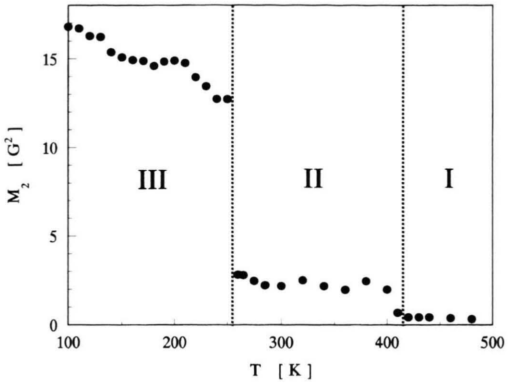

Fig. 1. The temperature dependence of the proton second moment for $GuPbI_3$.

Experimental

The measurements of the proton NMR second moments M_2 were carried out with a wide-line spectrometer operating at 28 MHz. The second moments were calculated by numerical integration of the first derivative of an absorption line and corrected for finite modulation amplitude.

The measurements of the proton spin-lattice relaxation times T_1 were performed with a 60 MHz pulse NMR spectrometer by a saturation recovery method. The temperature of the sample was controlled to an accuracy of 1 K.

Results

The temperature dependence of the proton second moment for $GuPbI_3$ is shown in Figure 1. Its value of about 17 G^2 registered at the lowest temperatures decreases to the plateau value of 14.8 G^2 observed between 150 and 210 K. Next it starts to decrease to 12.8 G^2 observed below 255 K. At this temperature an abrupt jump of the second moment to 2.3 G^2 is observed, and this value remains constant up to 400 K. At 410 K it falls down to 0.3 G^2 observed at higher temperatures.

The temperature dependence of the proton spin-lattice relaxation time for $GuPbI_3$ is presented in Figure 2. At low temperatures up to 255 K a nonexponential magnetization recovery is observed. The decay curves, decomposed into two exponential terms of comparable amplitudes, yield two T_1 values. At 255 K a discontinuity in T_1 plots is found and the relaxation behaviour becomes almost one-exponential, revealing a well defined T_1 minimum of 62 ms at 333 K. The next discontinuity is observed at 425 K, the temperature above which magnetization recovery becomes again evidently two-exponential.

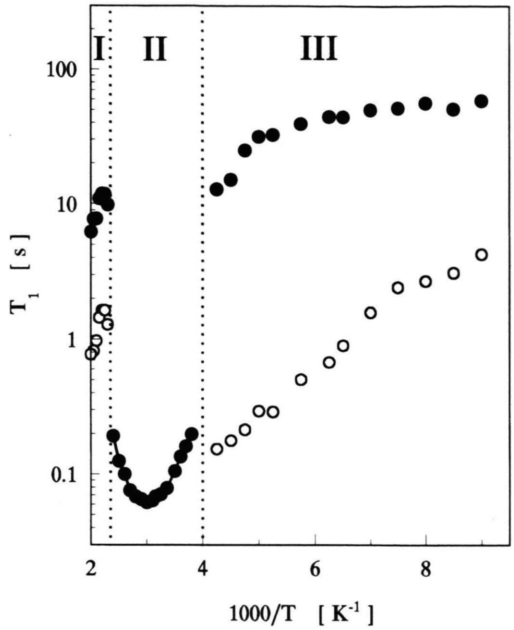

Fig. 2. The temperature dependence of the proton spin-lattice relaxation time for $GuPbI_3$; ● and ○: main and weak components of T_1, respectively. Solid line is a theoretical fit.

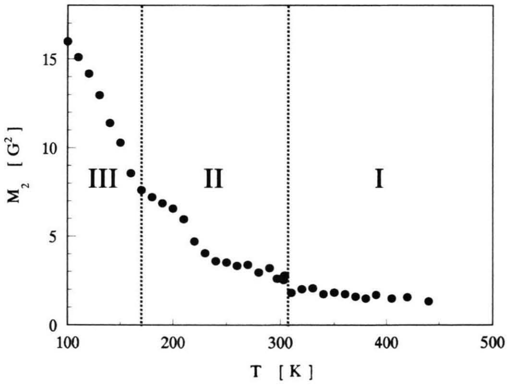

Fig. 3. The temperature dependence of the proton second moment for Gu_2PbI_4.

