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Origin of non-Arrhenius conductivity in fast ion conducting glasses

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We report the results of ac conductivity measurements on silver halide silver oxysalt glasses. Like Kincs and Martin [Phys. Rev. Lett. **76**, 70 (1996)], we find that these glasses exhibit non-Arrhenius behavior in the dc conductivity, which depends strongly on the silver halide content and on the type of the halide anion. From the frequency dependence of the conductivity, we draw conclusions on the origin of the non-Arrhenius behavior. In particular, we analyze the temperature dependence of the ions' mean square displacement, where the short-time subdiffusive dynamics passes over into the long-time diffusive dynamics. In the following, this "crossover" mean square displacement is denoted by $\langle R^2 \rangle_{cr}$. Glasses which exhibit non-Arrhenius behavior in their dc conductivity, are found to show a temperature dependent $\langle R^2 \rangle_{cr}$. A possible explanation for the temperature dependent $\langle R^2 \rangle_{cr}$ is an increase of the number of vacant sites for the mobile ions with increasing temperature. At higher temperatures, the number of these vacancies becomes constant, leading to a non-Arrhenius-type dc conductivity.

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I. INTRODUCTION

Solid ionic conductors are important materials for different technological applications such as batteries, supercapacitors, fuel cells, sensors, and electrochromic devices.[1–5] Much of the effort has been focused on crystalline solids in which the structural arrangement allows the motion of ions along specific crystallographic axis. Optimum materials for potential applications have a high density of weakly bonded ionic species as well as a high degree of disorder in the mobile ion sublattice. As the structural requirements are rather stringent, a high ionic conductivity is exhibited only by relatively few crystalline materials. Also, there are many limiting factors in the case of crystalline solids such as obtaining single crystals and in polycrystalline materials the inherent grain boundary effects.

In this context, glassy solid electrolytes are found to be promising candidates; the structural requirements are not so severe because of the high degree of disorder. To find glassy electrolytes with improved ionic conductivity, different strategies have been used. Kincs and Martin have optimized ion-conducting glasses by doping with metal halide salts in order to attain high ionic conductivity at room temperatures.[6] Subsequently, these glasses are frequently called fast ion conducting (FIC) glasses. At low temperatures, the dc conductivity of these glasses has been found to exhibit Arrhenius behavior similar to the most other glassy ionic conductors. However, upon increasing temperature the dc conductivity increases and approaches high ionic conductivity of the order of 10^{-2} S/cm near room temperature. Above this limit, the dc conductivity remains constant and departs from the Arrhenius behavior at higher temperatures. More quantitatively, similar non-Arrhenius behavior has been observed in the different series of FIC glasses as well as in crystals,[7,8] which exhibit high ionic conductivity at room temperatures. This ubiquitous non-Arrhenius behavior represents yet another challenge for the theorist as well as the experimentalist in the field. However, in the past few years considerable progress has been made using different experimental techniques to correlate the microscopic structure and fast ionic conductivity in these glasses.

Additionally, with the use of different experimental observations and by different theoretical concepts, few models have been proposed to understand the observed non-Arrhenius behavior and the underlying diffusion mechanism in these glasses.[9–11] As a result, there is no consensus regarding the experimentally observed non-Arrhenius behavior and the existing models for the diffusion mechanisms in these optimized ion-conducting solids. Most of the models involve more specific or indirect assumptions about the microscopic structure in general and/or in the distribution of site energy and energy barriers of the mobile cations in particular. However, a few empirical rules of thumb for high ionic conductivity have been postulated:[12] (i) the anion should be large and highly polarizable, (ii) the cation should be relatively small and also polarizable, (iii) a glass should contain more than one glass former, and (iv) a suitable microscopic structure which permits macroscopic motion of the ions with low activation energy are favored.

