
Dielectric and Dilatometric Properties of $\text{NH}(\text{CH}_3)_3\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ Low Dimensional Ferroics

YU. KORCHAK^a, V. KAPUSTIANIK^a, A. BATIUK^a, I. GIRNYK^b,
Z. CZAPLA^c AND S. DACKO^c

^aFerroics Physics Laboratory, Electronics Department
Lviv I. Franko National University
Tarnavskogo st. 107, 79017 Lviv, Ukraine

^bInstitute of Physical Optics, Dragomanova st. 23, 79005 Lviv, Ukraine

^c Institute of Experimental Physics, University of Wrocław
pl. M. Borna 9, 50-204 Wrocław, Poland

(Received May 10, 2004)

On the basis of dilatometric and dielectric investigations of $\text{NH}(\text{CH}_3)_3\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ crystals the earlier unknown phase transition with considerable temperature hysteresis was found at $T_1^c = 198$ K and $T_1^h = 223$ K, respectively, in cooling and heating runs. Existence of the characteristic dielectric dispersion was revealed within the high-temperature phase. It corresponds to the single dielectric relaxator below 250 K as well as to co-existence of two relaxators above this temperature. The determined values of the activation energy and relaxation time are characteristic of the co-operative reorientation of the trimethylammonium cation (high-frequency relaxator) whereas the combined reorientation motions of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ chains would be responsible for the low-frequency relaxation process. It was found that the above mentioned quasi-Debye type processes are involved into the mechanisms of the protonic conductivity.

PACS numbers: 64.70.-p

1. Introduction

The crystal of trimethylammonium trichlorocuprate $\text{NH}(\text{CH}_3)_3\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ (abbreviatedly TrMA-CuCl₃) should be considered as low dimensional materials that exhibit strong structural anisotropy [1]. The related crystals with general

formulae $\text{AMeCl}_3 \cdot 2\text{H}_2\text{O}$ and AMeCl_3 ($\text{A} = \text{N}(\text{CH}_3)_4, \text{NH}(\text{CH}_3)_3, \text{NH}_2(\text{CH}_3)_2$; $\text{Me} = \text{Cu}, \text{Co}, \text{Mn}, \text{Ni}$) have been the object of considerable attention during the past years [2–7] first of all due to their specific magnetic properties at low temperatures [2–5, 7].

The magnetic properties of the title compound have been the subject of several studies [8–10]. It corresponds to a linear chain compound and behaves as a very weak one-dimensional spin = 1/2 Heisenberg ferromagnet. Magnetic ordering occurs below 1 K.

At $T = 297$ K TrMA-CuCl_3 is monoclinic ($P2_1/c$). The structure of the title compound contains square-planar $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ subunits stacked along a (Fig. 1a) [1]. Two rather long Cu–Cl bonds with the next layers complete distorted octahedral coordination of Cu^{2+} . The octahedra form one-dimensional chains by edge-sharing. There is a clear correlation between the long and short Cu–Cl bonds. The shorter coordinative bond at Cu(2) causes a lengthening of the Cu(2)–Cl(1) single bond to 2.3060(5) Å, compared with a Cu(1)–Cl(2) bond length of 2.2770(5) Å. The Cl^- atom is involved in four hydrogen bonds with the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ chains. These hydrogen bonds are of intermediate strength and interconnect the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ chains along b (Fig. 1b). The cations are attached by

