Disordered conduction in single-crystalline dimer Mott compounds

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We study the temperature and frequency dependence of the dielectric constant and the ac conductivity in the dimer Mott insulator family $\beta'$-type Pd(dmit)$_2$ (where dmit denotes 1,3-dithiole–2-thione–4,5-dithiolate). We find that all compounds within this family have relaxorlike dielectric relaxation with a Curie-Weiss increase in the dielectric constant with decreasing temperature. An analysis of the dielectric data shows a clear relation between electronic correlation and the dipole-dipole interaction; also, geometrical frustration appears to weaken this interaction. Furthermore, the dc and ac conductivities are shown to be closely correlated and follow the same universal ac conductivity as disordered solids.

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I. INTRODUCTION

The electrical properties of glassy states have been extensively studied. Materials as diverse as amorphous semiconductors, ionic and electronic conducting polymers, ion conducting glasses, polycrystalline semiconductors, and doped single-crystal semiconductors at low temperatures have very common electrical properties.1 For instance, the ac conductivity $\sigma(\omega)$ of such materials can be scaled into a single curve independent of temperature and their dielectric constants $\epsilon$ have relaxations similar to dipolar fluids.1 The relaxations in question are not independent from the dc conductivity $\sigma(0)$, but are related by the Barton-Nakajima-Namikawa (BNN) relation

$$\sigma(0) = p\epsilon_0\Delta\epsilon\omega_m,$$

where $\Delta\epsilon = \epsilon(0) - \epsilon(\infty)$ is the dielectric loss strength, $p$ is a numerical constant close to 1, and $\omega_m$ is the dielectric loss peak angular frequency. The universality of those properties is such that we cannot distinguish the electrical response between electronic and ionic conductors.1

Molecular conductors are generally thought to form very clean single crystals. For insulating materials at ambient pressure, an application of pressure generally induces a transition toward a metallic state. The typical mean free path of the charge is in the neighborhood of thousands of angstroms at the lowest temperatures.2 As such, the electronic nature of the insulating states of those compounds is considered to be very homogeneous, as only a very low level of crystallographic defects results in such high values of the mean free path.

In molecular-based dimer Mott insulators, the conducting molecules are arranged such that molecule pairs with a large transfer integral can be defined as a unit. The band filling is in an effectively half-filled state. Geometrically frustrated arrangements of those units, e.g., a triangular lattice,3 can suppress the ground-state magnetic ordering. However, most cases are of the highly correlated and weak frustration type, with an antiferromagnetic (AFM) ground state expected from a Mott insulator.

Most of the theoretical works on dimer Mott insulators have been based on the half-filled single-band Hubbard model, namely, the dimer Mott model. Although this model neglects all charge degrees of freedom within the dimer unit, it correctly describes at least qualitatively the phase diagram of the dimer Mott systems under pressure. A few theoretical investigations have questioned the use of this model on various grounds, such as a very weak degree of dimerization4 or the absence of superconductivity.5 Our dielectric constant measurements in $\kappa$-(BEDT-TTF)$_2$$\tilde{\text{Cu}}$(CN)$_3$ [$(\kappa\text{-CN})_3$],6 where BEDT-TTF stands for Bis(ethylenedithio)tetra(thiatriafvalene), revealed that the temperature and frequency dependence of $\epsilon$ was similar to that of a relaxor ferroelectric compound. This result, combined with the 6-K anomaly found in thermal expansion,7 specific heat,8 and thermal conductivity9 data, has encouraged10 and inspired subsequent theoretical work focusing on the charge degree of freedom within the dimer unit. It has been previously noted that similar relaxor behavior for the dielectric constant was also present in a quasi-one-dimensional dimer Mott insulator $\beta'$-(BEDT-TTF)$_2$ICl$_2$; furthermore, this effect was probably common to the whole BEDT-TTF-based dimer Mott insulators.6