It is well established that in most crystalline solid ionic conductors diffusion of mobile ions can be described by the point defect model.[13,14] In this case, an interstitial pair (interstitialcy) or a vacancy type defect has been considered for ionic diffusion. According to the point defect model, only few ions may be able to perform a hop depending on the availability of the appropriate defect sites, while others are not able to hop at a given instant and temperature. In this respect, the ion transport in glass has been characterized by the "*weak electrolyte*" scenario, where the concentration of mobile cations varies with temperature but not their mobility.[15] On the other hand, in most cases, glassy electrolytes are viewed as "*strong electrolyte*," where all the ions are assumed to contribute to the experimentally measured dc conductivity, σ_{dc}. Since glass is a noncrystalline solid, the term "*point defect*" does not have a precise description as in the case of crystal.[16,17] There are models,[18] which describe the ion transport mechanism in glasses supporting the weak electrolyte scenario, and others, which consider the strong

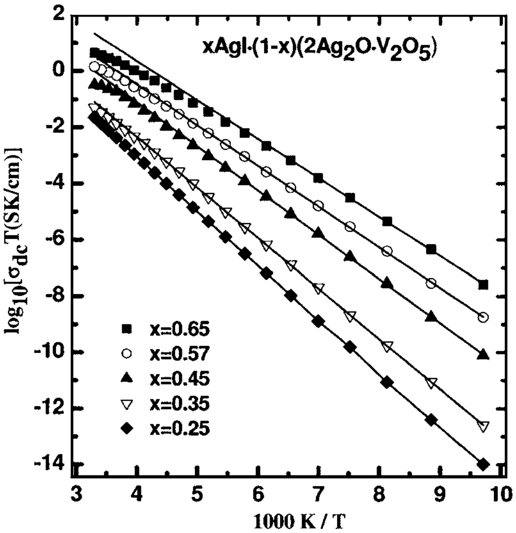

FIG. 1. Arrhenius plot of the dc conductivity (multiplied by the temperature) of $x\text{AgI}\cdot(1-x)(2\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ with $0.25 \leqslant x \leqslant 0.65$ glasses. The symbol represents the experimental data points and the fitted line corresponds to using the Arrhenius law.

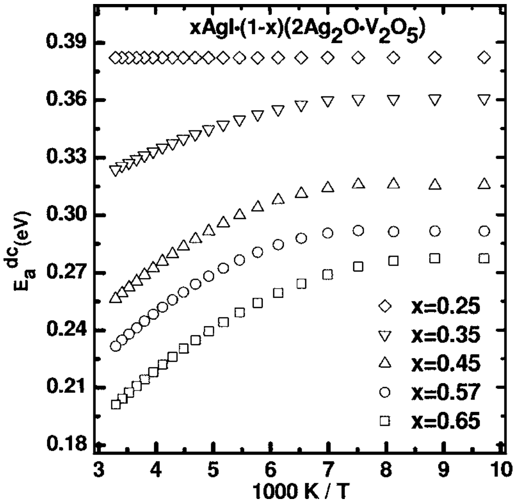

FIG. 2. The variation of the "apparent activation energy" with temperature in $x\text{AgI}\cdot(1-x)(2\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ with $0.25 \leqslant x \leqslant 0.65$ glasses.

electrolyte picture. The concept of the point defect model has been used to describe ion diffusion in glasses now and then over the decades, but they have not been widely accepted as in the case of crystalline solids. Recently significant progress has been made by different theoretical groups using computer simulation studies on ion conducting glasses, to correlate the glass structure, number of available ionic sites, and diffusion pathways volume with ion transport.[19–23] Additionally, the results of these different studies provide strong evidence that the ion transport in glasses can be described in terms of a concept that is well known from ionic crystals, namely, vacancy-like diffusion mechanism.

In order to check the applicability of different ideas and the concepts proposed by different theoretical models, we have carried out an experimental study on different FIC ion-conducting glasses using ac conductivity spectroscopy over wide range of temperatures and at different compositions. The analysis of the ac conductivity spectra of ion conducting glasses provides useful information regarding the diffusion mechanism of mobile ions, in particular the role of ion site energy distributions, number of available sites for diffusion, etc. In this context, recently it has been suggested that in glass with high electronic polarizability the ion transport is characterized by the small and temperature dependent ratio of empty ionic sites to number of mobile ions.[24] On the other hand, for glasses with low electronic polarizability ion transport is described by a relatively large and temperature independent ratio of empty ionic sites to the number of ions.[22] In this paper, we provide evidence from the frequency dependent conductivity study on FIC glasses and draw conclusions on the origin of the non-Arrhenius behavior. Furthermore, we present more conclusively that the applicability of vacancy type transport mechanism is responsible for the observed non-Arrhenius behavior in these FIC glasses.

