A possible glass-like state in θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ at low temperature

2008 J. Phys.: Condens. Matter 20 485211

(http://iopscience.iop.org/0953-8984/20/48/485211)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 485211 (6pp) doi:10.1088/0953-8984/20/48/485211

A possible glass-like state in θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ at low temperature

F Nad[1,2], **P Monceau**[1] **and H M Yamamoto**[3]

[1] Institut Néel, CNRS-UJF, 25 rue des Martyrs, BP 166, 38042 Grenoble cedex 9, France
[2] Institute of Radioengineering and Electronics, RAS, Mokhovaya 11/7, 125009 Moscow, Russia
[3] Condensed Molecular Materials Laboratories RIKEN, 2-1 Hirosawa Wako-shi, Saitama 351-0198, Japan

Received 2 June 2008, in final form 17 September 2008
Published 22 October 2008
Online at stacks.iop.org/JPhysCM/20/485211

Abstract

We present the results of measurements of conductivity and dielectric permittivity of the quasi-two-dimensional organic salt θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ along the in-plane direction in a wide temperature range from room temperature down to liquid helium temperature. At temperatures below about 20 K the ac conductivity corresponds to correlated electron motion in disordered systems. Temperature and frequency dependences of the dielectric permittivity exhibit the main features of the slowing down behavior characteristic of various disordered systems. We explain our results by assuming that this low temperature state represents one form of a glass state—a frozen conglomerate of domains of the two $\mathbf{q}_1$ and $\mathbf{q}_2$ short-range charge orders.

1. Introduction

The family of quasi-two-dimensional layered organic molecular crystals based on the donor molecule bis(ethylenedithio)-tetrathiafulvalene, (ET)$_2$X (ET = BEDT-TTF), displays a large variety of electronic states from insulating to superconducting. θ-Type (ET)$_2$X salts, namely θ-(BEDT-TTF)$_2$MM$'$(SCN)$_4$ (M = Rb, Tl, Cs; M$'$ = Co, Zn) have been synthesized and studied by Mori *et al* [1]. They consist of an alternating stack of anion and ET molecule layers. The ET layer can be regarded as a two-dimensional distorted triangular lattice with a 3/4-filled band. The properties of these θ-(ET)$_2$X salts have been successfully classified according to the physical nature of anions X, the dihedral angle θ_d between the molecular columns of ET molecules and the magnitude of the appropriate transfer integral t [1].

In addition to the known ground states exhibited in these compounds, a new ground state—a charge order (CO) state—has been found and studied. The driving force for this state is strong electron correlation effects which play the leading part in these compounds [2, 3]. The first convincing evidence of the existence of the CO state in θ-type (ET)$_2$X salts was obtained in θ-(ET)$_2$RbZn(SCN)$_4$ (abbreviated as RbZn salt, hereafter) in which a metal–insulator transition has been observed near the temperature $T_{\mathrm{MI}} \approx 200$ K [1]. From NMR [4, 5], polarized Raman and infrared spectroscopy [6] and x-ray [7] studies it has been established that in RbZn salt, indeed, a CO state develops below T_{MI} with a degree of charge disproportionation on ET molecules about 0.2:0.8 and with the concomitant formation of a $c^*/2$ superstructure along the stacking chains.

Subsequently, studies of this CO state have been considerably extended both by including new members of the θ-(BEDT-TTF)$_2$MM$'$(SCN)$_4$ family and by studying other phenomena in these compounds. In particular, the low frequency dielectric response and the effect of cooling rate on charge ordering have been considered in RbZn salt [8, 9]. It was found that, at slow cooling ($\approx$0.1 K min^{-1}), the magnitude of the dielectric permittivity, ε', grows monotonically from room temperature, and shows a tendency towards divergence in the close vicinity of T_{MI}. The large magnitude of ε' and its monotonic growth in the whole temperature range above T_{MI} give strong evidences for the formation of a short-range CO state already at temperatures far above the transition temperature T_{MI}. This conclusion is in agreement with the observation of the broadening of the NMR spectra [10, 11] and the appearance of diffuse planes and rods with $\mathbf{q} = (1/4, k, 1/3)$ above T_{MI}, those being replaced by the superstructure $c^*/2$ below T_{MI} [12].

