Spin-density-wave gap in the Bechgaard salts $(TMTSF)_2X$

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The electrodynamic response of the organic linear chain Bechgaard salts $(TMTSF)_2X$ ($X=PF_6$ and ClO_4) has been investigated over a very broad spectral range by applying a variety of optical spectroscopic tools. We focus our attention on the spin-density-wave ground state and, in particular, on its manifestation in the optical properties, with polarization perpendicular to the chains. Along this direction, we have clearly identified the spin-density-wave gap in the optical spectra of both compounds. We discuss the single particle excitation across the gap within a formalism similar to the one worked out for the superconducting state, but with Bardeen-Cooper-Schrieffer case I coherence factors, as well as an approach based on the two-dimensional Hubbard model. [S0163-1829(99)05235-2]

I. INTRODUCTION

For decades the physical properties of quasi-one-dimensional (1D) conducting systems have attracted a lot of interest, both with respect to their normal and to their broken symmetry ground states. The quasi-1D electronic structure leads to Fermi surface instabilities and therefore to phase transitions, reflecting the formation of electron-electron or electron-hole pairs, with the ground state at $T=0$ being a coherent superposition of the respective pair states.[1]

Solutions of models for the 1D electron gas (see, for example, the *g*-ology approach[1,2]) show that a superconducting, or a charge- or spin-density-wave (CDW, SDW), ground state can be reached, depending on the strength of the electron-electron or electron-phonon interaction. For the superconducting ground state, gauge symmetry is broken, while the density-wave states break translational symmetry, and in the SDW case the spin-rotation symmetry is also broken. For ''real'' quasi-1D materials, characterized by a non-negligible interchain coupling, a mean-field treatment might be applied, which then leads to a finite transition temperature T_{MF}.[1] Because of fluctuation effects the observed critical temperature for the phase transition is usually smaller than T_{MF}.

The various broken symmetry ground states have several common characteristics and their electrodynamic responses have been thoroughly explored, particularly with respect to the excitation spectra of the superconducting and charge-density-wave states.[1,3] In both cases, the response reflects the single particle and collective mode excitations, with the so-called coherence factors playing an important role. In the [Bardeen-Cooper-Schrieffer (BCS)] *s*-wave superconducting state at $T=0$, the zero frequency mode is followed, at finite frequency, by vanishing conductivity up to the gap frequency (2Δ) and then the absorption smoothly rises due to case II coherence effects.[3] At finite temperatures a smooth rise of the absorption develops due to absorption by uncondensed electrons. These effects have been accounted for by a steady stream of papers and are commonly connected to the calculations first performed by Mattis and Bardeen within the dirty limit (i.e., $2\Delta<\Gamma$, Γ being the scattering relaxation rate) of the BCS framework.[4] The situation is somewhat different for the density-wave states, in which case I coherence factors lead to a sharp maximum in the conductivity at the gap frequency.[1,3] The conductivity spectrum of charge-density-wave systems was first calculated by Lee, Rice, and Anderson.[5]

In contrast to the CDW and superconducting ground states, the electrodynamics of the SDW state is relatively poorly understood.[1,6] Despite a large number of optical experiments,[7–18] evidence for the SDW gap has not been clearly established. On the one hand, experimental results obtained along the highly conducting axis[8–17] of the linear chain Bechgaard salts $(TMTSF)_2X$ ($X=PF_6$, AsF_6, and ClO_4), generally display a very high reflectivity and consequently changes induced by the formation of the ground state are difficult to detect (particularly in the so-called clean limit where $2\Delta>\Gamma$ and changes are small). Moreover, the normal