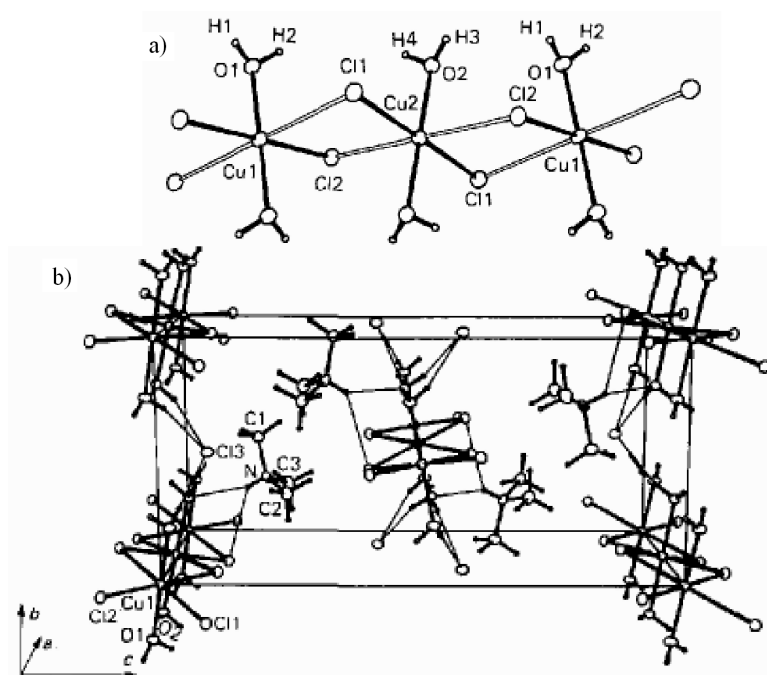


Fig. 1. Views of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ subunits stacked along a (a) and the crystal structure of $\text{NH}(\text{CH}_3)_3\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ along a (b) [1].

very weak bifurcated hydrogen bonds to the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ chains. The bonding along c consists of electrostatic interactions between the methyl H atoms and Cl atoms of the next $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ layers (shortest H–Cl contact: 2.85(2) Å) [1].

Studies of different crystals with alkylammonium cation showed that the change of the hydrogen bond network influences the lattice dynamics considerably and manifests itself in an essential transformation of the crystalline structure [11]. Unfortunately there is no report concerning possible high-temperature phase transitions (PTs) in TrMA- CuCl_3 and other phenomena connected with the hydrogen bonds dynamics. Under such circumstances we considered it worthwhile investigating them in detail. To complete the information about the structural changes and phase transitions in the trimethylammonium trichlorocuprate dihydrate crystals $[\text{NH}(\text{CH}_3)_3]\text{CuCl}_3 \cdot 2\text{H}_2\text{O}$ their dielectric parameters and thermal expansion were studied in the temperature range of 80 ÷ 300 K.

2. Experimental

The investigated green transparent crystals were grown by slow evaporation of an aqueous solution of $[\text{NH}(\text{CH}_3)_3]\text{Cl}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ salts taken in the stoichiometric ratio.

For the dielectric measurements the crystalline platelets of c -cut with a thickness of 0.8–1 mm were used. After polishing the samples were covered by conducting silver-paste electrodes. To avoid the influence of water absorption the samples were previously annealed at the temperature $T = 310$ K. The dielectric parameters were measured with an accuracy of nearly 1% at different frequencies of the measuring electric field (from 100 Hz up to 1 MHz) using a Hewlett-Packard 4284A multifrequency LCR-meter. The applied ac electric field did not exceed 1 V/cm. For the temperature investigations the samples were placed into a liquid nitrogen cryostat. The rate of the temperature change was 0.5 K/min.

Thermal expansion was investigated with employment of the quartz dilatometer with a capacity sensor on the crystalline platelets of a -, b -, and c -cuts with a thickness of 1.5–2 mm.

3. Results and discussion

The temperature dependences of the thermal dilatation measured along the principal crystallographic axes of TrMA- CuCl_3 crystal are presented in Fig. 2. In a cooling run they show the clear anomalies characteristic of phase transitions at $T_1^c = 198$ K. At heating this anomaly is observed at the higher temperature $T_1^h = 223$ K. The observed large temperature hysteresis (Fig. 2, insert) testifies that the supposed PT is of the first order. The temperature dependence of the thermal expansion coefficient α (Fig. 3) manifests the characteristic jump-like anomaly at the temperature $T_1^c = 198$ K (at cooling) reflecting a considerable change of the thermal dilatation behaviour in the different crystalline phases.