II. EXPERIMENT

For the preparation of silver halide containing glasses, appropriate amounts of high purity silver halides, Ag_2O, B_2O_3, and V_2O_5 were the starting materials. The mixtures were thoroughly mixed and melted in a quartz crucible slightly above the respective melting temperatures and kept there for about 30 min. Bulk glass samples were then obtained by pouring the homogenized melt into a stainless steel mold (with a diameter 22 mm and thickness ≈ 2 mm). For the conductivity measurements, the glass samples were then polished and sputtered on both surfaces with metal electrodes consisting of silver and platinum layer. Conductivity measurements were carried out by using the Novocontrol α-S high-resolution dielectric analyzer in a frequency range from 10 mHz to 3 MHz and in a temperature range from 103 to 303 K.

III. RESULTS

In Fig. 1 we present the Arrhenius plots of dc conductivity of $x\text{AgI}\cdot(1-x)(2\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ with $0.25 \leqslant x \leqslant 0.65$ glasses measured over wide range of temperatures. Clearly, at low silver iodide content level, the measured dc conductivity follows the simple Arrhenius form

$$\sigma_{\text{dc}}T = \sigma_0 \cdot \exp(-E_a^{\text{dc}}/k_B T). \tag{1}$$

With increasing AgI content level, the conductivity follows the Arrhenius behavior only at lower temperatures and becomes non-Arrhenius at higher temperatures, i.e., the slopes starts to decrease with increasing temperatures. It is significant to note that the onset of non-Arrhenius behavior shifts to lower temperatures when the AgI content becomes high. Additionally, these results are supported by measurements on $0.5\text{Ag}X\cdot 0.25\text{Ag}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3$ glasses with $X=\text{Cl}$, Br, and I. Like Kincs and Martin and by few others,[25,26] we find that the non-Arrhenius behavior of the dc conductivity depends strongly on the silver halide content level and on the type of the halide anion.

More evidently, we present the "apparent" activation energy of the glasses under investigation in Fig. 2. The apparent activation energy has been calculated with the use of running slope between adjacent temperature-conductivity points. It is interesting to note that the glasses with low silver iodide content exhibit higher activation energy and normal behavior of constant activation energy in the entire range of temperatures. On the other hand, with increasing AgI content the apparent activation energy is lower, remains constant only at lower temperatures and start decreases at higher temperatures. Therefore, it is clear that the measured dc conductivity and the apparent activation energy are strongly dependent on the AgI content.

According to linear response theory,[27–29] frequency dependent conductivity spectra of ion-conducting glasses can be directly related to the time dependent displacement of the mobile ions in thermal equilibrium. Hence, the many particle displacement function can be defined as

$$\langle R^2(t)\rangle = \frac{12k_BT}{N_Vq^2\pi}\int_0^t dt\int_0^\infty \frac{\sigma'(\nu)}{\nu}\sin(2\pi\nu t')d\nu, \qquad (2)$$

where N_V is the number density of the mobile ions, q denotes their charge. k_B and T are the Boltzmann's constant and temperature, respectively. On short time scales, diffusion of mobile ions are characterized by the subdiffusive behavior, i.e., the ions perform correlated forward backward hopping motions. This implies that when the time-dependent mean square displacement of mobile ions, $\langle R^2(t)\rangle$ is smaller than typically few Å^2, the mean square displacement increases sublinearly with time. On the other hand, at longer time scales the subdiffusive behavior passes over into a diffusive behavior, i.e., $\langle R^2(t)\rangle$ varies linearly with time. In the following, the value of $\langle R^2(t)\rangle$ at the crossover from the subdiffusive dynamics to the diffusive dynamics will be denoted by, $\langle R^2\rangle_{cr}$, i.e.,

