Giant Conductivity Resonance in the Spin-Density-Wave State of an Organic Conductor

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Frequency-dependent conductivity measurements between 4.5 and 35 GHz are reported in the spin-density-wave (SDW) state of the linear-chain organic conductor $(TMTSF)_2PF_6$, where TMTSF denotes tetramethyltetraselenafulvalenium. A giant conductivity resonance, implying long relaxation times, is observed at frequencies well below the single-particle gap. The frequency dependence is strongly depressed by small amounts of impurities. Either collective spin-density-wave conduction or excitations of the spin-density-wave mode are responsible for the observed frequency-dependent response.

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A considerable amount of work has been devoted recently to the dynamics of various collective modes which occur as the consequence of electron-phonon and electron-electron interactions in few-dimensional materials. Among four possible ground states,[1] the existence of singlet-superconductivity, charge-density-wave (CDW), and spin-density-wave (SDW) modes are well confirmed in various materials. Further, the dynamics of the single-superconductivity and CDW[2] condensates is well understood. An outstanding question to date has been the nature of the current-carrying state in the SDW mode.

The organic linear-chain conductor $(TMTSF)_2PF_6$, where TMTSF denotes tetramethyltetraselenafulvalenium, is the prototype of materials where a SDW ground state is well confirmed by various magnetic measurements.[3] Early experiments[4] on the frequency-(ω) and electric-field- (E) dependent response suggested that the dynamics and unusual spin-resurrection phenomena were also related to the SDW ground state. Subsequent experiments[5,6] verified that in the SDW state the conductivity $\sigma(\omega)$ is frequency dependent, but $\sigma(E)$ was found to be different from that observed in CDW systems. Also, attempts to induce nonlinear dc conduction by microwave fields and spin-resurrection experiments using dc electric fields were not successful.[7] The interpretation of results has been complicated by experimental problems due to contacts and thermal heating effects, and, consequently, a clear identification of the mechanism of transport in the SDW state has not emerged.

In this paper we report the results of experiments on the frequency-dependent response, measured in the SDW state of $(TMTSF)_2PF_6$ with contactless cavity-perturbation techniques up to 35 GHz. We find a dramatically temperature-dependent giant conductivity resonance which is strongly depressed by small amounts of impurities. It is difficult to understand our observation in terms of the dynamical response of a pinned collective SDW mode, and we suggest that excitations of the mode with extremely large mean free paths are responsible for the strikingly anomalous transport properties reported here.

The experiments were performed on high-purity $(TMTSF)_2PF_6$ and on alloys[8] with $(TMDTDSF)_2PF_6$, where TMDTDSF stands for tetramethyldithiadiselenafulvalenium, with 1% and 3% concentration. Linear and nonlinear dc conductivity measurements were performed with Ag-paint contacts by a four-probe technique.

The frequency-dependent conductivity measurements were performed with contactless cavity-perturbation techniques with cavities at 4.5, 9, 17, and 35 GHz, resonant in the TM_{010} (4.5 and 17 GHz) or TE_{011} (9 and 35 GHz) modes. In all cases, the sample was placed in zero microwave magnetic field and with the conducting axis parallel to the electric field. Approximately fifty needle-shaped samples were measured with different lengths and cross sections (typical diameters ~ 50–$100\ \mu m$ and lengths 2–8 mm), in order to ensure that size-dependent effects do not play a role in the experimental results and in the analysis. From the sizes of the samples and the measured conductivities, it was concluded that at temperatures below approximately 100 K, the surface-impedance limit[9] is appropriate. The results reported have been verified to be independent of microwave power and hence represent the small-signal linear response of the