In this paper we report on the frequency and temperature dependence of $\epsilon$ within the dimer Mott insulator $\beta'$-Pd(dmit)$_2$ (where dmit denotes 1,3-dithiole–2-thione–4,5-dithiolate) salts. Compared to BEDT-TTF molecules, the Pd(dmit)$_2$ molecule has a similar planar π-conjugated structure with two notable differences: The central carbon-carbon double bond is replaced by a Pd metal ion, and there are no terminal ethylene groups.13 The absence of terminal ethylene groups is important within this study, as they are a well-known source of disorder within the BEDT-TTF compounds that can affect the electronic properties.14 Similar to the $\kappa$-type BEDT-TTF salts, the $\beta'$-type of Pd(dmit)$_2$ salts are generally described in terms of dimer units of Pd(dmit)$_2$ that are arranged in a quasi-triangular lattice;15 however, the dimer units are stacked in a face-to-face configuration with a degree of electronic dimerization greater than that of the $\kappa$-BEDT-TTF salts.15 At ambient pressure, three different ground states can be found in $\beta'$-(cation)[Pd(dmit)$_2$]$_2$: cation denotes Me$_3$P, Me$_4$As, Me$_4$Sb, EtMe$_3$As, Et$_2$Me$_2$As, and Et$_3$Me$_2$P for the AFM insulators (Et denotes C$_2$H$_5$- and Me denotes CH$_3$-); cation denotes EtMe$_3$Sb for the spin liquid (SL) candidate; and cation denotes Et$_2$Me$_2$Sb for the diamagnetic charge-ordered (CO) insulator.15,16 A detailed study of the CO state is beyond the scope of the present paper.

We find that all $\beta'$-Pd(dmit)$_2$ salts have a relaxorlike dielectric constant with a different temperature scale unique...
to each cation. The electronic correlation and the degree of geometrical frustration are found to affect the dipole-dipole interactions, while the dipole moment seems to be independent of those two parameters. We emphasize in this paper that the conductivity and dielectric constant of dimer Mott insulators follow the same universal scaling and relationship as a disordered solid, while the crystal structure is at the clean limit.

II. EXPERIMENT

Single crystals of $\beta'-(\text{cation})[\text{Pd(dmit)}_2]^2$ were prepared by the air oxidation of $(\text{cation})_2\text{Pd(dmit)}_2$ in an acetone solution containing acetic acid at 5$^\circ$C–10$^\circ$C. Dielectric constant and ac conductivity measurements were conducted out with an autobalancing bridge (Agilent E4980A impedance analyzer). The samples were mounted in a parallel-plate setup and were cooled to a cryogenic temperature within a variable temperature insert placed into a liquid helium cryostat. The measured directions of all the samples presented here were limited to the out-of-plane direction of the crystal, the $c$ axis, as the parallel-plate setup required thin samples with large surfaces that are produced by crystal growth only along the out-of-plane direction. Gold paste or carbon paste was applied on opposite sides of the crystal surface as the parallel-plate electrodes. Both conducting pastes gave similar results. Furthermore, to ensure consistency of our results, at least four samples of each cation were measured from different crystal batch growths. Similar to the $\kappa-(\text{CN})_3$ case, we note that the values of $\epsilon_r'$ are independent of dc bias voltage up to the dielectric breakdown levels, which is in contrast to the relaxors. We further note the absence of any detectable hysteresis in $\epsilon_r'$, which excludes the extrinsic and internal barrier layer as the origin of the dielectric response. The bandwidth $W$ and the intradimer transfer integral $t_A$ values were calculated with a dimer Mott tight-binding model based on the extended Hückel method. Then $t_A/W$ represents the electron correlation, as the on-site Coulomb repulsion $U$ is approximately proportional to $t_A$.

III. RESULTS AND DISCUSSION

Figure 1 shows the typical behavior of the real part of $\epsilon_r$ measured in various $\beta'-$Pd(dmit)$_2$ compounds. The general trend is similar and follows the same response seen in relaxor ferroelectrics with $\kappa-(\text{CN})_3$, with strong frequency dispersion and an increase of $\epsilon_r'$ with decreasing temperature. This follows a Curie-Weiss law (Fig. 3, bottom inset), defined as

$$\Delta \epsilon(T) = \frac{C}{T - T_{\text{Curie}}},$$

where $C$ is the Curie constant and $T_{\text{Curie}}$ is the Curie temperature. Figure 2 (top inset) shows the typical behavior of the frequency dependence of $\epsilon_r'$ relaxation in $\beta'-$Pd(dmit)$_2$. This relaxation is best fitted by a Fourier-transformed stretched exponential function, the Kohlrausch-Williams-Watts (KWW) function typically used in glassy states. The dielectric function is then defined as