0953-8984/08/485211+06$30.00

At fast cooling (of the order of 10 K min^{-1}) the sharpness of the first-order transition and the divergence of ε' at T_{MI} are considerably suppressed. It was assumed [9] that, as a result of fast cooling, a disordered short-range metastable CO state, with different degrees of lattice transformation towards the $c^*/2$ superstructure, is probably formed in RbZn salt. This suggestion is in agreement with x-ray studies of RbZn salt in fast cooled conditions which show that the diffuse rods at $\mathbf{q} = (1/4, k, 1/3)$ remain below T_{MI} and that the lattice modulation at $c^*/2$ is disordered [12]. NMR studies of the fast cooling state also show that the appropriate spectral lines lose their structure and broaden considerably. Such a behavior could be the sign of formation in fast cooled RbZn salt of a glass-like charge disproportionated state [12].

Following the classification of the θ-(ET)$_2$X salts according to their dihedral angle, the RbZn salt (dihedral angle $\theta_{\mathrm{d}} = 111°$) is ranged in an intermediate position between the strong insulator θ-(ET)$_2$H$_3$I$_8$ ($\theta_{\mathrm{d}} = 133°$) and θ-(ET)$_2I_3$ (with minimum $\theta_{\mathrm{d}} = 100°$) which is close to being a metal [1]. In this context the study of another compound of this family, namely θ-(ET)$_2$CsZn(SCN)$_4$ (CsZn salt, hereafter), is of a great interest. This compound with $\theta_{\mathrm{d}} = 105°$ is placed between compounds with, respectively, a CO ground state and a metallic one. It has already been found [1] that the resistivity of CsZn salt changes little from room temperature down to 50 K, but grows sharply below 20 K. The thermoelectric power is small at room temperature; it begins to grow below 200 K, approaching a maximum at about 50 K and it falls down quickly at lower temperature. The magnetic susceptibility also changes little down to 20 K, showing a Curie type increase below 20 K. Near 20 K again a small jump in specific heat and entropy of CsZn salt has been also found [14]. One might think that these data could provide some evidence for the existence of a metal–insulator transition in CsZn salt near 20 K. However, subsequent studies show that the behavior of CsZn salt with decreasing temperature is more complicated.

The studies of infrared reflectance and Raman spectra show that no optical gap is observed in CsZn salt in the whole temperature range down to 10 K [15–17]. The authors of [17] suggest that the electronic state of CsZn salt at low temperature resemble the frozen (fast cooling) state of RbZn salt which consists of short-range CO domains. The nature of the electronic state of CsZn salt has also been studied by means of ^{13}C NMR lineshape analyses [18, 19]. Similar to the case of RbZn salt, at $T > T_{\mathrm{MI}}$ line broadening in CsZn salt is observed below about 180 K which is associated with charge disproportionation (CD). Below ≈140 K CD becomes almost static, corresponding to the formation of a short-range CO in this temperature range. However, with a further temperature decrease down to 5 K no long-range CO is stabilized, contrary to the case of RbZn salt [19]. Below about 30 K the ground state of CsZn salt remains very inhomogeneous, half of the molecular sites being non-magnetic while the other half have a finite magnetic moment. More detailed data about the structure of CsZn salt at low temperature have been obtained by x-ray studies, very similar to those in the isostructural θ-(ET)$_2$CsCo(SCN)$_4$ salt [20–22]. It was found that in these compounds strong diffuse sheets are observed along $2a^* + c^*$ and $2a^* - c^*$ directions in the temperature range 300–120 K. Below 90 K two-dimensional diffuse rods, corresponding to $\mathbf{q}_1 = (2/3, k, 1/3)$ and $\mathbf{q}_2 = (0, k, 1/2)$, develop from the diffuse sheets. With further cooling, the maximum intensity of $\mathbf{q}_2$ increases considerably, while that of $\mathbf{q}_1$ does not change.

Recent theoretical studies [23–25, 38] of the $\frac{1}{4}$ filled extended Hubbard model on the anisotropic triangular lattice have shown the existence of a three-fold state [26] due to geometrical frustration in the nearest neighbor Coulomb repulsion interactions. While in RbZn the lattice distortion at T_{MI} stabilizes the striped phase, in CsZn the three-fold sublattice structure and the two-fold striped state have almost comparable condensation energies and coexist at low temperature [24], as seen in x-ray studies.

Recently, studies of the dielectric constant and the ac conductivity in the out-of-plane direction (i.e. in the b-direction perpendicular to the well conducting molecular layers) have been carried out in CsZn salt in the narrow temperature range 4.3–7.1 K [27]. It was shown that the frequency dependence of the dielectric constant in this direction can be well described by the Havriliak–Negami formula. Unexpected strong nonlinear effects have also been observed at large electric fields. These findings have been explained by analogy with the behavior of collective excitations in charge density wave systems.