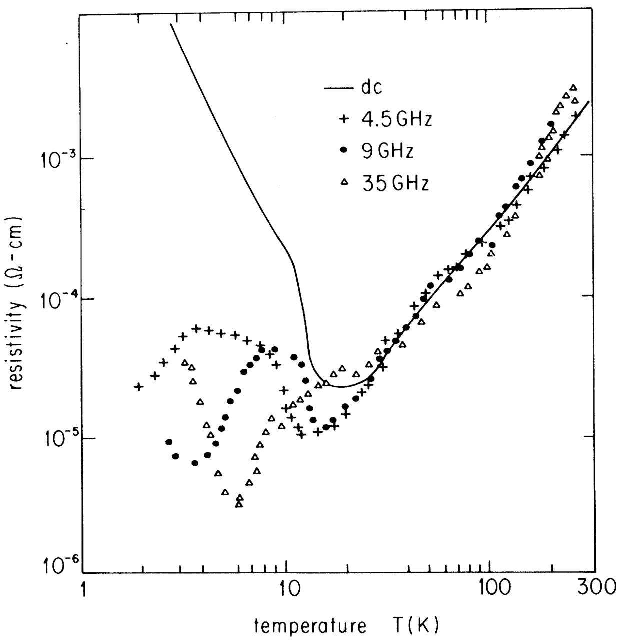

FIG. 1. Resistivity vs temperature for $(TMTSF)_2PF_6$ measured at dc and microwave frequencies.

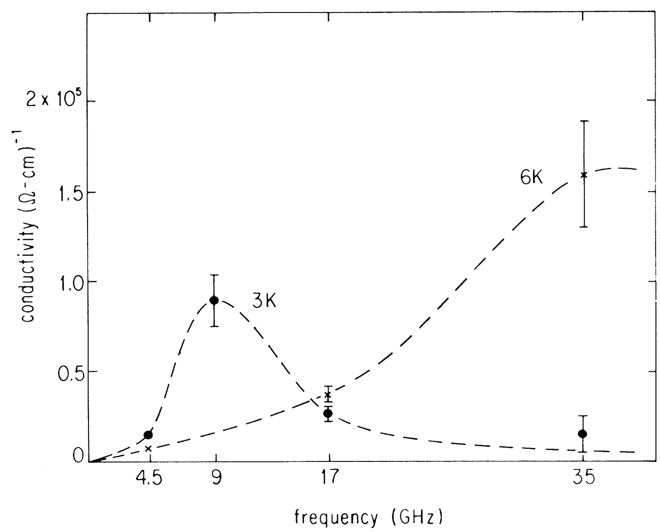

FIG. 2. Conductivity vs frequency for $(TMTSF)_2PF_6$ at 3 and 6 K. The dashed lines are guides to the eye.

material.

In Fig. 1 the dc and the high-frequency resistivities are displayed as a function of temperature. All data were normalized to the resistivities measured between 30 and 100 K. The resistivity is independent of frequency in this range, and the temperature dependence agrees with the results of earlier measurements. We also note that the breaks observed in the dc measurements are not seen in the high-frequency measurements.

In the so-called precursor region of temperatures between 30 K and the transition temperature at 11.5 K, we find that the conductivity is still relatively independent of frequency. Thus we see no evidence for a zero-frequency mode inferred[10] from far-infrared experiments with a predicted half-width of approximately 5 GHz. Our experiments show that if such a mode exists, its half-width should be considerably greater than 35 GHz, the maximum frequency of the present experiments.

In contrast to the behavior above T_c, a considerable frequency dependence develops in the SDW state below 11.5 K. Earlier experiments at 9 GHz by Walsh *et al.*[4] and by Janossy, Hardiman, and Grüner[7] indicated that the conductivity remains high in the SDW state, and considering their rather large experimental uncertainties, our results are in agreement with experiments at this frequency. However, the present considerably more accurate experiments at several frequencies reveal a rich structure in the temperature dependence as the temperature is lowered. A remarkable feature of our data is the broad minimum of $\rho(\omega)$ observed at each frequency with the minimum moving to lower temperatures and also to higher resistivity values with decreasing frequency. The ω-dependent conductivity, taken from the data points of Fig. 1, is shown in Fig. 2 at two different temperatures (the dashed lines are guides to the eye). A sharp resonance is clearly observed at the lower temperature, which broadens and whose center position increases with frequency as the temperature is increased. It is important to note that the scale of conductivities associated with this resonance is orders of magnitudes larger than the dc conductivity at that temperature and comparable to the high conductivity in the metallic state.