$$\langle R^2\rangle_{cr} = \langle R^2(t^*)\rangle \qquad (3)$$

with

$$t^* = \frac{1}{2\pi\nu^*}. \qquad (4)$$

Here, ν^* denotes the crossover frequency from the dc conductivity to dispersive conductivity, which we define by $\sigma'(\nu^*)=2\sigma_{\mathrm{dc}}$. It is important to understand the value, $\langle R^2\rangle_{cr}$ of mobile ions with respect to their dependences, i.e., temperature, composition, network structures, and electronic polarizabilities, since it carries information on a microscopic level about the ionic motions. If one consider that the typical jump distance between neighboring sites in the glassy network is "d" then $\langle R^2\rangle_{cr}/d^2$ represents an upper limit for the fraction of mobile ions that contribute to the conductivity at the crossover region. Thus, an analysis of the value of $\langle R^2(t)\rangle$ at the crossover region where the subdiffusive dynamics passes into the diffusive dynamics, provides valuable information about the fraction of ions that have moved from their equilibrium position. In most cases, it has been observed that the value of $\langle R^2\rangle_{cr}$ is independent of temperature in different ion conducting glasses and has been discussed in more detail elsewhere.[29] However, recently it has been shown that the value of $\langle R^2\rangle_{cr}$ depends strongly on the temperature in glasses with high electronic polarizabilities. This temperature dependence can be described by a power law:[24,30] $\langle R^2\rangle_{cr} \propto T^\beta$. Here, the exponent β is closely related to the electronic polarizabilities of the glass, α, which can be obtained by knowing the refractive index of the glass.

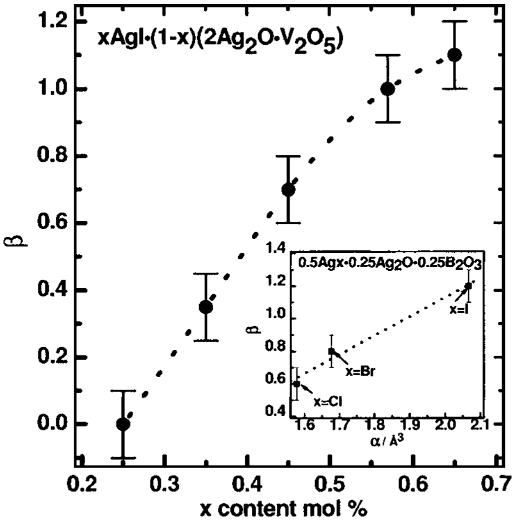

FIG. 3. Plot of the variation of the exponent β with different amount of AgI content in AgI$\cdot$ $(1-x)(2\mathrm{Ag_2O}\cdot\mathrm{V_2O_5})$ glasses. Inset shows the variation of the exponent β vs the average electronic polarizability per atom/ion, α, in 0.5Ag $X\cdot0.25\mathrm{Ag_2O}\cdot0.25\mathrm{B_2O_3}$ glasses. The dashed lines are drawn as guides to the eye.

In Fig. 3, we present the variation of the observed exponent β in $x\mathrm{AgI}\cdot(1-\mathrm{x})$ $(2\mathrm{Ag_2O}\cdot\mathrm{V_2O_5})$ glasses at different AgI content. Glasses with low silver iodide content, which possess the low electronic polarizability the exponent β is found to be zero. On the other hand, by increasing the AgI content level the electronic polarizability increases and correspondingly the exponent β increases to 1.1±0.1 at $x=0.65$. Furthermore, the frequency dependent conductivity measurements on $0.5\mathrm{Ag}X\cdot0.25\mathrm{Ag_2O}\cdot0.25\mathrm{B_2O_3}$ glasses with X=Cl, Br, and I confirm the above results. Here, the observed exponent β varies strongly with the type of the halide anion as shown in the inset in Fig. 3. The inset in Fig. 3, shows the exponent β versus the average electronic polarizability per atom or ion, α, of three different halide containing glasses. The values of α were calculated from the refractive indices of respective glasses using the Clausius-Mosotti equation.[31] Here, the glass containing iodide is found to show a higher exponent β than the chloride containing glass and correspondingly possesses higher electronic polarizability. Therefore, these results show clearly that the electronic polarizability plays an important role for the ion transport mechanism in glasses.