state properties along the chains are fundamentally different from those of a simple metal.[17,19,20] Sometimes the analysis of early optical measurements[10,11] in the direction parallel to the chains explained a peak around 200 cm^{-1} as evidence of a SDW-gap structure. However, this feature exists well above T_{SDW} with little change at the SDW transition temperature itself, and therefore it cannot be the single particle gap associated with the SDW ground state.[19,20] On the other hand, the experimental results obtained with the electric field polarization perpendicular to the chains[9–15] show that below some characteristic frequency the reflectivity drops as the temperature is lowered through T_{SDW}. This occurs at different frequencies depending on the experimental technique used, and while in general there is no sharp onset, gap values ranging from 30 to 100 cm^{-1} were asserted. Recently, transmission measurements through a gridlike structure of $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ crystals gave indications for a SDW gap perpendicular to the chains around 32 and 14 cm^{-1}, respectively.[18] We believe that this unsatisfactory variety of results is due to the investigation of small crystals and mosaics, often resulting in a reflectivity significantly smaller than the one which we have observed (in some cases exceeding our low frequency values of the absorptivity by one order of magnitude). In fact, the strong anisotropy of the electronic structure usually leads to long needlelike crystals, with typical transverse dimensions of less than 0.5 mm. In order to perform high quality optical measurements it is necessary to have large crystal faces, achieved in early pioneering work with mosaics. Surface scattering and interference effects due to misalignment of the crystals, gaps between the crystals, and diffraction effects from the composite sample as aligned needles in the mosaic configuration can induce spurious results and important alteration of the specular condition, even if the needles are coated with gold for the reference measurement.

We have embarked on a thorough and systematic investigation of the excitation spectrum of large single crystals of the Bechgaard salts $(TMTSF)_2X$, with $X=PF_6$ and ClO_4. It was initially supposed that the large scattering rate and the eventual realization of the dirty limit scenario perpendicular to the chain direction should make an exploration of the electrodynamics of the SDW state with respect to the gap excitation problem more accessible. Therefore, this paper will be focused only on the electrodynamics perpendicular to the chain direction, where we achieved a direct detection and complete analysis of the SDW gap. Parts of the results were presented before[21] and we also refer to Refs. 19 and 20 for a comprehensive discussion of the on-chain (i.e., parallel direction) electrodynamic response. In Sec. II we briefly present the sample growth techniques along with the experimental methods and results. Our findings and their theoretical implications are discussed in Sec. III, while in Sec. IV we conclude by addressing a few open issues and consequences of our results with respect to the general understanding of the physics in these quasi-1D organic systems.

II. EXPERIMENT AND RESULTS

The large single crystals used in this study were grown by an electrochemical growth technique,[22] at reduced temperature (0 °C) and at low current densities. These conditions give a slow growth rate and, over a period of four to six months, produce single crystals up to $4\times2.5\times1$ mm^3.[19,20] These large, high-quality faces in the ab' plane allowed us to perform reliable optical reflectivity measurements of these materials, both parallel ($E\|a$) and perpendicular ($E\|b$) to the highly conducting chain axis, down to low frequencies. The use of such large crystals led to significant enhancement of the accuracy obtained for the optical reflectivity with respect to previous investigations obtained by aligning multiple needlelike crystals into mosaics. We should remark that the directions a and b' define the face of the sample, on which the optical experiments were conducted, and therefore the axis characterized by the largest optical anisotropy. The b' direction is perpendicular to a but slightly different from the b direction of the triclinic crystal structure. This difference should not affect our overall conclusions.

The high quality of our large single crystals has been confirmed by dc transport measurements.[23] The resistivity $\rho(T)$ measured along the chain displays a typical metallic behavior at higher temperatures, a sharp phase transition around 10 K, and a thermally activated behavior of the resistivity below this temperature. The gap, using the expression $\sigma(T)=\sigma_0\exp(-E_{gap}/2k_BT)$ is $E_{gap}=2\Delta_\rho=35$ K and we refer to this value as the transport gap. It has been established that the ground state in both materials is a spin-density-wave, the onset of which is at $T_{SDW}=12$ K for $(TMTSF)_2PF_6$ and 6 K for $(TMTSF)_2ClO_4$.[23,24] The insulating behavior results from the opening of a gap in the single particle excitation spectrum at the Fermi level due to electron-electron interactions. The most recent dc-transport results on $(TMTSF)_2PF_6$ (Ref. 23) also confirm the huge anisotropy by orders of magnitude along the three crystallographic directions. In fact, the conductivity [i.e., $1/\rho(T)$], besides a metallic behavior for $T_{SDW}<T<100$ K in all directions, has an anisotropy of approximately $1:500:5\times10^4$ at about 20 K going from the c axis to the b' and a axes, respectively.[22,23] Electron-spin-resonance results also suggest anisotropic metallic behavior along all three directions.[25]

The electrodynamic response of these Bechgaard salts over an extremely broad energy interval ($7-10^5$ cm^{-1}) has been obtained by combining the results from different spectrometers in the submillimeter, far (FIR) and mid (MIR) infrared, optical, and ultraviolet (UV) spectral ranges. A detailed presentation of the experimental techniques is given in Ref. 20. Here, we just recall a few essential technical aspects. In the optical range from 15 to 10^5 cm^{-1} polarized reflectance measurements were performed employing four spectrometers with overlapping frequency ranges. In the submillimeter spectral range (7–20 cm^{-1}), we have used a coherent source spectrometer[26,27] based on backward wave oscillators, high power, tuneable, monochromatic light sources with a broad bandwidth.[28] This spectrometer was originally designed for transmission measurements and we have reconfigured it for reflection measurements on highly conducting bulk samples.

