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Phase transitions in ferroelectric nonachlorodiantimonate $[(\text{CH}_3)_3\text{NH}]_3\text{Sb}_2\text{Cl}_9$ studied by calorimetric and dielectric methods

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Résumé. — Nous avons étudié des transitions de phase dans les cristaux de tris (triméthylammonium) nonachlorodiantimonate (III) (TMACA) par microcalorimétrie différentielle (DSC), ainsi que par des mesures des propriétés diélectriques et pyroélectriques. A 364 K, TMACA présente une transition depuis une phase basse température ferroélectrique vers une phase haute température paraélectrique. Une anomalie a été aussi observée à environ 200 K, associée probablement à une relaxation. Les résultats obtenus montrent que la transition à 364 K présente en fait deux transitions très rapprochées, l'une étant probablement du premier ordre et l'autre du second ordre. La transition du deuxième ordre est observée à la même température ($364.0 \pm 0,3$) K quelle que soit la méthode utilisée, alors que celle du premier ordre est décelée par mesure de la constante diélectrique un degré plus bas que par calorimétrie. Celle-ci montre de plus un phénomène inhabituel, qu'on opère en programmation de température croissante ou décroissante : dans les deux cas, la transition du second ordre précède la transition du premier ordre. L'étude de la réponse pyroélectrique du cristal montre que le passage à l'état polaire est gouverné par la transition du premier ordre.

Abstract. — Phase transitions occurring in a ferroelectric crystal tris(trimethylammonium)nonachlorodiantimonate (III) (TMACA) were studied by calorimetric, dielectric and pyroelectric methods. Anomalies of dielectric and thermal properties were found around 200 K and at ca. 364 K. The anomalies in the low-temperature region exhibit a pronounced relaxational character. A detailed study of the behaviour of TMACA around 364 K clearly indicates that in fact TMACA undergoes two closely lying phase transitions, one of them being probably of the first order and the other of the second order. The temperature of the second order transition was determined to amount to (364.0 ± 0.3) K irrespective of the method employed, whereas the first order transition temperatures are detected by the dielectric measurements ca. 1 K below those found from the calorimetric measurements. An unusual sequence of the phase transitions was observed in DSC measurements : both on cooling and on heating the samples through the transition region, the second order phase transition precedes the first order one. The onset to ferroelectricity was found to be associated with the first order phase transition.

1. Introduction.

Tris(trimethylammonium)nonachlorodiantimonate (III), $[(\text{CH}_3)_3\text{NH}]_3\text{Sb}_2\text{Cl}_9$ (hereafter abbreviated as TMACA) is a representative of a new ferroelectric family of alkyl-ammonium metal halides of the general formula $[\text{NH}_{4-n}(\text{CH}_3)_n]_3\text{Y}_2\text{X}_9$ ($\text{Y} = \text{Sb}, \text{Bi}$; $\text{X} = \text{Cl}, \text{Br}$) which usually crystallize in perovskite-type layered structures. At room temperature, TMACA is monoclinic [1] with the space group Pc ($\beta = 90.17^\circ$, $Z = 2$). The ferroelectricity in this compound was found by Jakubas *et al.* [2], who reported on a phase transition from polar (ferroelectric) to nonpolar (paraelectric) phase at 367 K. Recently, we found this material to have interesting electrooptic properties [3], which make TMACA a promising candidate for application in electrooptic devices.

The structure of TMACA consists of distorted octahedra SbCl_6^{-3} , interconnected by the Cl^- anions into a two-dimensional network. The cavities between the octahedra contain three nonequivalent $\text{NH}(\text{CH}_3)_3^+$ cations, two of them forming $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds with bridge chlorine atoms. The third cation which occupies a free space inside a twelve-membered $(-\text{Sb}-\text{Cl}-)_6$ ring is reportedly linked to the chlorine atoms with a very weak bifurcated hydrogen bond [1]. Large thermal parameters show this cation to be disordered.

Preliminary dielectric [2], calorimetric [2] and pyroelectric [4] measurements suggested that the phase transition observed at ~ 367 K is of the order-disorder type and of the first order. The dielectric measurements [2] additionally revealed an anomaly around 207 K. A closer inspection of dielectric and Raman scattering data [5] in TMACA put some questions about the order of the 367 K transition and suggested the existence of an intermediate phase close to the phase transition temperature. These findings prompted us to carry out more careful measurements.