Figure 4 shows the temperature dependence of normalized quantity $\langle R^2\rangle_{cr}/(2.5\ \text{Å})^2$ in $x\mathrm{AgI}\cdot(1-x)(2\mathrm{Ag_2O}\cdot\mathrm{V_2O_5})$ glasses with different amount of AgI content. Here, we use 2.5 Å is an estimate for a typical jump distance between the neighboring positions in the glassy network. This estimate is in accordance with the jump distances found in the molecular dynamics simulation studies. If one assumes that there are no jumps over shorter distances, then the value of

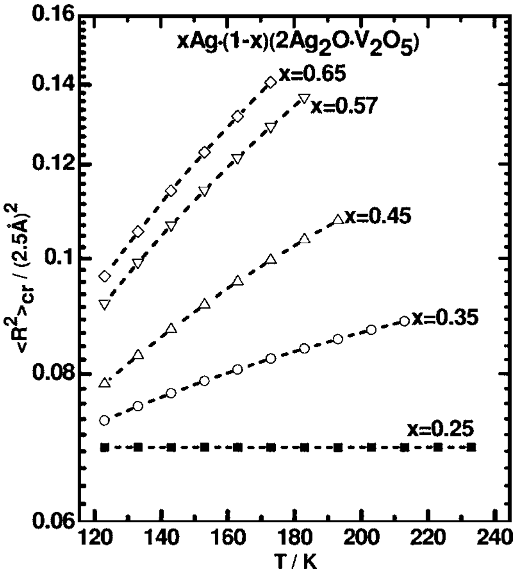

FIG. 4. The variation of the normalized quantity $\langle R^2\rangle_{cr}/(2.5\ \text{Å})^2$ vs temperature in $x\text{AgI}\cdot(1-x)(2\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ with $0.25 \leqslant x \leqslant 0.65$ glasses. Glass with low AgI content is characterized by a temperature-independent value of $\langle R^2\rangle_{cr}$. On the other hand, for glasses with higher AgI content the value of $\langle R^2\rangle_{cr} \propto T^{\beta}$ increases with increasing temperature T. The dashed lines are drawn as guides to the eye.

$\langle R^2\rangle_{cr}/(2.5\ \text{Å})^2$ represents an upper limit for the fraction of mobile ions that have left their original sites at the transition from subdiffusive to diffusive dynamics. As seen from the Fig. 4, the glass with low AgI content the fraction is small and independent of temperature. On the other hand, with increasing the AgI content level the fraction is of the order of few percent higher and it increases with increasing temperature. More apparently, investigations on $0.5\text{Ag}X\cdot 0.25\text{Ag}_2\text{O}\cdot 0.25\text{B}_2\text{O}_3$ glasses with X=Cl, Br, and I has been found to be similar temperature dependence.[24]

IV. DISCUSSION

Based on the above experimental results, we are now able to discuss the origin of non-Arrhenius behavior and its close relation to the observed exponent β in the optimized ion-conducting glasses. Taking into account structural considerations, the electronic polarizability has a strong influence on ion transport and dynamics in the highly polarizable network structures and has been discussed in the recent articles.[24,30] From the analysis of frequency dependent conductivity spectra of these glasses, we find that the value of $\langle R^2\rangle_{cr}$ is small and becomes a temperature dependent quantity. Additionally, it is interesting to note that glasses, which exhibit the non-Arrhenius behavior in the dc conductivity, are found to show a temperature dependent $\langle R^2\rangle_{cr}$.