At all frequencies up to and including the mid-infrared, we placed the samples in an optical cryostat and measured the reflectivity as a function of temperature between 2 and 300 K. For the $(TMTSF)_2ClO_4$ compound, we took particular care concerning the cooling procedure. In fact, the SDW state is achieved when the sample is quenched through the

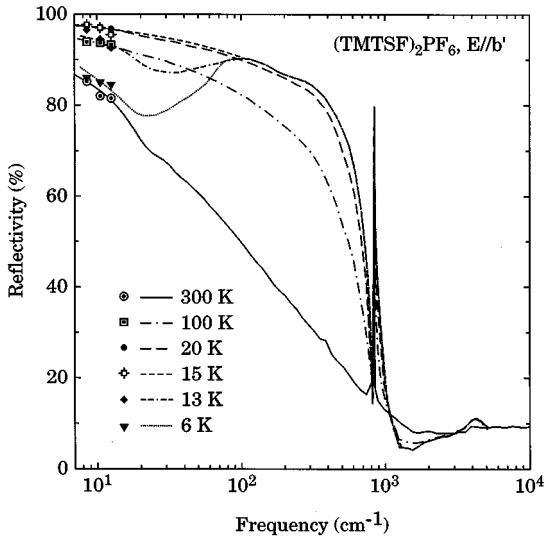

FIG. 1. Reflectivity spectra perpendicular to the chains ($E\|b$) for $(TMTSF)_2PF_6$ (note the logarithmic energy scale). At 835 cm^{-1} a phonon mode of the PF_6^- anion is seen. The points refer to the submm results, while the part of the curves below 20 cm^{-1} is the result of the interpolation (see text) of the submm data points with the FIR spectra.

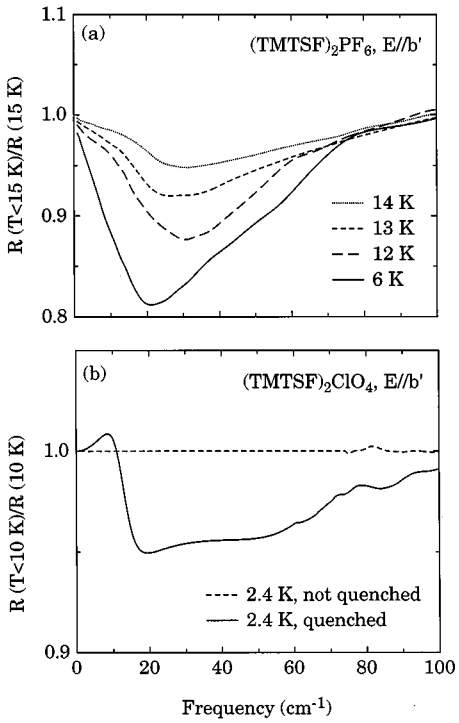

FIG. 2. Ratio between the FIR reflectivity perpendicular to the chains at $T<15$ and 10 K, and $T=15$ and 10 K for the $(TMTSF)_2X$ ($X=PF_6$ and ClO_4) compounds, respectively. The SDW gap opens at low temperature. For $(TMTSF)_2ClO_4$, the 2.4 K measurement is shown for the quenched and non-quenched (relaxed) state. The part of the curves below 20 cm^{-1} is the result of the interpolation (see text) between the submm data points and the FIR spectra.

anion ordering phase transition at 24 K.[29] Otherwise, a very slow cooling through the 24 K transition (with cooling rate of 0.1–0.3 K/min between 4 and 30 K) leads to a metallic state which undergoes a superconducting phase transition at 1.2 K.[29] We will present experimental data for both cases.