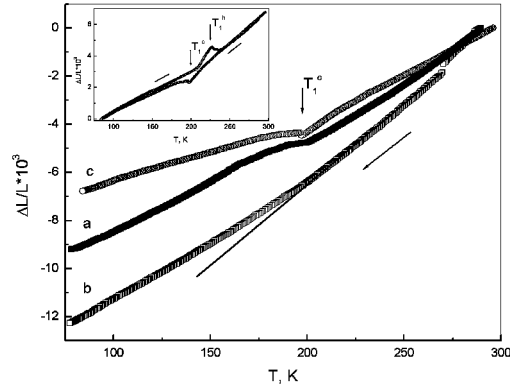


Fig. 2. Temperature dependences of the thermal dilatation measured at cooling on *a*-, *b*-, and *c*-cuts. Insert presents the temperature hysteresis of the phase transition on the example of temperature dependence of dilatation measured at cooling and heating on *c*-cut.

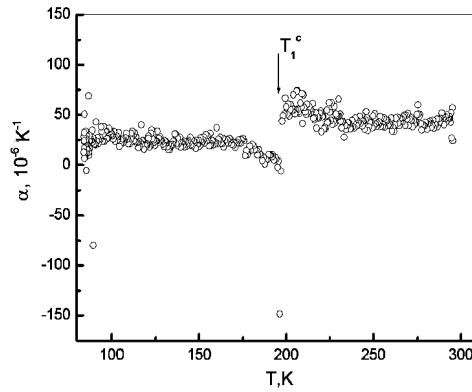


Fig. 3. Temperature dependence of the thermal expansion coefficient measured in cooling run along the [001] direction of TrMA-CuCl₃ single crystal.

As it follows from optical study the high temperature phase is ferroelastic (the corresponding data will be published in detail elsewhere) that correlates with its space group. The ferroelastic domains with 180° boundaries were clearly seen in a polarizing microscope on the *c*-cut of TrMA-CuCl₃.

The strong anisotropy of TrMA-CuCl₃ crystals and presence of the organic molecules with a dipole moment in their structure (Fig. 1) imply interesting dielectric properties. The temperature dependences of the dielectric parameter ϵ'_c are presented in Fig. 4. The specific dispersion of this parameter is connected with the thermal dipole relaxation. The detailed investigation of the dielectric relaxation was performed in the region lying below room temperature. It is necessary to note that the clear dielectric dispersion in the frequency range of 1 kHz–1 MHz

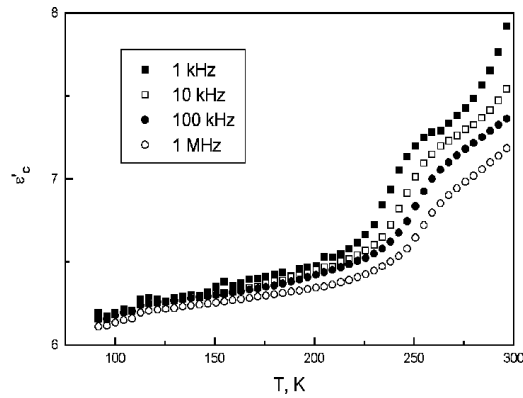


Fig. 4. Temperature dependences of the dielectric permittivity of TrMA-CuCl₃ crystal obtained at different frequencies of measuring electric field.

should be considered as a characteristic feature of the compounds with an alkylammonium cation and usually is related to a relaxation process connected with the reorientation of the organic molecules [12–14].

As it is seen from Fig. 4, the temperature dependences of the dielectric permittivity do not show clear anomalies that would be related to the phase transitions, first of all due to the masking role of the dielectric dispersion and obviously nonferroelectric nature of PT found from the dilatometric study.

It is known [15] that in general for an inhomogeneous insulator the spectrum of the real part of the dielectric permittivity is described by

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + \omega^2\tau^2}, \quad (1)$$

where ε_0 and ε_{∞} are the low and high frequency limits of the permittivity, ω is the frequency, τ is known as the relaxation time. Figure 5 shows that the frequency

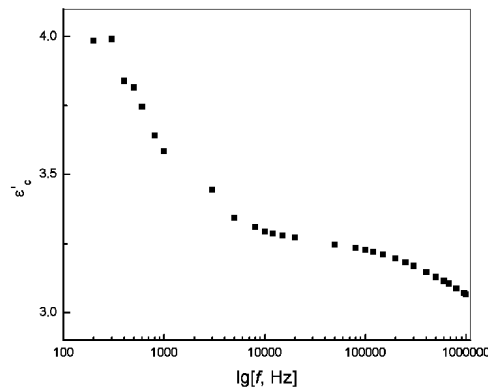


Fig. 5. Frequency dependence of ε'_c in the semi-logarithmic scale at $T = 265$ K.

dependence of ε' at the temperature 265.1 K consists of the two frequency intervals at $0.5 \div 10$ kHz and 100 kHz \div 1 MHz respectively, that should be connected with two different relaxation processes. The nature of these relaxation processes becomes clear only when to consider their temperature evolution.