Figure 3 shows the temperature dependence of the proton second moment for Gu_2PbI_4. A fast decrease of the second moment from 16 G^2, registered at 100 K, is observed up to 170 K. Then a slower decrease leads to a nearly constant value of about 3.2 G^2 found above 250 K. At 307 K the second moment falls down to

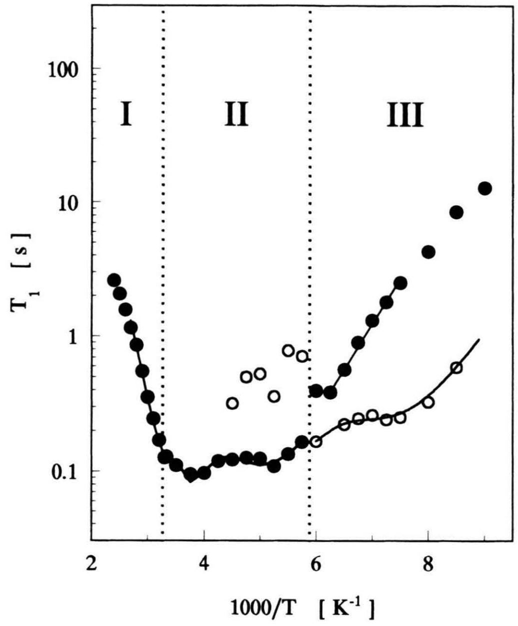

Fig. 4. The temperature dependence of the proton spin-lattice relaxation time for Gu_2PbI_4; ● and ○: main and weak components of T_1, respectively. Solid line is a theoretical fit.

1.7 G^2, the value which is observed almost constant to 440 K.

Figure 4 shows the temperature dependence of the spin-lattice relaxation time T_1 for Gu_2PbI_4. A non-exponential magnetization recovery, observed in the temperature range 110 - 220 K, was decomposed into two exponential terms yielding two T_1 values. At low temperatures a short, weaker T_1 reveals a minimum of 240 ms at 138 K, while at higher temperatures two minima for the main T_1 value of 110 and 95 ms can be observed at 190 and 267 K, respectively. Both T_1 components show evident discontinuities at about 170 K.

Discussion

a) Guanidinium Triiodoplumbate

To describe molecular dynamics of the guanidinium cation, the experimental value of the second moment must be compared with the theoretical one. The latter is calculated by using the Van Vleck formula [9], which for a polycrystalline sample containing two kinds of nuclei with spins I and S is given by

$$M_2 = \frac{3\gamma_I^2\hbar}{5N} I(I+1)\sum_{jk} r_{jk}^{-6} + \frac{4\gamma_S^2\hbar}{15N} S(S+1)\sum_{jm} r_{jm}^{-6}, \tag{1}$$

where r_{jk} and r_{jm} are the distances between respective nuclei, N is a number of nuclei over which the sum is taken. Equation (1) corresponds to the rigid lattice, while in the case of molecular reorientation the intramolecular part of the second moment is reduced by the factor

$$\rho = (3\cos^2\alpha - 1)^2/4, \tag{2}$$

when rotation takes place about the n-fold ($n \geq 3$) symmetry axis (α is the angle between the internuclear vector and the reorientation axis) or by

$$\rho = 1 - 3\sin^2\alpha\cos^2\alpha, \tag{3}$$

when a motion around the two-fold axis is considered.