2. Experimental.

The TMACA single crystals were obtained by isothermal evaporation at 293 K of aqueous solutions of a stoichiometric mixture of $(\text{CH}_3)_3\text{NHCl}$ and SbCl_3 with an excess of HCl . Thick hexagonal-shaped plates of TMACA with a perfect cleavage plane (perpendicular to the a axis) were colourless and transparent.

Single crystals of TMACA were calorimetrically examined in the temperature range 160 to 270 K and 355 to 375 K with a Perkin-Elmer DSC-2 differential scanning calorimeter, controlled by a Hewlett-Packard HP86 micro-computer for data acquisition and processing. The temperature calibration of the instrument was made using the melting point of naphthalene (353.4 K). Single-crystalline samples weighting about 30 mg were carefully encapsulated in aluminium pans in order to ensure good heat transfer. The measurement head was flushed with dry helium gas. The measurements of isobaric heat capacity were carried out at scanning rates of 5 and 10 K/min (according to the standard procedure), though some heat flow measurements were also carried out at 2.5 K/min. A part of the calorimetric measurements in the high-temperature range was performed using a Setaram DSC111 calorimeter controlled by the HP microcomputer. The measurements in this case were carried out at 1, 2, 5 and 10 K/min, both on heating and cooling.

The measurements of static electric permittivity were performed at 1 kHz ($E = 5$ V/cm) with a Meratronic E 315A automatic C bridge. Some experiments were performed at 300 Hz, 1 kHz and 10 kHz with a Tesla semi-automatic C bridge BM 484 ($E = 3$ V/cm). Cooling (or heating) rates were kept constant in the vicinity of the phase transition and amounted to ± 0.05 K/min.

The pyroelectric measurements in TMACA were performed by a modification of the dynamic Chynoweth technique [6], using HeNe (5 mW) laser light chopped at the 75 Hz

frequency. The pyroelectric response was measured after suitable amplification with a lock-in nanovoltmeter. The scanning rate was about ± 1 K/min.

3. Results.

3.1 DSC MEASUREMENTS. — Specific heat (c_p) measurements performed on heating single crystalline samples of TMACA in the range 355-375 K revealed two distinct endotherms with the maxima at 365.6 K and 364.9 K. The existence of two peaks around 365 K confirms that there might indeed be two phase transitions in this region, and not a single one as reported earlier [2]. In order to check this hypothesis, we performed several DSC experiments on heating and on cooling the samples, using various scanning rates. The exotherms recorded in the cooling runs show two neatly separated peaks. One of them, rather narrow, shows features characteristic of a first order phase transition, the other, much broader, resembles a second order transition (see Fig. 1). The apparent orders of the transitions can also be deduced from the magnitudes of the thermal hystereses measured for both of them.

We observed an appreciable thermal hysteresis for the narrower peak ($\Delta T = 4.4$ K at 2.5 K/min) and a much smaller for the broad one ($\Delta T = 1.3$ K at 2.5 K/min). From the DSC measurements performed at different scanning rates and then extrapolated to the zero scanning rate, the temperature of one of the transitions can be determined to amount to $T_{II} = 363.7$ K, and the thermal hysteresis to 0.0 K. Hereafter, we shall refer to this transition as to the second order one. The temperature of the other phase transition extrapolated to the zero scanning rate was found equal to $T_I^c = 363.0$ K or $T_I^h = 364.2$ K depending on whether it

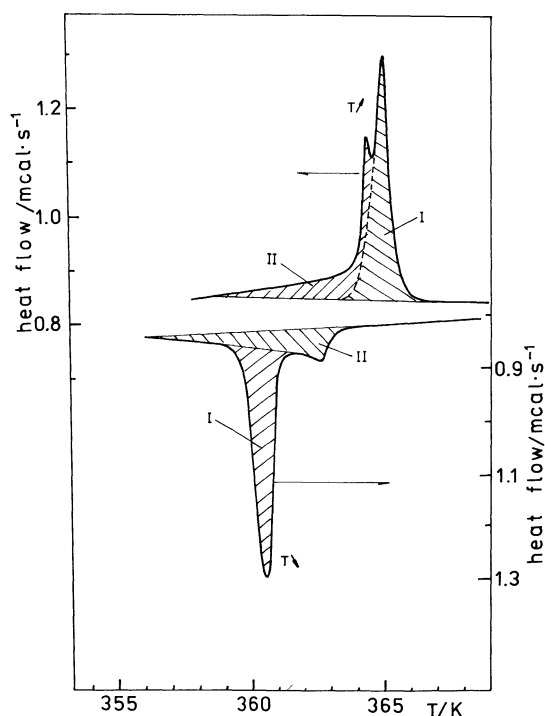


Fig. 1. — Heat flow curves measured in TMACA single crystals on heating (upper curve) and cooling (lower curve). Scanning rate ± 2.5 K/min. Separation of the first and second order phase transitions is schematically shown.