In the present paper, the results of studies of the conductance and the dielectric permittivity of CsZn salt are presented in the direction along the molecular planes with the largest conductivity, i.e. in the direction where the basic transport properties due to CO phenomena ought to be exhibited. The measurements have been carried out in a wide temperature range from room temperature down to liquid He temperature, which overlap the change of properties of CsZn salt from metallic to insulating. Our results give a better understanding of the evolution of CsZn salt states with decreasing temperature and of the physical nature of its low temperature state.

2. Experimental results

We have measured the real and imaginary parts of the complex conductance of six θ-(ET)$_2$CsZn(SCN)$_4$ samples with characteristic dimensions of length 1.5–2 mm, width 50–100 μm and thickness 10–15 μm. Electrical contacts to the samples were prepared by attaching thin (17 μm diameter) gold wires by silver paste to gold pads evaporated onto the sample ends. The magnitude of the conductivity at room temperature of the CsZn samples we measured as equal to about 50 S cm^{-1}, which corresponds to the value published earlier [1]. Measurements of the complex conductance were carried out using a HP 4192 A impedance analyzer in the frequency range 10^3–10^7 Hz at temperatures between 300 and 4.3 K. The amplitude of the ac voltage applied to the sample was within its linear response. The temperature regulation (cooling rate was about 0.1 K min^{-1}) and the conductance measurements were carried out in an automatic regime under computer control.

Figure 1 shows the temperature dependence of the real part of the conductance, G, of CsZn salt versus inverse temperature

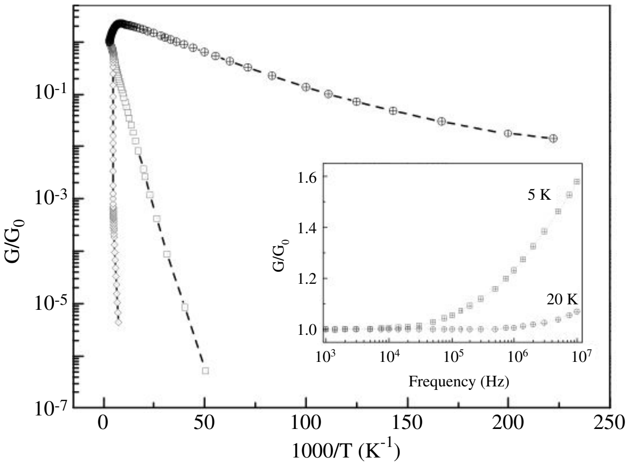

Figure 1. Arrhenius plot of the conductance G, normalized by its room temperature value G_0, at frequency 1 kHz for slow cooling (0.1 K min^{-1}) of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ (⊕); same plots for θ-(BEDT-TTF)$_2$RbZn(SCN)$_4$ with slow cooling (0.1 K min^{-1}) (○) and fast cooling (9 K min^{-1}) (□). The inset shows the frequency dependence of the conductance G of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ normalized by its value G_0 at two temperatures, 5 and 20 K.

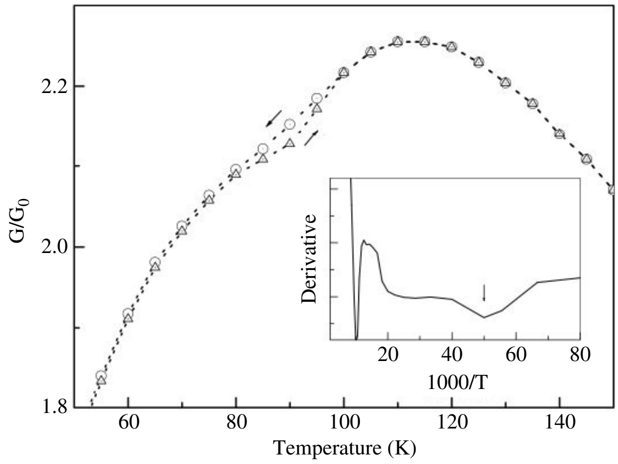

Figure 2. Temperature dependence of the conductance G of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$, normalized by its room temperature value G_0, in the temperature range where the conductance is maximum. The inset shows the variation of the derivative $d(\log G)/d(1000/T)$ as a function of inverse temperature for θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$.