The intramolecular part of the second moment for the rigid structure of the compound was calculated for the standard geometry of the guanidinium cation [10] with C-N = 1.32 Å, N-H = 1.02 Å, H-H = 1.77 Å, since the X-ray analysis has not yielded precise hydrogen atom positions. Considering all proton-proton (I-I) and proton-nitrogen (I-S) spin-interactions, we obtained the intramolecular part of the second moment equal to 16.5 G^2. The intermolecular part, calculated for the room temperature phase II, gave the very low value of 0.7 G^2, resulting from the long cation-cation distances in the lattice. Thus the calculated total second moment value of 17.2 G^2 corresponds very well to the experimental 16.9 G^2 registered at the lowest temperatures studied. This means that the cations are rigid on the NMR time scale. At higher temperatures a reduction in the second moment reflects an onset of reorientations. Experimental plateau values of 14.8 G^2 and then 12.8 G^2 can be well ascribed to the consecutive reorientations of two amino groups around their two-fold symmetry axes (flipping). Theoretical calculations of the reduced second moment for a model of only one NH_2 group flipping give 15 G^2, while a consecutive onset of another amino group flipping reduces the value of M_2 to 13 G^2. Both values compare well with the experimental plateau values observed in the low-temperature phase. The activation energies for two consecutive NH_2 group motions, estimated from the Waugh-Fiedin formula [11], are 18.9 kJ/mol and 32.7 kJ/mol. An abrupt jump of the second moment, registered at 255 K, reflects the phase transition involving a drastic change in dynamical behaviour of the cations in phase II. To interpret the value of 2.3 G^2 observed in the phase II we had to consider different models of the guanidinium cation reorientations. First we considered C_3 reorientation of the cation, which was revealed in all the guanidinium salts previously studied. Such a motion should yield a value of about 6 G^2. When the C_3 reorientation is preceded by the NH_2 groups flipping, the M_2 value is reduced to 3.5 G^2, often observed by us for a number of guanidinium salts [10, 12 - 18]. To get the observed value of 2.3 G^2 we had to assume a dynamical inequivalence of the guanidinium cations: half of them perform the C_3 reorientation preceded by the NH_2 groups flipping and the rest undergo a tumbling process, that is an isotropic reorientation around their centers of gravity. This statement corroborates the order-disorder character of the III→II phase transition. At the II→I phase transition the second moment diminishes to 0.3 G^2. Though such a value is very often ascribed to a self diffussion process, in our case the observed non-zero linewidth of about 0.7 G and very weak internuclear interactions point rather to the tumbling of all the cations. The activation energy for the tumbling of the less mobile part of cations was estimated to be about 63 kJ/mol.

Our T_1 experiment, revealing at most temperatures two-exponential magnetization recovery confirms the dynamical inequivalence of the guanidinium cations. Probably two types of the cations of different mobility, well separated by PbI_3 anion chains, relax independently to the lattice producing two different components of spin-lattice relaxation time T_1. The minimum of 62 ms observed in the intermediate phase II corresponds to the ΔM_2 reduction value of 9.1 G^2. A similar value we obtained theoretically by assuming C_3 reorientation of the cations preceded by the consecutive two NH_2 groups flipping. Such a motion is the most effective mechanism for the relaxation in phase II producing the T_1 minimum observed. The slower tumbling motion of the rest part of cations revealed in the wide-line experiment does not affect the relaxation in the phase considered. The activation parameters for the C_3 reorientation could be extracted from a least-squares fit to the experimental T_1 data, described by the expression

$$T_1^{-1} = \frac{2}{3}\gamma_I^2 \Delta M_2[\tau/(1+\omega_I^2\tau^2) + 4\tau/(1+4\omega_I^2\tau^2)]. \tag{4}$$

The fitting procedure yielded the surprisingly low activation energy of 16.8 kJ/mol and the preexponential factor $\tau_0 = 4.9 \cdot 10^{-12}$s. For most of the investigated guanidinium salts the C_3 reorientation of the cation was hindered by the energy barrier of about 40 kJ/mol [12 - 18]. A similar value could be expected for the compound studied if the phase III had existed up to sufficiently high temperatures. The III→II phase transition evidently lowers the energy barrier producing much greater dynamical freedom for the cation reorientation in phase II. The drastic change in the dynamical behaviour of the guanidinium cation as well as evident discontinuities in the M_2 and T_1 values at the III→II phase transition suggest a significant change in the crystal structure of the compound.

b) Bis-Guanidinium Tetraiodoplumbate

The crystal structure determined at 285 and 309 K allowed us to calculate, (1), the theoretical second moment values for the rigid structure of the compound in phase I and II. The total values obtained are the same in both phases and equal to 19.7 G^2. However, the calculations revealed stronger inequivalence of the cations in phase I than in phase II. The intermolecular parts for the two inequivalent cations are 1.76 G^2 and 4.50 G^2 in phase I, while in phase II they do not differ significantly, being equal to 2.98 G^2 and 3.33 G^2. The value of 19.7 G^2 corresponding to the rigid structure of the compound was not reached in our experiment. The value of 16 G^2 registered at 100 K proves that a reorientation has already set in, reducing the second moment value. Two components of the NMR spectrum observed at low temperatures point to the existence of two dynamically inequivalent guanidinium cations. A plateau value of 3.2 G^2, observed above 220 K, can be well interpreted in terms of C_3 reorientations of all the guanidinium cations, preceded by the NH_2 groups flipping motion. At the phase transition II→I the second moment is reduced to 1.7 G^2. Such a value can be theoretically obtained by assuming that one of the cations still undergoes C_3 reorientation preceded by the NH_2 groups flipping while another one is already submitted to a tumbling or diffusive motion. A fine structure of the NMR spectrum in phase I well supports such a model of a different dynamical behaviour of two crystallographically inequivalent cations.