The complete set of optical properties is then obtained through Kramers-Kronig (KK) transformation of the $R(\omega)$ spectra measured over the wide spectral range.[19,20] For this purpose, we have interpolated the sub-mm points at 7, 10, 12, and 20 cm^{-1} with the spectra obtained over a continuum of frequencies above 15 cm^{-1}. The interpolation was achieved either by smoothly connecting the data points by hand or by modelling the optical response within the more sophisticated, phenomenological Lorentz-Drude classical dispersion theory.[30] Both ways give equivalent results. The implications of the low-frequency interpolations are particularly relevant in view of the discussion about the anisotropic electrodynamic response between the a and b' axes, which will be done elsewhere.[31] Because the KK integral extends from zero to infinity, it is necessary to make suitable high and low frequency extrapolations to the measured reflectivity data. We have chosen to use the power law $[R(\omega)\sim 1/\omega^4]$ at high frequencies and the Hagen-Rubens (HR) extrapolation for $\omega\rightarrow 0$ at $T>T_{SDW}$. For $T<T_{SDW}$, the reflectivity was extrapolated to 100% for $\omega\rightarrow 0$. The extrapolations for $\omega\rightarrow 0$ have no practical influence on the KK results in the spectral range of interest, where the SDW gap opens. Nevertheless, it is notorious that there is an apparent discrepancy, particularly for $(TMTSF)_2PF_6$, between the dc conductivity[23] and the HR extrapolation at $T>T_{SDW}$ [see Fig. 3(a) of Ref. 21]. This might be indicative of a non-Drude behavior at low frequencies.[31] From $R(\omega)$ and the corresponding phase $\phi(\omega)$ it is then possible to calculate the components of the complex optical conductivity $\sigma(\omega)=\sigma_1(\omega)+i\sigma_2(\omega)$.[19,20]

Figure 1 displays the measured optical reflectivity $R(\omega)$ as a function of temperature for the $(TMTSF)_2PF_6$ compound with polarization perpendicular to the chain. Both sets of data (in the submm range and from FIR on) are shown. Below 20 cm^{-1}, the curves smoothly going through the submm points and merging in the FIR spectra are the results of the above mentioned interpolation procedures. Equivalent results have been obtained for $(TMTSF)_2ClO_4$. At 300 K, the reflectivity is characterized by an overdamped behavior (i.e., $\Gamma\gg\omega_p$, ω_p being the plasma frequency) while at low temperature we find a well-developed plasma edge at approximately 0.1 eV. Moreover, a sharp phonon absorption can be seen at 835 cm^{-1}. Optical investigations from FIR up to UV were also performed on $(TMTSF)_2AsF_6$, which displays similar spectra. Since for this latter compound there is no data below FIR, we will limit our discussion on $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ only.

The main topic of this paper is the SDW gap, leaving the interpretation of the rather anomalous and complex (i.e., non-Drude-like) low frequency excitation spectrum at $T>T_{SDW}$ for a future publication.[31] In this respect and in order to only highlight the SDW gap feature, we present in Fig. 2 the ratio between $R(\omega)$ at temperatures below 15 and 10 K, and $R(\omega)$ at 15 and 10 K for $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$, respectively. The chosen reference temperatures of 15 and 10 K are above the corresponding T_{SDW} for the two compounds.

When the temperature is reduced the reflectivity significantly decreases at frequencies below 70–100 cm^{-1} (Figs. 1

and 2), which is seen as evidence that a well-defined single particle (SDW) gap develops. In this context, the results for the $(TMTSF)_2ClO_4$ compound are particularly compelling. In fact, the FIR absorption signalling the possible opening of a gap only developed in the quenched state, while the slowly cooled spectra do not display any significant temperature dependence down to 2.4 K [Fig. 2(b)]. At the low frequency end of our measured spectral range for both the $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ compound, we see an upturn in reflectivity even at $T<T_{SDW}$, possibly associated with the uncondensed carriers. This effect becomes less pronounced at low temperatures (i.e., for $T\rightarrow 0$), where the upturn is shifted to lower frequencies. Indications of these FIR features were partially seen in early optical investigations of these salts.[11,13–15] The high quality of our large single crystals combined with the very broad energy spectral range covered by our experiments (never attained up to date) allows us to considerably improve the available experimental data and to present a compelling set of results.