was determined from cooling or heating runs, respectively. This transition will hereafter be referred to as the first order one. (Superscripts refer to heating — h and cooling — c , and subscripts to the first or second order nature of phase transition.) It is interesting to note that, on heating, the first order transition is observed above the second order one, whereas on cooling an inverse sequence is observed: the first order transition appears at lower temperature than the second order one.

Different shifts observed at various scanning rates allowed us to perform a separation of exotherms corresponding to the two transitions, as is shown in figure 1. A more complicated situation is encountered for endotherms recorded in heating runs where the temperature of the second order transition lies just below that of the first order one but, again, an arbitrary separation can be made (cf. Fig. 1). The enthalpy of the first order phase transition obtained employing the separation procedure described above and integrating the areas under the heat flow curves, amounts to $1.02 \text{ kJ.mole}^{-1}$, thus the entropy of the transition (ΔS_T^I) equals to $2.97 \text{ JK}^{-1} \text{ mole}^{-1}$. The entropy of the second order phase transition (ΔS_T^{II}) was found equal to $1.67 \text{ JK}^{-1} \text{ mole}^{-1}$. These values are likely to be charged with an error as large as 10-15 %, due mainly to the inaccurate separation procedure of the two peaks and arbitrarily constructed baseline, though the reproducibility of the measurements on different samples was satisfactory.

Supplementary DSC measurements performed in the low temperature region (170-260 K) on a virgin TMACA sample, showed also a thermal anomaly in the region 197-204 K, its enthalpy amounting to $\Delta H = 42.3 \text{ J.mole}^{-1}$. The same measurement, when repeated immediately after the first one, showed no sign of any anomaly around 200 K. However, the samples were found to recover: the effect measured on the sample stored at ambient temperature over 30 min amounted to $\sim 30 \%$ of that observed on the virgin sample.

3.2 DIELECTRIC MEASUREMENTS. — The temperature dependences of the electric permittivity measured quasi-statically at the rate $\pm 0.05 \text{ K.min}^{-1}$ along the c axis (ϵ'_c) both on heating and cooling are shown in figure 2 (the c axis is the one for which the highest values of the electric permittivity were observed). One can notice two anomalies at 363.4 K and 364.2 K on heating, and at 363.8 K and 361.7 K on cooling the sample. The peak at $(364 \pm 0.2) \text{ K}$ remains at a practically constant temperature irrespective of the direction of temperature changes. On the contrary, the other anomaly exhibits an appreciable thermal hysteresis. The anomaly at 364 K is superimposed on high values of ϵ'_c and thus difficult to measure precisely, but in perfect crystals (with the highest values of $\epsilon'_c \sim 680-700$) it is always present and well reproducible.

In order to better visualize the anomalies of dielectric permittivity we performed precise measurements of $\epsilon'(T)$ along the a crystallographic direction which is almost perpendicular to the c axis, but for which the values of ϵ' are more than an order smaller as compared to ϵ'_c . As shown in figure 3, in the heating run those anomalies are indeed easy to observe, and changes of ϵ' for both directions are comparable. However, the peaks observed on cooling were far less pronounced. Measurements of ϵ'_a were performed on several samples. The anomalies were observed in all series of measurements, although minute details of the temperature dependences and, in particular, the phase transition temperatures were found to depend on the quality and history of samples.