(Arrhenius plot) normalized by its value at room temperature G_0, measured at a frequency of 1 kHz. For comparison, in the same figure 1 the appropriate dependences for RbZn salt for fast cooling (9 K min^{-1}) and slow cooling (0.1 K min^{-1}) are shown [9]. From this figure the difference in the temperature dependence of conductance of CsZn and RbZn salts is obvious. The conductance of RbZn salt, for both slow and at fast cooling, decreases from room temperature, corresponding to a non-metallic type of conductivity. When cooled further in slow cooling conditions the conductance of RbZn salt exhibits a sharp decrease with hysteresis below 200 K; that corresponds to a first-order transition into the CO charge state which is accompanied by lowering the lattice symmetry and by the doubling of its period along the c axis [7]. With fast cooling, the first-order character of the transition is greatly suppressed and a smaller and more diffuse decrease of the conductance is observed near 167 K [9].

As can be seen from figure 1, the conductance of CsZn salt grows when the temperature decreases below room temperature, indicating metallic type conductivity. The growth of G becomes slower from about 130 K and G exhibits a maximum in the range 110–115 K (figure 2). Below this maximum, for all the CsZn samples we measured, we have observed that $G(T)$ exhibits a small bend in the temperature range 100–80 K with respect to the background of the monotonic decrease of conductance. The variation of conductance in this temperature range displays hysteresis: the curves of $G(T)$ at decreasing and increasing temperature differ from each other by $\Delta T = 4$–5 K (figure 2). The temperature dependence of the derivative $d(\log G/G_0)/d(1000/T)$ shows a sharp minimum near 100 K (inset in figure 2).

From figure 1 it is clearly seen that, in the temperature range below the maximum of G, the slope of the decrease of G, that is to say the 'activation energy', is considerably smaller than in the case of RbZn salt for both cooling rates. The quotation marks around 'activation energy' indicate that the Arrhenius plot of $G(1/T)$ is not linear in the whole temperature range 100–4.3 K, i.e. it means that no real well-defined energy gap can probably be ascribed to this low temperature CsZn ground state.

A further marked decrease of G is observed near 20 K; this is in agreement with the wide minimum of the derivative in the inset in figure 2. A noticeable frequency dispersion of G appears only below 20 K, and it only becomes significant with decreasing temperature (inset of figure 1). However, as can be seen from the inset, even in this temperature range the magnitude of G does not practically depend on frequency below about 10 kHz, that corresponds to dc conductance. Below 20 K, the $G(T)$ dependence is rather similar to hopping type conductivity in a sample with disorder [28, 29]. The evaluation of the ac hopping conductivity for disordered systems taking into account electron correlation effects shows that the ac conductance is proportional to T^3 [29]. Our attempts to approximate the temperature dependence of the ac conductance of CsZn in the temperature range 4.3–20 K show that the more accurate fit indeed corresponds to the relation $G \sim T^n$ with $n = 2.9$ (see figure 3), i.e. it is very close to the theoretical value $n = 3$.

Figure 4 shows the temperature dependences of the real part of the dielectric permittivity, ε', at various frequencies 10^4–10^7 Hz. When T is decreased below room temperature the magnitude of ε' begins to increase. The rate of this increase is especially marked below about 200 K. Below 100 K, the $\varepsilon'(T)$ curves show a maximum, ε'_m, at some temperature T_m dependent on frequency. With decreasing frequency this maximum shifts to lower temperatures and simultaneously the magnitude of ε'_m increases considerably up to large values of the order of 10^6. For temperatures below T_m, ε' decreases more rapidly than its growth above T_m. Such forms of $\varepsilon'(T)$ dependence and their variation with frequency bear a strong resemblance to the known so-called slowing down behavior

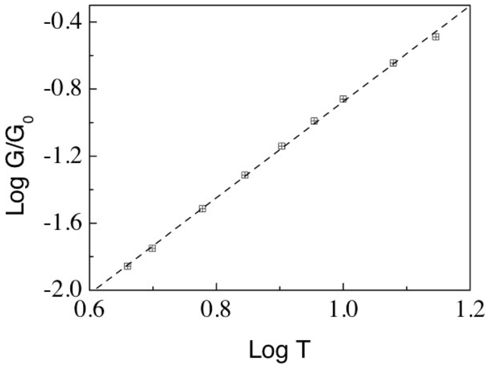

Figure 3. Variation of the logarithm of the conductance G of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$, normalized by its room temperature value G_0, as a function of logarithm of temperature in the temperature range below 20 K.

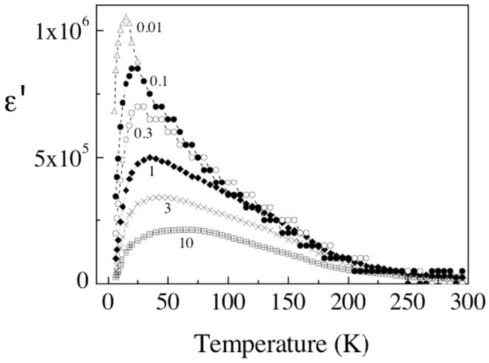

Figure 4. Temperature dependences of the real part of dielectric permittivity ε' of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ at different frequencies (in MHz).