The large high-frequency conductivity is strongly depressed by small amounts of impurities. In Fig. 3, the conductivity measured at 9 GHz is shown for the pure material and for the alloys as functions of temperature. Similar depression was found at 4.5 and 35 GHz. The dc conductivity is hardly affected except for a slight increase in T_c with impurities, which we attribute to disorder.[8]

We have also studied in detail the nonlinear conductivity in both the pure materials and alloys. Nonlinear conduction,[5] with no threshold field, was found in all cases, but no correlation with the length of the specimens for given voltage (as would be expected if the electric field E is the relevant parameter) or with impurity concentration was found. Instead, the magnitude of the nonlinear conduction was found to be correlated with the resistance jumps which developed during cooling. We conclude, therefore, that the nonlinear conductivity (up to fields of 10 V/cm) is a spurious phenomenon, and is not an intrinsic property of

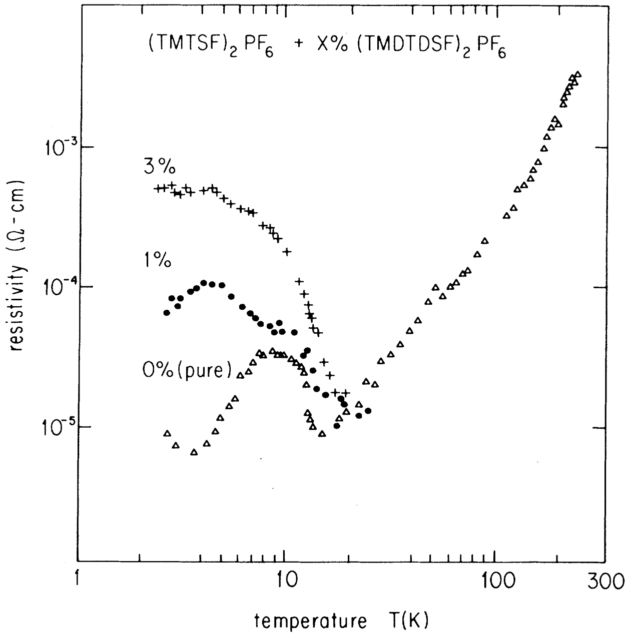

FIG. 3. Resistivity at 9 GHz vs temperature of pure $(TMTSF)_2PF_6$ and of alloys with $(TMDTDSF)_2PF_6$. For clarity the data on the alloys above 30 K is not shown.

the SDW ground state.

Our results are in agreement with experiments[6] performed in the radio-frequency spectral range, where $\sigma(\omega)$ increases with frequency at frequencies below approximately 1 GHz. On the high-frequency side of our frequency window, our results are consistent with far-infrared measurements[11] on $(TMTSF)_2PF_6$. Below T_c, far-IR measurements at 6 K yield a low σ at approximately 300 GHz comparable to σ_{dc}. The same has also been observed[12] for the related materials $(TMTSF)_2X$ ($X = SbF_6$, AsF_6).

We first note that our measurement frequencies correspond to energies $\hbar\omega$ much smaller than the single-particle gap[11] ($\Delta \sim 45\ \mathrm{cm}^{-1} = 66$ K, $\hbar\omega/\Delta < 2\times10^{-2}$) and consequently the observed $\sigma(\omega)$ clearly is not related to single-particle excitations across the gap. Also, the magnitude of σ measured at microwave frequencies is orders of magnitude larger than that observed in materials where the frequency-dependent conductivity reflects the contribution of states localized in the gap.[2] We conclude, therefore, that impurity states in the gap cannot explain our experimental results.

