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Microwave conductivity and dielectric constant of tetramethyltetrathiafulvalene salts $[(\mathrm{TMTTF})_2X,\ X = \mathrm{SCN},\ \mathrm{ReO_4},\ \mathrm{SbF_6}]$

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Microwave conductivity and dielectric constant at 6.5 GHz are reported for three tetramethyltetrathiafulvalene salts: $(\mathrm{TMTTF})_2X$, $X = \mathrm{SCN}$, $\mathrm{ReO_4}$, and $\mathrm{SbF_6}$. A divergence of the dielectric constant ϵ is observed at the *structureless* transition temperature for $\mathrm{SbF_6}$ (160 K) and $\mathrm{ReO_4}$ (220 K), contrasting with a stepwise change at the anion ordering transition of the latter salt (160 K). The dielectric constant of $(\mathrm{TMTTF})_2\mathrm{SCN}$ shows a broad maximum above the anion ordering transition and a sharp decrease at T_c. Moreover the microwave conductivity exceeds dc conductivity above the *structureless* transition in $(\mathrm{TMTTF})_2\mathrm{SbF_6}$. Also, conductivity becomes frequency dependent below the anion ordering of $(\mathrm{TMTTF})_2\mathrm{SCN}$. These data support the pseudogap picture describing the structureless transition, a complete gap for the anion ordering transition, and the absence of charge-density waves in these materials.

Study of radical cation salts $(\mathrm{TMT}C\mathrm{F})_2X$ ($C = \mathrm{S}$, Se) have introduced a wealth of new physics in the last decade. Apart from first organic superconductor,[1] many interesting phases such as charge- or spin-density waves stabilize at low temperatures in these low-dimensional salts. Although they show the same structural arrangement, with *zig-zag* stacking of the organic molecules surrounding the anions,[2] the physical properties of the TMTTF and tetramethyltetraselenafulvalene (TMTSF) salts are quite different. In particular the chains in the sulfur compounds are more dimerized.[3] Narrower bandwidths and the presence of an electron-electron interaction lead to greater electronic localization and a lower electrical conductivity than in the TMTSF salts.[4] For the TMTTF compounds a simple band model is no longer sufficient to describe the electronic properties, and electron-electron and electron-phonon correlations have to be introduced, usually via an extended Hubbard model.[5] In this context the electronic and magnetic properties of TMTTF salts are generally described using a large $\mathcal{U}$ approximation (where $\mathcal{U}$ is the intrasite electronic correlation)[6] and introducing umklapp scattering.[7] This term accounts for the $4k_F$ component (where k_F is the Fermi vector) of potentials external to the organic chain such as those of the surrounding chains or of the anion lattice.

$(\mathrm{TMTTF})_2X$ salts have been synthesized with a wide variety of anions, which can be classified into different groups according to their symmetry: centrosymmetrical ones, such as $\mathrm{SbF_6}$ or noncentrosymmetrical ones, which either have a permanent dipole moment like SCN, or do not, like $\mathrm{ReO_4}$. The anions usually occupy a center of symmetry of the structure[2] and, in the case of noncentrosymmetrical anions, this can only be consistent with a temporal disorder of the anions at room temperature, allowing an ordering and a superstructure at low temperature.[8]

Measurement of the T-dependent structure,[9] conductivity σ,[4,9,10] thermopower S,[10,11] and magnetic susceptibility χ (Refs. 10, 12, and 13) reveal the presence of one or two transitions in each of these three salts for $T > 100$ K. These transitions have been attributed to anion ordering (for noncentrosymmetric anions),[14] plus large $\mathcal{U}$,[7,11] and electron localization.[10]

We report here the results of T-dependent 6.5-GHz microwave conductivity measurement on $(\mathrm{TMTTF})_2X$ salts with centrosymmetric anions ($\mathrm{SbF_6}$), noncentrosymmetric anions with permanent dipole moment (SCN), and noncentrosymmetric anions without permanent dipoles ($\mathrm{ReO_4}$). The results clearly demonstrate the absence of a Peierls (CDW) transition in these materials, and the presence of two different types of transition, one leading to a real gap associated with anion ordering, and the second associated with pseudogap picture and electron localization.