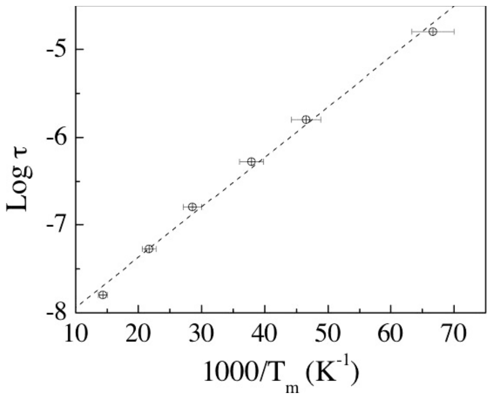

Figure 5. Variation of the logarithm of the relaxation time τ of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ as a function of inverse temperature T_m.

which is typical for various systems with certain degree of disorder [30]. In such a case, it is usually considered that, at T_m, the condition $\omega\tau \approx 1$ ($\omega = 2\pi f$, τ: relaxation time) is reached, at which the response of the sample begins to slow, i.e. it does not have enough time to follow the faster variation induced by the ac voltage, thus leading to a decrease of the magnitude of ε'. A plot of the relaxation time $\tau = 1/\omega$ as a function of inverse temperature $1000/T_m$ is shown in figure 5. It can be seen that this $\log\tau$ versus $1000/T$ dependence is close to linear, i.e. it can be well approximated by a thermo-activated type relation: $\tau = \tau_0 \exp(-\Delta/kT)$ with $\tau_0 \approx 10^{-9}$ s and $\Delta \approx 130$ K.

3. Discussion

As it appears from our results presented above as well as from results published earlier [1], several different states are developed in CsZn salt with decreasing temperature. In the temperature range 300–100 K the increase in conductance (figures 1 and 2), generally speaking, corresponds to a metallic type of conductivity. Evidence for this is also provided by spectral studies [15] which show a Drude-like type of energy spectrum without noticeable energy gap. However, a number of experimental results indicate that this 'metallic' state in CsZn salt is actually more complicated. As it was already noted in the Introduction, x-ray studies have shown that, in this temperature range, diffuse sheets develop in CsZn salt that correspond to the tendency for charge disproportionation along some crystallographic directions [20]. In addition, NMR spectra begin to broaden at temperatures below 180 K [19]. Similarly, from our data about the temperature dependence of $\varepsilon'(T)$, the dielectric constant ε' begins to increase in the same temperature range (figure 4). This means that the first indications of the appearance of CD are observed in CsZn salt, i.e. already in this state some features of inhomogeneous charge distribution develop, although the state maintains a metallic type nature.

Below about 110 K, the character of the temperature dependence of the conductivity changes: beyond a maximum, G slowly decreases (figure 1). In all this temperature range the decrease of the conductivity of CsZn salt is considerably smaller than in the case of RbZn salt. In addition, the measured $G(1/T)$ dependences show that several peculiarities are observed over the background of its monotonic decrease. We found that a sharper decrease of G with hysteresis occurs near 90 K, which can be associated with a structural modulation coupled with local charge ordering [31]. These features appear characteristic for a 'diffuse' first-order transition, namely near this temperature the logarithmic derivative of the conductance shows a well-defined minimum (inset in figure 2). It is also in this temperature range that the significant growth of ε' begins (figure 4). All these features give some indications that, probably, some new phase with a new charge distribution may develop or be enhanced in part of the CsZn sample. These results agree with the results of x-ray and NMR studies [20, 21]. The structural studies show that in CsZn and CsCo salts, in the temperature range 120–50 K, two-dimensional diffuse rods located at $\mathbf{q}_1 = (2/3, k, 1/3)$ and $\mathbf{q}_2 = (0, k, 1/2)$ grow from the diffuse sheets already visible at higher temperatures. It should be noted that the appearance of the superstructure with $\mathbf{q}_2$ corresponds to CO analogous to RbZn salt [7].