The non-exponential behaviour of the relaxation times observed at the low temperatures reflects a dynamical inequivalence of the cations. A decomposition of the magnetization recoveries into two exponential terms yields two different T_1 values. A theoretical fitting of (4) to the experimental T_1 plot with a minimum observed for the shorter component yielded the following parameters: E_a = 10.5 kJ/mol, τ_o = $1.4 \cdot 10^{-13}$s and ΔM_2 = 1.8 G^2. The latter value indicates that the minimum observed may result from the flipping of the NH_2 group in one type of the cations. The low energy value shows that such a motion could not be seen in the wide-line experiment performed, since it would reduce the second moment already at about 70 K. The main T_1 component, decreasing with temperature, yielded the activation energy of 13.0 kJ/mol which could correspond to an onset of C_3 reorientation of the other guanidinium cation. At about 170 K the observed discontinuities of both T_1 components strongly suggest the existence of a second phase transition III→II not yet revealed by other methods. The temperature behaviour of the second moment corroborates this conclusion. In the phase II two T_1 minima observed could be well described by the following fitted parameters:

E_a = 13.0 kJ/mol, $\tau_o = 4.8 \cdot 10^{-13}$s and ΔM_2= 4.3 G^2 (the lower minimum),

E_a = 18.4 kJ/mol, $\tau_o = 4.3 \cdot 10^{-13}$s and ΔM_2 = 4.9 G^2 (the higher minimum).

Both minima, characterized by such similar values of τ_o and ΔM_2, can be well ascribed to the consecutive onsets of C_3 reorientations of two types of cations reorienting with different activation energies which are low and comparable with the value determined for the triiodoplumbate. In phase I, T_1 increasing with temperature yields the activation energy of 31.4 kJ/mol which could be ascribed to the tumbling of the cations.

A comparison of the peculiar cation dynamics revealed in both compounds under study with the results previously obtained by us for a number of guanidinium salts [10, 12 - 18] shows the role of the cation-anion interaction in determining the hindering barriers. The unusually high mobility of the tumbling cations and the low hindering barriers for their C_3 reorientation appear to result from the very weak guanidinium cation-iodoplumbate anion interaction. The mean charge density on the iodide ions must be much lower than on the other investigated anions. The cation-anion interaction in both iodoplumbates must be weaker than in a simple guanidinium iodide [12]. The contribution to the hindering potential from interionic hydrogen bonding in both salts under study must also be much smaller than in the salts previously studied.

Conclusions

$GuPbI_3$:

a) NMR study has confirmed the existence and order-disorder character of two phase transitions and revealed a dynamical inequivalence of two types of highly mobile guanidinium cations.

b) Different dynamical behaviour of guanidinium cations was found in all three phases:

phase III – consecutive flipping of two amino groups (E_a = 18.9 and 32.7 kJ/mol),
phase II – C_3 reorientation of half of the cations (E_a = 16.8 kJ/mol) and tumbling of the rest,
phase I – tumbling motion of all cations.

c) III→II phase transition evidently lowers the energy barrier for the cation reorientations, triggering much greater dynamical freedom of the ions in phase II.

Gu_2PbI_4:

a) NMR study has confirmed the existence of an order-disorder phase transition at 307 K and disclosed a new phase transition at 170 K.

b) Dynamical inequivalence of two crystallographically inequivalent highly mobile guanidinium cations was found.

c) Different dynamical behaviour of guanidinium cations was found in all three phases:

phase III – flipping of NH_2 group with E_a = 10.5 kJ/mol,
phase II – consecutive onset of C_3 reorientations of two types of cations reorienting with different activation energies (13.0 and 18.4 kJ/mol),
phase I – C_3 reorientation and the tumbling motion (E_a = 31.4 kJ/mol).

Acknowledgements

This work was partially supported by the Scientific Research Committee under Grant No. 2PO3B06508.

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