It would be appealing to describe the observed frequency-dependent response in terms of the oscillatory motion of the SDW mode. In the presence of pinning and damping, such a mode would lead (to a first approximation, with neglect of disorder effects) to a frequency-dependent conductivity[13,14]

$$\mathrm{Re}\,\sigma(\omega) = \frac{ne^2\tau}{m^*}\frac{\omega^2}{\tau^2(\omega_0^2-\omega^2)^2+\omega^2}, \tag{1}$$

where ω_0 and τ are the phenomenological pinning frequency and damping time constant, respectively, n is the number of condensed electrons in the SDW mode, and m^* is the effective mass of the condensate. At 3 K, fitting the data to Eq. (1) yields $\omega_0/2\pi = 9$ GHz, $1/2\pi\tau = 10$ GHz. With $n = 1.4\times10^{21}/\mathrm{cm}^3$ evaluated from the unit cell size, on the assumption of a quarter-filled band, this leads to $m^* \sim 69m_e$, where m_e is the free-electron mass.

For a SDW,[13] $m^* = m_b$, the band mass, since the SDW ground state arises from electron-electron interactions. In contrast, for a CDW, $m^*_{\mathrm{CDW}} \sim (10^2\text{–}10^3)m_b$, because of electron-phonon coupling.[13] Since $m_b \approx m_e$, our result for the effective SDW mass (although smaller than m^* found in CDW[15] systems) implies that the SDW is probably coupled to the much heavier lattice. This can arise if the SDW is commensurate with the lattice, as is the case if the band were exactly quarter filled.

While nonmagnetic impurities do not pin the collective SDW mode in first order, recent calculations[14,16] have shown that including higher-order terms can lead to pinning by nonmagnetic impurities. This would then explain our findings on the concentration dependence of the high-frequency conductivity. In $(TMTSF)_2X$ salts, pinning can also arise due to commensurability, in which case the commensurability potential is apparently affected by the impurity concentration.

It is difficult, however, to explain the strong temperature dependence observed for the resonance, apparent from Fig. 2, in terms of a pinned SDW mode alone. While a strongly temperature-dependent damping is expected as a result of the interaction of the oscillating mode with spin-wave excitations,[14] the experimental results presented in Fig. 2 suggest that the low-frequency spectrum of $\mathrm{Re}\,\sigma(\omega)$ moves down to lower frequencies as the temperature is decreased. An oscillator sum rule for the area under the $\sigma(\omega)$ resonance for a collective mode can be written as

$$\int_{\mathrm{SDW}} \mathrm{Re}\,\sigma(\omega)\,d\omega = \frac{\pi}{2}\left(\frac{ne^2}{m^*}\right). \tag{2}$$

This suggests (Fig. 2) that the number of modes associated with the conductivity decreases with decreasing temperature. In contrast to this, within the framework of mean-field theory, the area under $\sigma(\omega)$ should be independent of T, since n/m^* is independent of T.

We believe that our results imply that charged, massive, thermally excited modes are responsible for the unusual frequency-dependent conductivity observed here. Nonlinear modes[17] (such as solitons) are likely candidates for such modes. For a commensurate SDW with commensurability four, general arguments[18] allow the existence of charged, spinless solitons with energies much smaller than the gap, which can contribute to $\sigma(\omega)$.[19] If these modes are responsible for the observed $\sigma(\omega)$, they are expected to be extremely mobile. Describing the decrease of σ with increasing ω (found at low temperatures above 10 GHz) in terms of a Drude expression leads to $1/2\pi\tau \sim 10$ GHz, and this with the magnitude of σ would lead to an effective mean free path of $l \sim V_F\tau \sim 10^4$ Å, an enormous value. The concentration dependence of the frequency-dependent conductivity is, furthermore, in agreement with the above estimate. If we assume that the mean free path is limited by the impurity concentration n_i, and $l \sim 1/n_i$ (for a highly anisotropic electron motion), then a depression of σ by a factor of 20 for 1% impurity concentration would imply $l \sim 10^3$ Å in the pure material. While it is possible to understand the decrease of peak height with temperature as being due to the decreasing number of excitations, the shift of the peak frequency to lower frequencies implies that the restoring forces are temperature dependent.

In conclusion, we have observed for the first time a conductivity resonance in the SDW state, which has large amplitude and is strongly temperature dependent. These results are clearly not explainable in terms of a single-particle band-transport mechanism. Furthermore, the resonance properties are quite unlike that of related collective ground states such as CDW's suggesting that the transport in this system is due to a novel mechanism, possibly involving excitations of the SDW.

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