Following from structural studies, below 100 K the intensity of rods with $\mathbf{q}_2$ increases appreciably while the intensity of $\mathbf{q}_1$ remains practically unchanged [21]. These data indicate the tendency for the formation of a more homogeneous CO state, although charge modulation with $\mathbf{q}_1$ is also present. However, even at 20 K, the intensity of $\mathbf{q}_2$ diffuse spots remains very weak. The correlation lengths of $\mathbf{q}_1$ and $\mathbf{q}_2$ modulations are not very large (50–70 Å) [20]. Studies of NMR spectra in this temperature range show that CD becomes more static and corresponds to short-range ordering, but not to long-range ordering [19]. Such a ground state corresponds rather to the division of CsZn samples in domains with different structural factors and different charge distribution which are competing with each other [27, 32, 33].

In this temperature range we have observed a considerable growth of ε', approaching a maximum $\varepsilon'_{\mathrm{m}}$ at T_{m}; the magnitude of $\varepsilon'_{\mathrm{m}}$ increases and T_{m} decreases when frequency is reduced (figure 4). Such a behavior corresponds to a slowing down behavior and is typical for many ferroelectrics with some degree of disorder, so-called relaxors [34], and for different types of glasses. In such systems, when temperature decreases the relaxation rate of the response to the ac field becomes slower, corresponding to a considerable broadening of the distribution of relaxation time, the width of which becomes proportional to $\ln\tau$ [35]. In this case, in a wide interval of time, the relaxation can be described as a logarithmic dependence of some order parameter on time [35]. In accordance with our measurements, we can consider the polarization as such an order parameter. Because ε' is proportional to the polarization, it has to be proportional to $\ln\tau$. Figure 6 shows the magnitude of $\varepsilon'_{\mathrm{m}}$ as a function of $\log(1/\omega)$, i.e. $\log\tau$. As can be seen from this figure the proportionality is indeed realized in our CsZn samples under investigation. That gives additional evidence for the explanation we propose to describe the behavior of CsZn salt in this temperature range.

As can be seen from figure 5, the relaxation time grows with the decrease of temperature following a thermo-activated law with activation energy $\Delta_\tau = 130$ K. We saw above (figure 1) that, below 100 K, the dependence of $\log G(1/T)$ is nonlinear and no any definite activation energy can be ascribed to this dependence. We should remember that in this temperature range the intensities of $\mathbf{q}_1$ and $\mathbf{q}_2$ are very weak (less than 5×10^{-5} of the Bragg intensity) and structural correlation lengths are very small. These features are apparently insufficient for the formation of a well-defined energy gap in the conduction band [21]. Additionally, spectroscopic studies also show that any gap is absent while electron localization occurs at low frequency [15]. If one would like to estimate an 'activation energy' Δ_G from the slope of the tangent to the $\log G(1/T)$ curve in some appropriate temperature range one will obtain $\Delta_G \approx 65$ K in the range 50–20 K and $\Delta_G \approx 23$ K in the range 10–7 K. The latter value of Δ_G corresponds to the value determined in [36] from conductivity studies in the temperature range 10–1 K. The difference in magnitude of activation energies, Δ_G for conductivity and Δ_τ for relaxation time, can be explained in the following way. The ac conductivity of our samples is determined by the motion of free electrons in a disordered system, the character of which is closed to hopping conductivity [28]. The appropriate 'activation energy' characterizes some average value of energy barriers for such a single electron motion. From the other hand, the magnitude of ε' is determined mainly by the polarization of domains. As in the case of usual ferroelectrics, the ac polarization results from the cooperative motion of many elementary dipoles within the coherence distance, i.e. within a given domain. In that case, the reorientation of a domain in the applied ac electric field requires a considerably larger energy which is proportional to the domain volume. Namely this energy will correspond to the energy barrier Δ_τ in the thermo-activated variation of the relaxation time. As follows from figure 5, the average magnitude of the barrier is equal to about 130 K. Hence, it appears that at temperatures near 100 K this barrier can be overcome by thermal fluctuations, which can lead to a change of the direction of the polarization vector. In external ac electric fields such ferroelectrics exhibit a behavior similar to that of so-called superparaelectrics [34] which are the electrical analogue of superparamagnets first considered by Néel [37]. With decreasing temperature, in the range 40–20 K, the magnitude of kT becomes smaller than Δ_τ. As a result, the stability of domains towards reorientation increases and the relaxation time grows in a thermo-activated manner (figure 5).

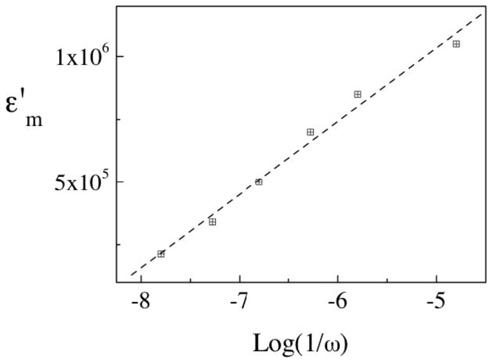

Figure 6. Variation of the magnitude of the maximum of the real part of dielectric permittivity $\varepsilon'_{\mathrm{m}}$ of θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ as a function of logarithm of the inverse frequency.