It is worthwhile to recall that $R(\omega)$ parallel and perpendicular to the chain are very different. This is particularly manifested by the anisotropy in the plasma edge, which parallel to the chains is at about 1 eV, one order of magnitude larger than perpendicular to the chains (Fig. 1).[19–21] Furthermore, the temperature dependence of $R(\omega)$ parallel to the chains ($E\|a$) is also quite peculiar.[19,20,32] What is important for the following discussion of the electrodynamics of the SDW state is that optical measurements conducted parallel to the chains give no clear-cut evidence for a single particle gap of the SDW state.[19,20] In other words, at the SDW phase transition, the spectra for $E\|a$ display the development of a collective excitation in the microwave range but do not show any significant temperature dependence in the FIR spectral range.

With respect to our results, we shall mention another interesting work,[18] where the magnetic field induced SDW subphases in the Bechgaard salts were studied with FIR spectroscopy. There seems also to be evidence for a SDW gap, besides the indication of a large electron lattice coupling manifested by the strong phonon renormalization in the SDW state. The gap values of Ref. 18 are, however, lower than 70 cm^{-1}, extracted from our spectra. It is still unclear the reason for such a difference. Nevertheless, it should be observed that, even though the transmitted power in Ref. 18 depends mainly on the conductivity along the b' axis, incident light was not polarized and contributions (such as, e.g., phonon modes or midgap states[31]) from other directions (i.e., projections of absorptions from other polarizations) can affect the spectra in Ref. 18. Our data, obtained with polarized light, allow us a more firm determination of the various excitations characterizing the different polarization (crystallographic) directions. Further possibilities for the apparent disagreement in the gap values evaluated from different experiments will be discussed later (see Conclusions).

The KK transformation was subsequently applied in order to obtain $\sigma(\omega)$. Using the same layout as in Fig. 2, Fig. 3 displays the corresponding ratio of the real part $\sigma_1(\omega)$ of the FIR optical conductivity of $(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ along the perpendicular direction. We clearly identify a gaplike feature developing at about 70 cm^{-1} for $T<T_{SDW}$, which is rather sharp in the

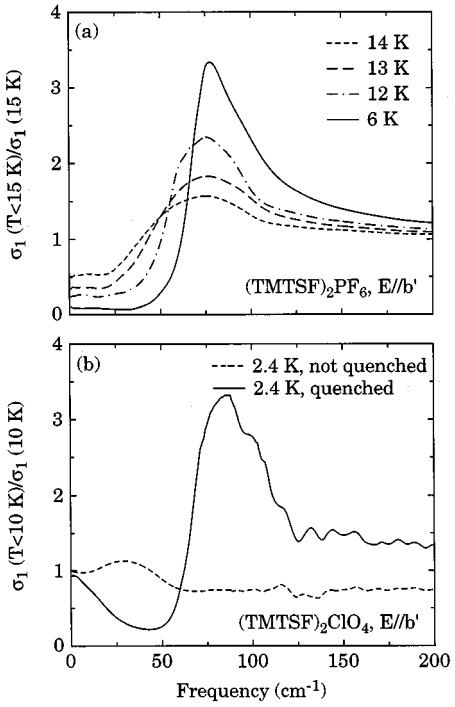

FIG. 3. Ratio of the real part of the FIR optical conductivity perpendicular to the chains below and above T_{SDW} for the $(TMTSF)_2X$ ($X=PF_6$, and ClO_4) compounds, as obtained from KK transformation of the reflectivity spectra. The data are shown in the same way as in Fig. 2.

$(TMTSF)_2PF_6$ and $(TMTSF)_2ClO_4$ compound and moves to slightly lower frequencies and decreases in intensity as the temperature increases in $(TMTSF)_2PF_6$. As already anticipated by Fig. 2(a), this feature seems to persist at temperatures slightly above T_{SDW} (particularly for the $(TMTSF)_2PF_6$ compound). In the case of the $(TMTSF)_2ClO_4$ compound, the optical conductivity displays the opening of the gap only in the quenched state, while it remains temperature independent from 10 K down to 2.4 K for the relaxed (slowly cooled) state [Fig. 3(b)]. Unfortunately, our cryostat does not allow us to follow the temperature dependence of the gap feature between 3 and 5 K in $(TMTSF)_2ClO_4$.