As it is known [16], the pure Debye-type relaxation implies the frequency dependent complex permittivity obeying an equation of the form

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + i\omega\tau}. \quad (2)$$

Equation (1) should be considered as a sequence of relation (2). The relaxation time τ is connected with the loss peak frequency as $f_p = 1/2\pi\tau$. In this case the relaxation time follows a temperature dependence of Arrhenius type [17]:

$$\tau = \tau_0 \exp\left(\frac{E_r}{kT}\right), \quad (3)$$

where τ_0 is a pre-exponential factor which is inverse to the oscillation frequency of the dipole (or charge) in its potential well and E_r stands for the activation energy of the relaxation. If the dipoles interact with each other, the used equation is slightly different from (2) [18]:

$$\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau)^{1-\alpha}}, \quad (4)$$

where α is an empirical parameter ($0 < \alpha < 1$) which measures the degree of departure from the Debye model [16]. Equation (4) describes the relaxation time distribution that manifests itself in the shape of the Cole–Cole diagrams (ε'' versus ε'). In the pure Debye model ($\alpha = 0$), as was mentioned above, the dipoles are assumed to be non-interacting with each other. Consequently the Cole–Cole plot is a semicircle centred on the ε' -axis. In the opposite case ($\alpha > 0$) the semicircles are centred below this axis.

In our case the Cole–Cole diagrams obtained for the c -cut (Fig. 6) appear as semicircles centred below the ε' -axis. One can note that at the temperatures higher than 250 K the two relaxators are observed (Fig. 6a) whereas at the lower temperatures (below 250 K) only one relaxation process manifests itself as a single semicircle (Fig. 6b). The Cole–Cole plot for the high temperature range (above 250 K) correlates with the corresponding frequency dependence of the ε' (Fig. 5). Analysing the Cole–Cole diagrams for different temperatures using the well-known methods [19] one could calculate the values of the relaxation time. For the high-frequency relaxator these parameters were found to be $10^{-5} \div 10^{-6}$ s whereas for the low-frequency one — $10^{-3} \div 10^{-5}$ s. The inverse temperature dependence of $\ln\tau$ for the high-frequency relaxator (Fig. 7) manifests slight anomaly at $T^* = 250$ K. Perhaps, it would be connected with appearance of the additional low-frequency relaxator above T^* (at least, in the investigated frequency window). As one can see from Fig. 7 the inverse temperature dependences of the relaxation

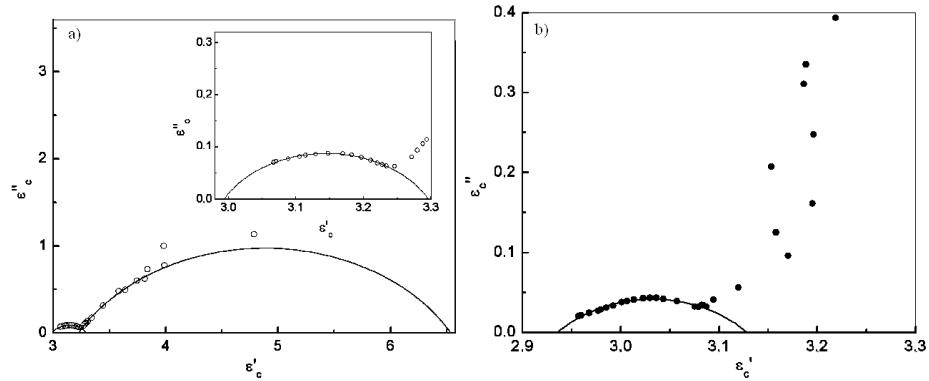


Fig. 6. Cole-Cole diagrams for TrMA-CuCl₃ crystal obtained at 265 K (a) and 243 K (b).