Samples were grown with the classical electrochemical method at a constant current of a few μA as described previously.[9] Microwave measurements were performed using a cavity perturbation technique[15] which has been a successful tool in earlier studies of metal-insulator transitions, Peierls gaps, CDW and spin-density waves (SDW's) and their ground-state excitations such as bipolarons, and the effects of disorder in low-dimensional systems.[16–20] A $\mathrm{TM_{010}}$ cavity resonating at 6.5 GHz was used. Changes in resonance frequency and Q of the cavity were measured at each temperature for the sample (placed inside a quartz tube) in and out of the cavity, and analyzed using *perturbation analysis*.[15] When skin depth remained larger than the sample thickness in the whole temperature range, both the microwave conductivity σ and the dielectric constant ϵ were calculated according to *depolarization regime* analysis. For thicker samples the skin depth might become progressively comparable to sample thickness as T increases toward room temperature and deplorization regime analysis gives accurate account of σ and ϵ only at low temperature.

Figure 1 shows the temperature dependence of the dielectric constant for the three compounds. The thickness of the SCN and $\mathrm{ReO_4}$ samples does not allow a high accuracy of the measurements for these two salts in the vicinity of room temperature. $(\mathrm{TMTTF})_2\mathrm{ReO_4}$ at 220 K

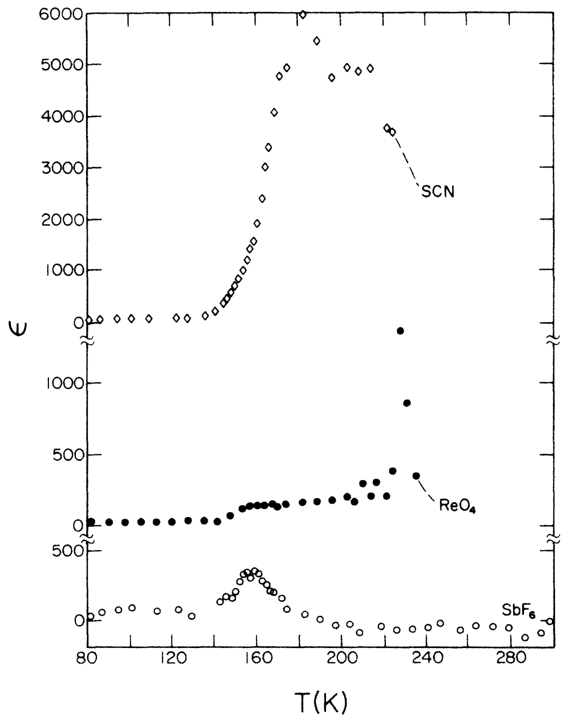

FIG. 1. Temperature dependence of dielectric constant for the three salts $(TMTTF)_2X$. Note the change of the Y-axis scale between the curves.

and $(TMTTF)_2SbF_6$ show a divergence of ϵ around the temperature of the *structureless* transition. At 160 K the dielectric constant of the ReO_4 salt decreases stepwise and remains constant at lower temperatures. In the case of $(TMTTF)_2SCN$, ϵ increases when the temperature is decreased from room temperature and reaches a broad maximum around 180 K. Below the maximum a sharp decrease of ϵ is observed at the temperature of the anion ordering.

Figure 2 is a plot of both the dc (Refs. 4, 9, and 10) and microwave conductivity for the three salts vs $1/T$. The data have been normalized at room temperature to ensure an easy comparison. The general behavior previously observed on dc measurements is well reproduced on microwave experiments. In particular the two transitions of $(TMTTF)_2ReO_4$ are clearly visible on the high-frequency data. For $(TMTTF)_2SbF_6$ and SCN microwave conductivity deviates from dc at low temperatures. However, it is noteworthy that a smooth and continuous deviation is observed in the case of SbF_6 while the deviation appears more suddenly at the transition temperature of $(TMTTF)_2SCN$. Both the microwave and dc conductivity of $(TMTTF)_2SbF_6$ are reported in Fig. 3 as a function of the temperature. This figure points out the divergence of the two conductivities as the temperature approaches the structureless transition from above.