As seen from figure 4, after having reached its maximum ε' decreases sharply below about 20 K. Near the same temperature a minimum has been observed in the temperature dependence of the derivative $\mathrm{d}(\log G/\mathrm{d}1000/T)$ (inset in figure 2). Below 20 K we have shown that the temperature dependence of the ac conductance follows a power law relevant to hopping conductivity in disordered systems (figure 3). Moreover I–V curves measured from 19 K down to 0.29 K have a nonlinear character and they follow a power law like $I \sim V^\alpha$ with the value of α much larger than 1, approaching 8.4 at 0.29 K [36]. These forms of I–V curve resemble those measured in the CDW compound, m-TaS$_3$ (with the value of α approaching 15) [39], where it was shown that such a form corresponds to hopping conductivity in a strong enough electric field [40]. For a precise determination of a glass transition at low temperature in the CsZn salt, it would be necessary to perform measurements of the dielectric permittivity in a broad frequency range [41]. Our measurements are practically limited to only three octaves (10^4–10^7 Hz). Therefore, at the present stage, we can only give a qualitative picture based on the similarity of the observed dependences to that corresponding to a glassy-like behavior. Thus, we consider that the most probable explanation of all these low temperature features is the transition of CsZn salt into a glass-like state [13]. Indeed, the existence of at least of two types of domains with different structure, each competing with the other, leads to the development of frustration, i.e. the situation when incompatible and competing two-fold ($\mathbf{q}_2$) and three-fold ($\mathbf{q}_1$) states probably correspond to two degenerate free energy minima with energy very close in magnitude [23–26]. As a result of such frustration, some glassy-like state develops, which corresponds to a frozen degree of disorder on the long-range scale with conservation of short-range order [13, 23] with small coherence length, which is still less than 200 Å along each crystallographic axis.

4. Conclusion

In summary, our experimental data bring some insight into the physical nature of the transition of CsZn salt taking place at low temperatures near 20 K. The temperature dependence of the ac conductance does not have a pure thermo-activated character but it corresponds to a cubic power of temperature $G \sim T^3$, which follows from the theory for ac hopping conductivity in disordered systems taking into account electron correlation effects [29]. Both the temperature and frequency dependences of the dielectric permittivity ε' show a slowing down behavior which is typical for ferroelectrics with a considerable degree of disorder similar to a glass-like state [30, 33–35]. With decreasing temperature the relaxation time increases in a thermo-activated manner with an activation energy corresponding to the energy barrier which has to be overcome for reorientation in the ac electric field. The frequency dependence of the maximum of the dielectric permittivity, $\varepsilon'_{\mathrm{m}}$, has a logarithmic character $\varepsilon'_{\mathrm{m}} \approx \ln(1/\omega)$ that is in agreement with the theory for various glass states [30, 33, 35]. Thus, the data we have obtained provide strong arguments for the assumption that the low temperature ground state of CsZn salt represents a combination of frustrated domains which, with decreasing temperature, are frozen into a glass-like short-range charge ordered state.

Acknowledgments

We are grateful to T Takahashi for sending us the results of NMR lineshape analyses of single crystal θ-(BEDT-TTF)$_2$CsZn(SCN)$_4$ before publication [19]. This work was supported in part by the Russian Foundation for Basic Research (grant no. 06-02-72551) in the frame of the CNRS-RAS Associated European Laboratory of the Institut Néel and the Institute of Radioengineering and Electronics RAS, and partially by INTAS (grant no. 05-1000008-7972) and RFBR (grant no. 08-02-01093-a).