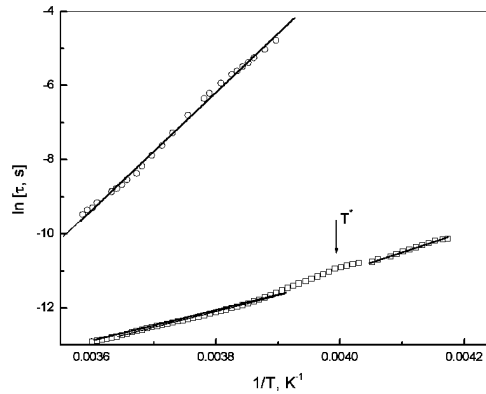


Fig. 7. The inverse temperature dependences of the relaxation time τ for the high- (\square) and low- (\circ) frequency relaxators.

times in the logarithmic scale manifest a linear character for both relaxators. This allows determining the activation energy for each relaxator using the Arrhenius equation (3). The values of E_r for high-frequency relaxator was found to be equal to 0.485 ± 0.005 eV ($T < 250$ K), 0.370 ± 0.005 eV ($T > 250$ K) and for the low-frequency relaxator — 1.360 ± 0.005 eV.

On the basis of the available structural [1] and dielectric data for related materials [13, 14, 20, 21] one can suppose that in the case of the high-frequency relaxator the determined values of the relaxation time are characteristic of the co-operative reorientation of the trimethylammonium groups between neighbour copper-chlorine chains along [011]. The values of the relaxation time for the low-frequency relaxator are considerably larger. Therefore, in this case the relaxator should be connected with reorientation of the much more massive complex than the

single organic groups. It is quite possible that this dielectric relaxation concerns the cooperative motion of the whole $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ chains.

The clearly seen quasi-vertical segment observed in the Cole–Cole plot (at least in Fig. 6b) should be related to the low-frequency conductivity. For the high-temperature region (Fig. 6a) influence of the conductivity manifests itself in the observed clear deviation of the Cole–Cole diagram from the behaviour characteristic of the Debye-type relaxation: the semicircle corresponding to the low-frequency relaxator is not centred on the ε' -axis. The mentioned conductivity is determined from the relation [6]:

$$\sigma = \varepsilon_v \omega \varepsilon'', \quad (5)$$

where ε_v is the dielectric permittivity of vacuum, ε'' is the imaginary part of the dielectric permittivity. The temperature dependence of the electric conductivity measured at the frequency 100 kHz in a cooling run, is depicted in Fig. 8. It is clearly seen that the conductivity depends exponentially on temperature that is characteristic of hopping conductivity. This type of conductivity is described by equation [20]:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right), \quad (6)$$

where σ_0 is a pre-exponential factor and E_a is the activation energy of conductivity. According to (6) the dependences of $\ln\sigma$ on the inversed temperature should be linear that is observed in the experiment. In the same time the linear segments are limited by the temperatures $T_1^c = 198$ K and $T^* = 250$ K (Fig. 8). The anomaly at $T_1^c = 198$ K would be related to the phase transition observed in the dilatometric measurements. The anomaly at $T^* = 250$ K probably is connected with the change of conductivity mechanism as well as with the change in the nature of the relaxation processes. Indeed, as it was mentioned above, at the temperatures higher than T^* the two types of relaxators appeared to be active whereas at lower temperatures only single relaxator was observed. One could assume that the processes of dielectric relaxation and conductivity are closely related to each other. The dependence $\ln\sigma = f(1/T)$ consists of three linear segments (Fig. 8, insert). From their slopes one can calculate the activation energy E_a of conductivity. The determined values for the three above mentioned temperature regions were found to be equal to 0.530 ± 0.005 eV ($T > 250$ K), 0.110 ± 0.005 eV (198 K $< T < 250$ K) and 0.225 ± 0.005 eV ($T < 198$ K), respectively. These values are commensurate with the energies of weak hydrogen bonds [21]. This testifies to the proton character of the conductivity in the investigated crystalline compounds. On the basis of obtained data one can suppose that in the high-temperature phase ($T > 198$ K) the conductivity is realized through two possible mechanisms characterized by different E_a values.