Depending upon the symmetry of the anion and the superstructure, structural distortions occur and are accompanied by instabilities of the electronic and/or magnetic behavior.[21] Centrosymmetrical anions are not expected to display such ordering. However, displacement of the anions away from the symmetry center could have similar effects on the conduction chains.[14,22]

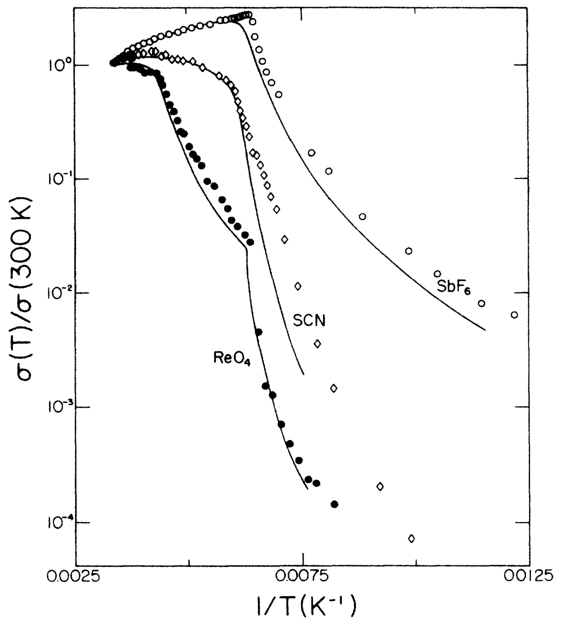

FIG. 2. Normalized microwave conductivity vs $1/T$ for the three salts $(TMTTF)_2X$. The lines are dc conductivity taken from the references (Refs. 4, 7, and 8).

The ordering of the ReO_4 anions occurs at 160 K and is clearly evidenced by a sudden decrease of both the electrical conductivity and the magnetic susceptibility, and a sharp increase of the thermopower,[10] corresponding to the

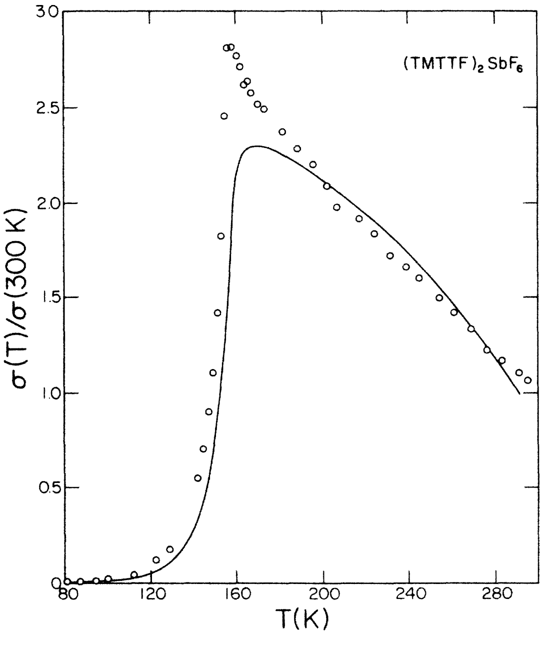

FIG. 3. Temperature dependence of microwave conductivity for $(TMTTF)_2SbF_6$. The line is dc conductivity (Ref. 7).

opening of a gap in the electronic and magnetic excitations. X-ray studies[22] have shown the condensation of a $(\frac{1}{2},\frac{1}{2},\frac{1}{2})=2k_F$ superstructure below 160 K. On the contrary, the SCN anions order with a $(0,\frac{1}{2},\frac{1}{2})=4k_F$ superstructure[12] at $T_c=160$ K. The resulting transition is observed in conductivity and thermopower measurements, but the magnetic susceptibility remains unchanged below T_c.[23]

In the case of $(\mathrm{TMTTF})_2\mathrm{SbF}_6$, a metal-insulator transition is visible at 154 K on electrical conductivity[9] and thermopower,[10] but no change is observed on the magnetic susceptibility.[13] Moreover, x-ray studies have failed to reveal any superstructure, neither at $2k_F$ nor at $4k_F$, down to 15 K.[9] The same kind of transition, so-called structureless transition, has been observed in $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ at 220 K.[10] Among other hypotheses, small displacements of the anions respective to the organic chains leading to the opening of a gap in the charge excitation spectrum have been postulated to account for this transition.[10] However, its origin remains still unclear.