$$\epsilon(\omega) = \epsilon_{\infty} + (\epsilon_s - \epsilon_{\infty}) \int_0^{+\infty} \frac{d e^{-(t/\tau)^\beta}}{dt} e^{-i\omega t} dt,$$

where $\tau$ is the relaxation time and $\beta$ is the stretching exponent. Equation (3) reduces to a simple Debye relaxation when $\beta = 1$. If the entire relaxation is not within our frequency window of 20 Hz to 1 MHz, the KWW model is overparametrized and we cannot estimate the parameters of this model reliably. The temperature range where all the relaxation occurs within our frequency window varies between compounds. In the case of EtMe$_3$Sb[Pd(dmit)$_2$], for instance, this temperature range is from roughly 30 to 40 K. Reliable estimates of the stretching

FIG. 1. Frequency and temperature dependence of the real part of the relative dielectric constant of $(\text{cation})[\text{Pd(dmit)}_2]^2$, where the frequency range and the cation are specified within the graph. The inset shows the ac conductivity of the respective compounds.
exponent value $\beta$ are found to never exceed the value of 3/5 and to decrease with decreasing temperature in all $\beta'$-Pd(dmit)$_2$.

The mean relaxation time $\langle \tau \rangle$ can be deduced from the KWW fits of the frequency dependence or by estimating the midpoint of the relaxation when $\epsilon'/(\langle \tau \rangle) = \epsilon'(+\infty)/2+\delta\epsilon(T)/2$ is true. Although both methods yield similar results, the midpoint of the relaxation method was used as the temperature range where we can estimate $\langle \tau \rangle$ reliably is greater than that from the KWW method. Within this temperature range, we find that $\langle \tau \rangle$ follows a simple Arrhenius temperature dependence with an activation gap $E_A$ similar to that estimated from the dc conductivity. The BNN relation is obeyed in all $\beta'$-Pd(dmit)$_2$ salts, as shown, for instance, in the SL sample in Fig. 2 (bottom inset). The implication of the BNN relation is that the dc conductivity and the excess polarization share the same physical origin. Then $\Delta\epsilon$ may arise entirely from mobile charges as from a dipolar polarization perspective and the hopping of a charge between neighboring sites can be seen as the rotation of a permanent dipole. However, this is unlikely as the estimated hopping distance or the mean displacement is less than 1 Å, while the minimum distance between the sites within the dimer unit is longer than 3 Å. Moreover, $\Delta\epsilon$ follows a Curie-Weiss temperature dependence, while models based purely on hopping conduction yield a simple $1/T$ function. The frequency dependence of the dielectric response is also of the dipolar-dominated response type and the ferroelectricity has been recently reported in $\kappa$-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl (Ref. 24) and $\beta'$-(BEDT-TTF)$_2$ICl$_2$. As such, we still believe that bulk dielectric dipoles are the main contributors to $\Delta\epsilon$.

Disorder is found to significantly affect the charge mobility in molecularly doped polymers, in which both charge carriers and permanent dipoles are present. As stated previously, charge-transfer salt single crystals are of such high quality that the disorder cannot have a crystallographic nature. However, Fig. 2 shows that the ac conductivity can be scaled into a master curve whose shape is similar between cations and those found in ion conducting glass, conducting polymers, and other highly disordered compounds. The flat region of this Taylor-Isard scaling consist of the high-temperature frequency-independent part of the ac conductivity, while the curved region consist of the frequency-dependent part of the ac conductivity. Its significance lies in the shape of the master curve being independent of the details of the system even though it approximates $\Delta\epsilon$ as a simple $1/T$ Curie dependence. This universal behavior of the ac conductivity to the details of the disorder occurs when the local mobility covers many order of magnitude and approaches the extreme-disorder limit. The hopping of charge carriers in a random energy landscape, as in the symmetric random-barrier model, describes well all the major features of the conductivity. It is then possible that this random energy landscape originates from the randomly oriented polar nanoregions, which give rise to the relaxorlike dielectric constant. Percolation then explains the common $E_A$ between $\sigma(0)$ and $\langle \tau \rangle$ of the polar nanoregions. The largest energy barriers between the percolation clusters act as bottlenecks for $\sigma(0)$ (Ref. 1) and delimit the polar nanoregions.