In the case of $x\text{AgI}\cdot(1-x)(2\text{Ag}_2\text{O}\cdot\text{V}_2\text{O}_5)$ glasses, we find the value of $\langle R^2\rangle_{cr}$ is of the order of 0.5 Å at 123 K. In this context, it is interesting to consider the distances between the Ag^+ sites in the single crystal of $\text{Ag}_8\text{I}_4\text{V}_2\text{O}_7$ as determined by the x-ray diffraction studies.[32] In the present case, it has been found that Ag^+ exists in two different coordination environments with partially occupied fivefold and completely occupied sixfold coordinated sites. The distance between the octahedrally coordinated Ag^+ sites is 3.5 Å, while the distance between the fivefold coordinated Ag^+ sites is 2.85 Å. Within the framework of bond valance method, a long range transport of Ag^+ requires infinite pathways between the equilibrium positions and such pathways include the completely occupied and the partially occupied sites in the network structure. Furthermore, it has been suggested that the Ag^+ conduction takes place in the layers that extent perpendicular to the c direction via jump between these completely occupied and the partially occupied sites. Taking into account the most preferred conduction pathways and minimal valance mismatch leads to an average jump distance of 3.3 Å between the equilibrium sites.[19,32] Molecular dynamics simulation studies on alkali ion conducting silicate glasses yield typical jump distances of between 2 and 3 Å.[33,34] We note that in the case of our glasses, $\langle R^2\rangle_{cr}$ is much smaller than the square of such a typical jump distance. This extremely small value of $\langle R^2\rangle_{cr}$ suggests that only a small fraction of ions have moved away from their original sites when the subdiffusive dynamics passes over into the diffusive dynamics. That is most of the ions occupy their original sites are performing localized motions, which do not contribute to the subdiffusive behavior. Only the remaining, i.e., the most mobile ions ($<10\%$), which have moved from their original sites contribute to the subdiffusive behavior. Hence, following analogy of ionic crystals, we propose that ion transport in highly optimized ion conducting glasses is mainly governed by the low number of vacancy sites.

Thus, the main decisive result from this study with quantitative analysis is that only the fraction of cations in these glasses contributes to the measured conductivity at the crossover region. At low temperatures, the number of available empty sites is small, but it increases with increasing temperature, since many more sites become available. The number of available sites and its variation with temperature depends on the distribution of site energy of the disordered potential landscape. This distribution seems to be influenced strongly by the electronic polarizability of the given glass. Recent work done by Heuer and his co-workers on lithium silicate glasses using Molecular dynamics simulations suggests that the number of available sites is only few percent larger than the number of ions.[34] Experimentally, we observe that the value of $\langle R^2\rangle_{cr}$ is found to increase with increasing temperature in the optimized ion conducting glasses. This indicates that the temperature variation of mobile ion concentrations increases since the number of vacant sites for the mobile ions increases. It is well known that an important prerequisite for a high ionic conductivity is achieved by large number of empty sites. At higher temperatures, number of sites available for the ion hopping becomes constant, leading to a non-Arrhenius-type conductivity.

It is worthwhile to compare the observed non-Arrhenius behavior in optimized ion conducting glasses with other ion conducting glasses with respect to their electronic polarizability. There are ion-conducting glasses that possess high electronic polarizability but do not lead to deviation from the

Arrhenius law well below their glass transition temperatures. Pan and Ghosh carried out experimental investigations on lithium ion conducting bismuthate and lead bismuthate glasses.[35] Remarkably, these glasses possess high electronic polarizabilities of the network structures. Using the Almond and West formulism, they calculated the charge carrier concentrations and were found to be temperature dependent at low lithium oxide content level, i.e., the number density of mobile ions increases with increasing temperatures. With increasing lithium oxide content level, the temperature dependency of number density decreases and becomes independent of temperatures. Unfortunately, the glass transition temperature determines the upper limit of measurement of σ_{dc} for these glasses. Thus, generally one observes only linear relation in the Arrhenuis plot. However, within the measurement range, it is significant to note that the temperature dependent variations of number density of mobile ions in these glasses indicate that vacancy type transport should be responsible in analogous to the situation in ionic crystals.

V. CONCLUSIONS

In conclusion, optimized ion conducting glass that possesses high electronic polarizability are found to exhibit a non-Arrhenius behavior in the dc conductivity. The strength of the non-Arrhenius behavior depends strongly on the amount of silver halide content and on the type of the halide anion. More specifically, we find that in glasses with high electronic polarizabilities, the number of available sites for ions to hop seems to be smaller than the number of ions at sufficiently low temperatures and becomes strongly temperature dependent. From our results, we propose that vacancy type transport mechanism is responsible for the observed non-Arrhenius behavior in the optimized ion conducting glasses. Glasses exhibit the non-Arrhenius behavior in their dc conductivity is inherent to show temperature dependent $\langle R^2\rangle_{cr}$. A possible explanation for the temperature dependent $\langle R^2\rangle_{cr}$ is an increase of the number of vacant sites for the mobile ions with increasing temperature. At higher temperatures, the number of these vacancies becomes constant, leading to a non-Arrhenius-type dc conductivity.

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