In low-dimensional systems, metal-insulator transitions are expected to be surrounded by a wide range of fluctuative behavior. In this intermediate regime, in the presence of finite coherence length, such systems can be well characterized by the study of their dielectric constant, in vivid distinction from metallic (small and negative ϵ) and insulating (small and positive ϵ) phases.[16,19,24] The divergence of ϵ in $(\mathrm{TMTTF})_2\mathrm{SbF}_6$ and ReO_4 at the structureless transition (154 K for SbF_6 and 220 K for ReO_4) could be accounted for by contributions of critical fluctuations toward the formation of a $4k_F$ partial gap at the Fermi surface as the temperature reaches T_c from above, and fluctuations of the order parameter below T_c.[25] Considering a plasma frequency $\omega_p \simeq 9000\ \mathrm{cm}^{-1}$ (Ref. 26) and a conductivity gap $\omega_g \simeq 530\ \mathrm{cm}^{-1}$ for the insulating phase of $(\mathrm{TMTTF})_2\mathrm{SbF}_6$, dielectric constant could be estimated as $\epsilon = 1+0.65\omega_p^2\omega_g^2 \simeq 72$,[27] in good agreement with the measured value $\epsilon \simeq 50$. If we account for the divergence of ϵ as the temperature reaches T_c from below, the ratio $\epsilon_{(T_c)}/\epsilon_{(T\rightarrow 0)} \simeq 4$ indicates that 44% of the zero temperature gap persists at T_c. This suggests the presence of a pseudogap in this system near T_c. Moreover, the frequency dependence of the conductivity below the transition is inconsistent with the presence of a normal semiconductor gap in this system. In the case of ReO_4, the ratio $\epsilon_{(T_c=220\,\mathrm{K})}/\epsilon_{(T>160\,\mathrm{K})} \simeq 6$ leads to the persistence of 40% of the full gap at T_c. In the insulating phase between the two transitions ($160\ \mathrm{K} < T < 220\ \mathrm{K}$), the gap may be estimated as $E_g \simeq 1900$ K,[10] leading to $\epsilon_{\mathrm{calc}} \simeq 18$, far from the measured value, $\epsilon_{\mathrm{meas}} \simeq 220$. However, the occurrence of the second-phase transition at 160 K prevents an accurate evaluation of the zero-temperature gap. The extent of divergence of ϵ from its low-temperature value is consistent with the variation of the gap as expected from a Bardeen-Cooper-Schrieffer- (BCS-) like temperature dependence; divergence of ϵ as T reaches T_c from above may be due to critical fluctuations. More pronounced effects have been observed in SbF_6 than in ReO_4. Not only is the ϵ divergence extended for a larger temperature interval above T_c, but also a deviation of the microwave conductivity from dc is observed. However, it should be noted that the weak temperature dependence of the conductivity in the "metallic" phase of $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ makes the deviation between microwave and dc conductivity harder to observe.

The ordering of the anions in $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ at 160 K opens a real gap at the Fermi surface as previously observed both on dc conductivity and magnetic susceptibility measurements.[10] The activation energy of the conductivity is doubled, again leading to a calculated dielectric constant of the order of 6 (3 times smaller than ϵ above the 160-K transition), while the measured dielectric constant is of the order of 50 (4–5 times smaller than ϵ measured above the 160-K transition). The stepwise drop of ϵ is consistent with the opening of a gap at the Fermi surface. It should be noted that the estimation of the gap from the susceptibility measurements leads to a smaller value, and therefore to a better agreement between measured and calculated dielectric constants.

The behavior of the dielectric constant $(\mathrm{TMTTF})_2\mathrm{SCN}$ is more complicated. Dielectric constant above $T_c=160$ K could be attributed to the presence of orientational disorder of the SCN anions, whose permanent dipole moments influence the electron motions in the TMTTF chains. Independent SCN^- dipole motion is insufficient to account for the maximum of dielectric constant. The behavior of the dielectric constant may be related then to a cooperative ordering of these SCN dipoles.

Whatever the origin of the structureless transition in $(\mathrm{TMTTF})_2\mathrm{ReO}_4$ at 220 K and $(\mathrm{TMTTF})_2\mathrm{SbF}_6$ at 160 K, this study evidences the different nature of this transition compared to an anion-ordering transition. The divergence of the dielectric constant clearly shows the occurrence of a real phase transition at the electronic anomaly. Moreover, the observed behavior is consistent with the pseudogap picture usually used to interpret this transition. Finally, the existence of wide range of fluctuative regime around the transition is demonstrated. In the case of $(\mathrm{TMTTF})_2\mathrm{SCN}$ the behavior at the electronic anomaly is complicated by the simultaneous occurrence of the anion ordering. Nevertheless, the frequency dependence of the conductivity below the transition is in agreement with a pseudogap description rather than a complete three-dimensional semiconducting gap.

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