References

[1] Mori H, Tanaka S and Mori T 1998 *Phys. Rev.* B **57** 12023
[2] Seo H 2000 *J. Phys. Soc. Japan* **69** 805
[3] Seo H, Hotta C and Fukuyama H 2004 *Chem. Rev.* **104** 5005
[4] Miyagawa K, Kawamoto A and Kanoda K 2000 *Phys. Rev.* B **62** 7679
[5] Chiba R, Yamamoto H M, Hiraki K, Nakamura T and Takahashi T 2001 *Synth. Met.* **120** 919
[6] Yamamoto K, Yakushi K, Miyagawa K, Kanoda K and Kawamoto A 2002 *Phys. Rev.* B **65** 085110
[7] Watanabe M, Noda Y, Nogami Y, Mori H and Tanaka S 2003 *Synth. Met.* **133/134** 283
[8] Nad F, Monceau P and Yamamoto H M 2006 *J. Phys.: Condens. Matter* **18** L509
[9] Nad F, Monceau P and Yamamoto H M 2007 *Phys. Rev.* B **76** 205101
[10] Chiba R, Hiraki K, Takahashi T, Yamamoto H M and Nakamura T 2004 *Phys. Rev. Lett.* **93** 216405
[11] Takahashi T, Chiba R, Hiraki K, Yamamoto H M and Nakamura T 2004 *J. Physique* IV **114** 665
[12] Watanabe M, Noda Y, Nogami Y and Mori H 2003 *Synth. Met.* **135/136** 665
Watanabe M, Noda Y, Nogami Y and Mori H 2004 *J. Phys. Soc. Japan* **73** 116
[13] Kanoda K, Ohnou K, Kodama M, Miyagawa K, Itou T and Hiraki H 2005 *J. Physique* IV **131** 21
[14] Nishio Y, Nihei Y, Tamura M, Kajita K, Nakamura T and Takahashi T 1999 *Synth. Met.* **103** 1907
[15] Tajima H, Kyoden S, Mori H and Tanaka S 2000 *Phys. Rev.* B **62** 9378
[16] Wang N L, Feng T, Chen Z J and Mori H 2003 *Synth. Met.* **135/136** 201
[17] Suzuki K, Yamamoto K, Yakahi K and Kawamoto A 2005 *J. Phys. Soc. Japan* **74** 263
[18] Takahashi T, Hiraki K, Moroto S, Tajima N, Takano Y, Kubo Y, Satsukawa H, Chiba R, Yamamoto H M, Kato R and Naito T 2005 *J. Physique* IV **131** 3
[19] Chiba R, Hiraki K, Takahashi T, Yamamoto H M and Nakamura T 2008 *Phys. Rev.* B **77** 115113
[20] Nogami Y, Pouget J-P, Watanabe M, Oshima K, Mori H, Tanaka S and Mori T 1999 *Synth. Met.* **103** 1911
[21] Watanabe M, Nogami Y, Oshima K, Mori H and Tanaka S 1999 *J. Phys. Soc. Japan* **68** 2654
[22] Watanabe M, Noda Y, Nogami Y, Oshima K and Mori H 2002 *J. Physique* IV **12** 231
[23] Kaneko M and Ogata M 2006 *J. Phys. Soc. Japan* **75** 014710
[24] Watanabe H and Ogata M 2006 *J. Phys. Soc. Japan* **75** 063702
[25] Hotta C and Furukawa N 2006 *Phys. Rev.* B **74** 193107
[26] Mori T 2003 *J. Phys. Soc. Japan* **72** 1469
[27] Inagaki K, Terasaki I, Mori H and Mori T 2004 *J. Phys. Soc. Japan* **73** 3364
[28] Mott N F and Davis E A 1979 *Electron Processes in Non-Crystalline Materials* (Oxford: Clarendon)
[29] Shklovskii B L and Efros A L 1981 *Sov. Phys.—JETP* **54** 218
[30] Jonscher A K 1983 *Dielectric Relaxation in Solids* (London: Chelsea Dielectrics)
[31] Mori H, Okano T, Tanaka S, Tamura M, Nishio Y, Kajita K and Mori T 2000 *J. Phys. Soc. Japan* **69** 1751
[32] Imry I and Ma S 1975 *Phys. Rev. Lett.* **35** 1399
[33] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Clarendon)
[34] Cross L E 1987 *Ferroelectrics* **76** 241
[35] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
[36] Takahide Y, Kanoike T, Enomoto K, Nishimura M, Terashima T, Uji S and Yamamoto H M 2006 *Phys. Rev. Lett.* **96** 664
[37] Néel L 1949 *Compt. Rend. Acad. Sci.* **228** 664
[38] Tanaka Y and Yonemitsu K 2007 *J. Phys. Soc. Japan* **76** 053708
[39] Itkis M E, Nad F and Monceau P 1990 *J. Phys.: Condens. Matter* **2** 8327
[40] Apseley N and Hughes H P 1974 *Phil. Mag.* **30** 963
Apseley N and Hughes H P 1975 *Phil. Mag.* **31** 1327
[41] Kutnjak R P, Levstik A, Levstik I, Filipic C, Blinc R and Kind R 1994 *Phys. Rev.* B **50** 12421