Measurements of ferroelectric hysteresis loop confirmed that during cooling, the polar (ferroelectric) phase appears just below the temperature assigned to the first order transition suggesting that this transition is responsible for appearance of the ferroelectric state of the crystal. Thus the « intermediate » phase should be nonpolar. On heating, a proper hysteresis loop again can be measured until the temperature of the first order transition. Slightly above

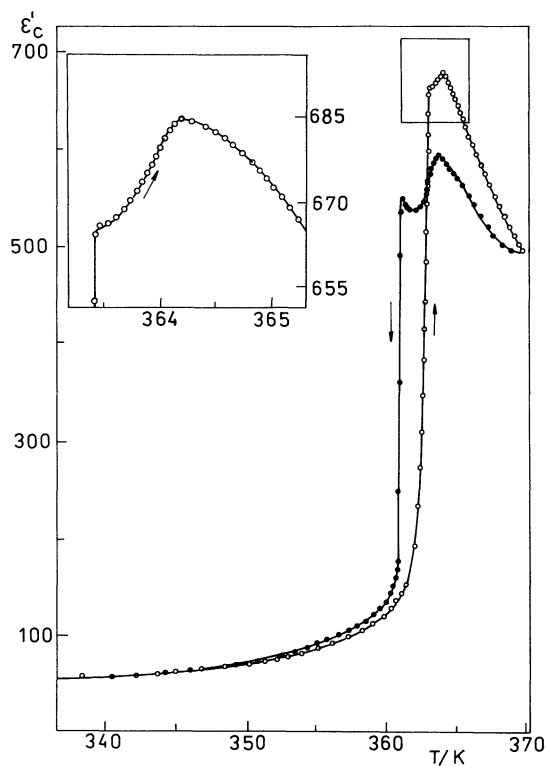


Fig. 2. — Temperature dependence of static electric permittivity ϵ'_c measured along the **c** axis in a TMACA single crystal (heating and cooling runs are indicated by the arrows). Insert: the phase transition region.

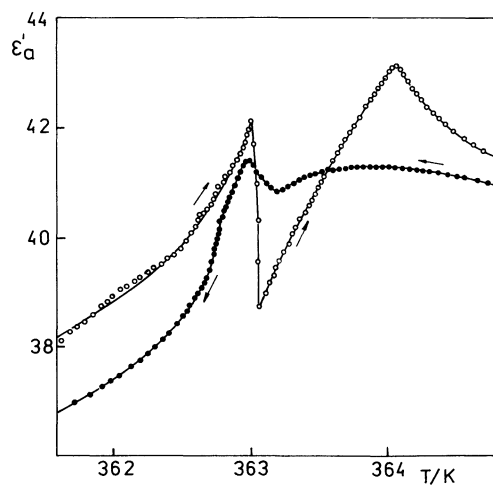


Fig. 3. — Temperature dependence of static electric permittivity ϵ'_a measured along the **a** axis in a TMACA single crystal. Heating and cooling runs are indicated by the arrows.

this temperature a loop is also observed ; it is, however, difficult to distinguish whether it is a single or double one (a double hysteresis loop can exist within a limited temperature range above a first order ferroelectric transition — see, e.g. Ref. [7]).

We performed cyclic measurements of ϵ'_c in the vicinity of the paraelectric-to-intermediate phase transition without entering the ferroelectric phase. As mentioned in the preceding section, the rate of temperature changes was in this case very low and amounted to only ± 0.05 K/min. We found that the position of the maximum of the $\epsilon'(T)$ dependence measured on cooling and heating remains essentially unchanged, confirming the second-order nature of the transition connected with this maximum. The dielectric properties of the « intermediate » phase are well reproducible provided the condition of not entering the polar phase is fulfilled.

Measurements of electric permittivity performed in the range 170-260 K at several frequencies clearly establish the relaxational mechanism of the low temperature anomaly (cf. Fig. 4). The ϵ'' maxima exhibit a distinct temperature shift toward lower temperatures on decreasing the measurement frequencies.