Since $\Delta\epsilon$ follows a Curie-Weiss temperature dependence, $T_{Curie}$ should reflect the dipole-dipole interaction strength. Plots of $T_{Curie}$ as a function of the electronic on-site correlation are shown in Fig. 3 (top). A linear increase of the Curie temperature with increasing electronic correlation is clearly visible for $\beta'$-Pd(dmit)$_2$ compounds with low geometrical frustration. This increase of the dipole-dipole interaction with increasing electronic correlation is to be expected if the dipole nature is electronic. However, above some critical value, $T_{Curie}$ appear to decrease with further increases of $\tau_A/U$. We attribute this decrease of $T_{Curie}$ to geometrical frustration as the increase of $\tau_A/U$ is small in comparison to the increase of the degree of frustration $t/t'$. In addition to this, the decrease of $T_{Curie}$ coincides with values of $t/t'$ in proximity to 1, where a spin-liquid state is thought to exist (see Fig. 3, top inset). This relation with $t/t'$ implies that spin interactions are assisting the electronic ordering as predicted in the paired-electron crystal model. A comparison of the Néel temperature $T_N$ and $T_{Curie}$ shows the interesting case in which an AFM ordering temperature is greater than the dipole ordering in Me$_4$P ($T_N \approx 40$ K) and Me$_4$As ($T_N \approx 35$ K). Previous reports of $T_{Curie}$ in $\kappa$-BEDT-TTF salts and $\beta'$-(BEDT-TTF)$_2$ICl$_2$ (Ref. 25) were above or equal to $T_N$. Those results gave the impression that the charge freezing was essential for stabilizing the AFM state. Our result seems to contradict this hypothesis at first, but we should note that the AFM transition in Me$_4$P[Pd(dmit)$_2$] is unusually weak.

As in Ref. 6, we converted the Curie constant estimates into the charge disproportionation values shown in Fig. 3 (bottom). Illustrations of what the charge disproportionation pattern may look like can be found in Ref. 25, as $\beta'$-Pd(dmit)$_2$ salts have a similar arrangement of the conducting molecules to $\beta'$-(BEDT-TTF)$_2$ICl$_2$. Surprisingly, the estimated charge disproportionation appears to have only small changes within the $\beta'$-Pd(dmit)$_2$ salts, implying that the dipole moments are independent of $U/W$ and spin fluctuations. We note,
FIG. 3. (Color online) The top is a plot of the Curie temperature from the dielectric constant as a function of on-site correlation. The top inset shows the relation between the electronic correlation and the frustration parameter \( t'/t \) in the \( \beta'\)-Pd(dmit)\(_2\) salts. The bottom is an estimate of the charge disproportionation as a function of on-site correlation from the Curie constant, where 0 indicates equal charge occupancy of the two molecules of a dimer structure. The lower (blue) dashed line is related to the minimum dipole moment value for a three-dimensional state converted to charge disproportionation. The bottom inset shows a plot of the inverse dielectric constant in EtMe\(_3\)Sb[\( \beta'\)-Pd(dmit)\(_2\)] used to estimate the Curie parameters (red dashed straight line).

IV. SUMMARY

In conclusion, our dielectric and conductivity data show a direct link between dc and ac conductivity through the BNN relation and confirm that both are electronic in origin. This electronic origin of the excess polarization is further confirmed with the correlation between the Curie temperature dependence and the electronic properties of \( \beta'\)-Pd(dmit)\(_2\) salts. In this case, the dipole-dipole interaction is found to depend on both the electronic correlation and the spin interaction, while the dipole moment is found to be independent of interdimer transfers integrals. Most importantly, the BNN relation, the KWW frequency dependence of the relaxation, and the ac conductivity scaling into a single master curve all confirm that the conductivity in dimer Mott compounds is electronically disordered, but in a crystallographically clean system. One of the implications of this result is that the metal-insulator transition occurs between a clean correlated metal and an electronically correlated and disordered insulator. This insight into the electronic nature of dimer Mott compounds should help us understand some of the peculiar properties of dimer Mott insulators, such as the increase in conductivity with additional crystallographic disorder in the insulating state, whereas these same types of defects decrease the conductivity in the metallic state. The nature of disorder at the electronic level within dimer Mott insulators has been reported previously; here we state that this behavior is intrinsic to all dimer Mott systems.

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