Comparing the values of both types of activation energies (E_r and E_a), one can suggest that the nature of protonic conductivity at least at $T > 250$ K should

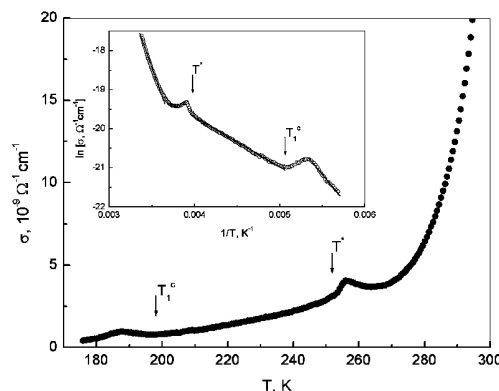


Fig. 8. Dependence $\sigma(T)$ measured along $[001]$ in a cooling run at frequency of electric field 100 kHz. Insert — inverse temperature dependence of $\ln\sigma$.

be related to the so-called “Grotthus” mechanism involving correlated jumps of the bare proton between the host molecules and correlated reorientation of the latter [22]. In this case the trimethylammonium cations would be treated as the host molecules. Within the mentioned temperature region they can occupy two possible positions determined by the directions of the N–H...Cl bonds between neighbor copper-chlorine chains along $[011]$ (high-frequency relaxator). One can suggest that the co-operative reorientation of the organic groups proceeds along $[011]$ whereas the translocation of protons between the neighboring chains of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ is observed in the perpendicular direction, that is along $[0\bar{1}1]$ [20]. In this case, to permit a proton transport, the activation energy of conductivity E_a has to be larger than the sum of the activation energy E_r of the host molecule reorientation and the energy barrier U between the two different H-bonds. Such a situation would be realized at $T > 250$ K for conductivity with $E_a = 0.420$ eV. In the same time, one can suppose that the proton conductivity at $T < 198$ K is connected with another mechanism.

What concerns the second type of the high temperature proton conductivity with $E_a = 0.110$ eV it also could be related to the “Grotthus” mechanism. The latter would involve the jumps of protons between the O–H...Cl bonds created by single Cl^- (3) anions. These bonds also can occupy two possible positions between the neighbor copper-chlorine chains along $[011]$. The translocation of protons in such a case would be observed along the $[0\bar{1}1]$. Due to the comparatively small overall mass of the atoms involved into this mechanism the corresponding relaxator is expected to be observed at the frequencies considerable higher than 1 MHz. In the same time one can suggest that the broad anomalies of dielectric parameters observed at T^* are connected with activation of additional mechanism of protonic conductivity.

4. Conclusion

As it follows from the dilatometric and dielectric investigations the crystals of TrMA-CuCl₃ undergo the first-order phase transition at the temperatures: $T_1^c = 198$ K and $T_1^h = 223$ K (at cooling and heating, respectively). Taking into account the shape and the magnitude of the dielectric anomalies as well as the data of structural and optical study one can suppose that this is a transition between two ferroelastic phases.

The thermal dipole relaxations of quasi-Debye-type were observed in the high-temperature phase of TrMA-CuCl₃. At the temperatures higher than 250 K the two relaxators were found whereas at the lower temperatures (below 250 K) only one relaxation process manifests itself. The high-frequency relaxator is connected with the co-operative reorientations of the comparatively massive trimethylammonium complexes. The low-frequency relaxator would be related to co-operative motion of the whole CuCl₂ · 2H₂O chain. It has been also found that TrMA-CuCl₃ crystals are characterized by pronounced protonic conductivity, which is realized through the Grotthus mechanism at least at temperatures higher than 250 K. The anomalies of the dielectric parameters around $T^* = 250$ K probably are connected with the change of conductivity mechanism as well as with diminishing influence of the low-frequency relaxator on cooling (in the investigated frequency window). These changes would be hardly related to the phase transition since they do not manifest themselves in the dilatometric and optical investigations. Finally, one can note that protonic conductivity and Debye relaxation in the investigated frequency window have to be considered as a rather characteristic feature of TrMA-MeCl₃ group compounds [11]. This requires a more detailed study of these materials. Moreover, the complicated origin of the observed phenomena demands the application of various experimental methods sensitive to the proton dynamics, such as NMR and vibration spectroscopy.

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