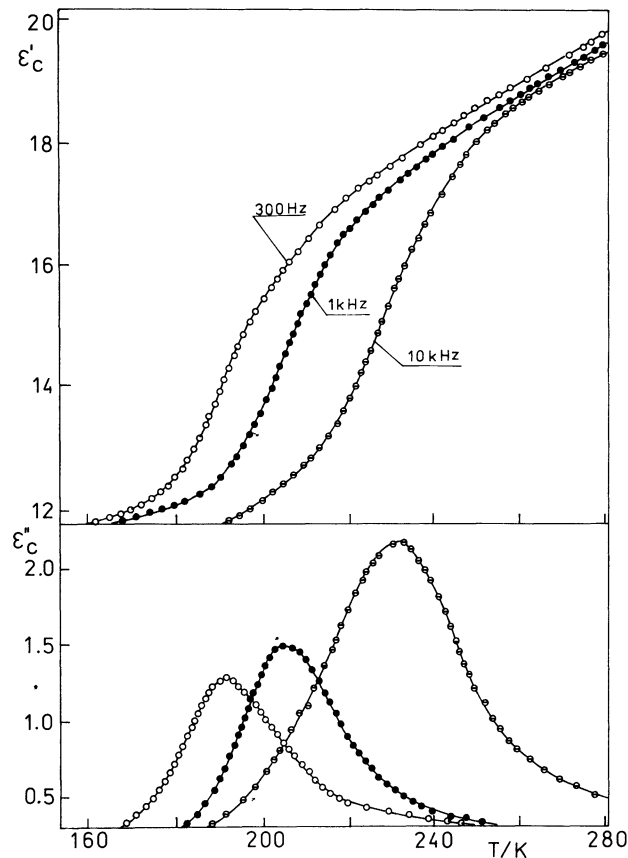


Fig. 4. — $\epsilon'_c(T)$ and $\tan \delta(T)$ dependences in TMACA in the low temperature region.

3.3 PYROELECTRIC MEASUREMENTS. — Pyroelectric measurements were already performed in TMACA [4] using the continuous current method [8]. We employed the Chynoweth method [6], allowing for studies of pyroelectric responses of materials under externally

applied electric field and at arbitrarily low temperature scanning rates (the latter condition cannot be realized with the continuous current pyroelectric method). Neither a measurable effect on the behaviour and magnitude of the pyroelectric coefficient nor any shift of phase transition temperature under the influence of externally applied electric fields have been found up to 7×10^5 V/m. An example of pyroelectric responses obtained in TMACA on heating and cooling is shown in figure 5. The thermal hysteresis observed at the scanning rate of ~ 1 K/min amounted to 2.4 K. It is unusual that the pyroelectric response depends so strongly on the direction of temperature changes.

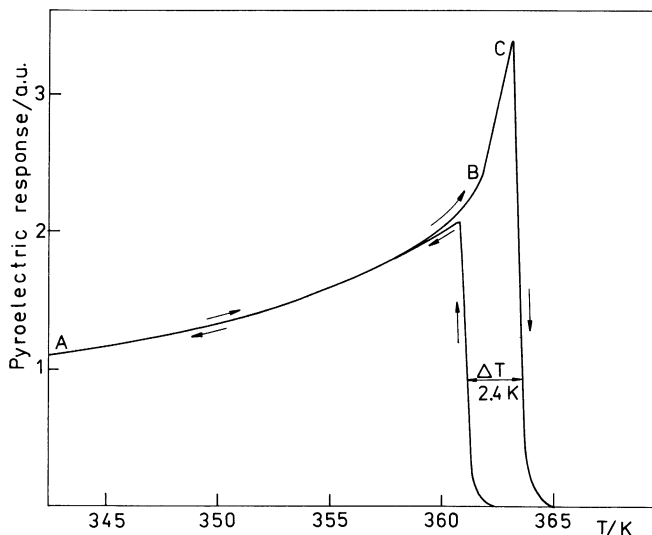


Fig. 5. — Pyroelectric response curves obtained for TMACA along the *c* direction using the Chynoweth technique. The rate of temperature changes amounted to ± 1 K/min. Heating and cooling runs are indicated by the arrows.

4. Discussion.

For the sake of clarity the results of calorimetric, dielectric and pyroelectric measurements presented in the preceding section will be discussed separately for the high temperature (355-375 K) and the low temperature (~ 200 K) transition regions.

4.1 HIGH TEMPERATURE REGION. — All experimental techniques employed to study the behaviour of crystalline TMACA strongly indicate the existence of two closely lying phase transitions :

- i) two anomalies of heat capacity are observed, whose features can be assigned to a first and a second order transitions ;
- ii) two anomalies of dielectric permittivity appear in the same region, one of them showing features characteristic of a first order transition ;
- iii) pyroelectric measurements point out that the rise of the spontaneous polarization in TMACA is linked with the first order transition. A hysteresis of the pyroelectric response as large as 2.4 K has been observed ;
- iv) Raman scattering data [9] revealed the existence of a splitting of two bands assigned to internal vibrations of the CH_3 group (asymmetric stretching), its temperature dependence

being characteristic of a second order phase transition: $\Delta(\Delta\nu)$ was found to vary as $(T - T_c)^\beta$ with $T_c = 364$ K and $\beta = 0.47$.

In our opinion, the existence of two structural phase transitions in the high temperature region in TMACA is well documented. However, the interpretation of all the experimental data in a coherent way is by no means simple.

The results of calorimetric measurements give the transition entropies $\Delta S_T^{\text{II}} = 1.67 \text{ JK}^{-1} \text{ mole}^{-1}$ and $\Delta S_T^{\text{I}} = 2.97 \text{ JK}^{-1} \text{ mole}^{-1}$. Such large values of ΔS suggest that both transitions are of the order-disorder character. The entropy change assigned to the first order transition comes very close to the value $1/2 R \ln 2$ ($= 2.88 \text{ JK}^{-1} \text{ mole}^{-1}$) which can be understood as a conformational entropy of two entities in the unit cell, ordered below the phase transition point and disordered above it. A possible candidate might be a reorientation of one among three nonequivalent $\text{NH}(\text{CH}_3)_3^+$ cations, presumably the one linked by a bifurcated hydrogen bond to chlorine atoms in the inorganic sublattice. The value of transition entropy assigned to the second order transition indicates that most probably we do not deal with a pure order-disorder case, but, on the other hand, ΔS_T^{II} is too large to be connected with a pure displacive-type transition. These facts put a question about the nature of this transition, which seems to have a rather complex character.

A comparison of the phase transition temperatures determined from dielectric and calorimetric measurements leads to an interesting finding: on heating, the first order transition appears at 364.2 K in DSC runs and at 363.4 K in dielectric measurements, while on cooling it is observed at 363.0 K and 361.7 K, respectively. In other words, the dielectric measurements systematically locate the transition at the temperature ca. 1 K below that determined from the DSC measurements. This difference cannot be due to any problem with the temperature calibration because the temperature of the second order transition has been found to amount to 364.0 ± 0.3 K irrespective of the method employed. The shift, albeit small, gives rise to a qualitative difference in the sequence of the phase transitions as seen by the two methods: while in the DSC measurements the second order transition always precedes the first order one (i.e. appears at a lower temperature on heating, and at a higher temperature on cooling the samples) such an inversion is not observed in the dielectric measurements, and the first order transition always appears on the low temperature side. The difference is probably due to a different signature of the first order phase transition in the experimental techniques employed. At present we cannot offer any quantitative explanation for the observed behaviour of our samples. In particular, because of lack of structural information about the « intermediate » and high-temperature phases, we feel unable to put forward a thermodynamical description of the transitions. However, it should be stressed that, to our knowledge, a sequence of the phase transitions such as that observed in our DSC experiments has been observed for the first time.

The difference between the pyroelectric signal measured in heating and cooling runs (the BC section of the curve in Fig. 5) indicates that the onset to a non-zero spontaneous polarization coincides with the first order transition.

Some features of calorimetric and dielectric $\epsilon'(T)$ measurements in TMACA resemble those found in RbLiSO_4 where an incommensurate phase has been found between two closely lying phase transitions at 475 and 477 K [10]. Similar features were found in NH_4HSeO_4 where again the presence of an incommensurate phase has been postulated [11]. One may speculate that also in the case of TMACA the intermediate phase is of an incommensurate character.

4.2 LOW TEMPERATURE REGION. — The dielectric anomalies observed in TMACA around 200 K, and presented in figure 4, exhibit features characteristic of those due to relaxational-

type dipolar motions. The activation energy determined from the ($\ln \omega$ vs. $1/T$) plot amounts to ca. 30.6 kJ mol^{-1} . This value falls within the range of energies of weak hydrogen bonds [12]. Such a character of dielectric anomalies and observed thermal anomalies reported in section 3 suggest that the process responsible is most probably freezing of motions of some entities on decreasing the temperature. The Raman scattering data [9] seem to support the above conclusion, because in the temperature region 130-250 K only minor line shifts and intensity changes were observed in the spectra. The observation of the 305 cm^{-1} band assigned to a torsion of methyl groups [9] which changes its halfwidth and intensity in a thermally activated way suggests that the organic cations are involved in the described process.

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