The rather important temperature dependence at the onset of the SDW phase transition for $E\|b'$ contrasts with the already mentioned situation for $E\|a$, where the $\sigma_1(\omega)$ spectra display the pinned collective mode excitation appearing at 0.3 cm^{-1} for $T<T_{SDW}$ and a rather broad FIR mode at about 200 cm^{-1}.[16,17] This latter feature for $E\|a$ persists up to very high temperature above T_{SDW} and was interpreted as the optical manifestation of a charge (Mott) correlation gap, as predicted by models associated with a Tomonaga-Luttinger liquid approach.[19,20]

III. DISCUSSION

Figures 2 and 3 clearly show, for the two investigated compounds, a strong temperature dependence of the FIR optical properties, the onset of which is coincident with the SDW phase transition at T_{SDW}. In this respect, the results on $(TMTSF)_2ClO_4$ obtained with different cooling rates [Fig.

2(b)] undoubtedly support the interpretation that the FIR absorption developing below T_{SDW} is indeed associated with the SDW phase transition. Consequently, we ascribe this absorption to excitation across the SDW gap.

For the formation of the SDW gap, the spectral weight arguments [i.e., $\int_0^{\omega_0} d\omega \sigma_1(\omega), \omega_0$ being a cutoff frequency] play an important role. We have checked, first of all, that the total spectral weight ($\omega_0 \rightarrow \infty$) is conserved at all temperatures. Moreover, we will assume in the following discussion that the low frequency $\sigma_1(\omega)$ [i.e., below $\sim 50\ cm^{-1}$ where a possible non-Drude behavior can emerge above T_{SDW} (Ref. 31)], although it is intrinsic, does not affect our discussion of the gap feature. In the normal phase, and for $E \| b'$, a significant amount of spectral weight, obtained by integrating $\sigma_1(\omega)$ between 0 and $\omega_0 \sim 200\ cm^{-1}$ at $T > T_{SDW}$, is located in the spectral range where the mean field theory would predict the SDW gap to be (i.e., at $2\Delta = 3.52 k_B T_{SDW}$). Furthermore, contrary to the measurements parallel to the chains[17,19,20] there is no experimental data nor theoretical anticipation for a contribution of the collective mode in the direction perpendicular to the chains at $T < T_{SDW}$. Since the collective excitation would appear at low frequencies, its absence implies a shift of the spectral weight to higher frequencies. As the temperature is lowered below T_{SDW} all the spectral weight below approximately $50\ cm^{-1}$ [see, e.g., Fig. 3(a) in Ref. 21] is removed from the gap region and transferred to the single particle excitations at approximately $70\ cm^{-1}$ (Fig. 3). This implies that the gap opens over the entire Fermi surface. Recent ^{77}Se NMR studies below 4 K at high magnetic fields are also consistent with a simple model of the temperature dependence of the spin lattice relaxation rate (T_1^{-1}) in a fully gapped and low-dimensional conductor.[33] Nevertheless, these latest NMR results also suggest an incomplete SDW transition at T_{SDW}, leaving residual carriers at the Fermi level, and a subsequent consummation of the transition at 4 K.[33] Our optical data cannot clearly discriminate between ungapped charges and thermally activated ones across the SDW gap. Some of the low frequency spectral weight, seen just below T_{SDW} in the gap spectral range, might be associated with the residual ungapped Fermi surface, envisaged by the NMR data. Optical experiments at even lower temperatures and frequencies could help in further pinning down this issue.

On the contrary, for measurements with the light polarization along the chain direction ($E \| a$) $\sigma_1(\omega)$ at $T \geq T_{SDW}$ is characterized by a very narrow zero-frequency mode with a width Γ of approximately $0.15\ cm^{-1}$. This mode, which contains a small fraction of the total spectral weight,[31] can be described by a renormalized Drude behavior[30] with an average width (i.e., scattering rate Γ) considerably smaller than the expected mean field SDW gap 2Δ of the order of 20 cm^{-1}. Moreover, the on-chain excitation spectrum is dominated in the FIR spectral range by the mode at about 200 cm^{-1} at all temperatures, collecting the great majority of the total spectral weight and being ascribed to the Mott correlation gap.[19,20] It might be speculated that the SDW gap for $E \| a$ develops in the low frequency tail of the Mott-gap feature and cannot be clearly seen, meaning that the SDW gap falls right into the Mott gap. Alternatively, one could argue that a so-called clean limit scenario (i.e., $\Gamma < 2\Delta$) prevents the detection of the SDW gap for $E \| a$.

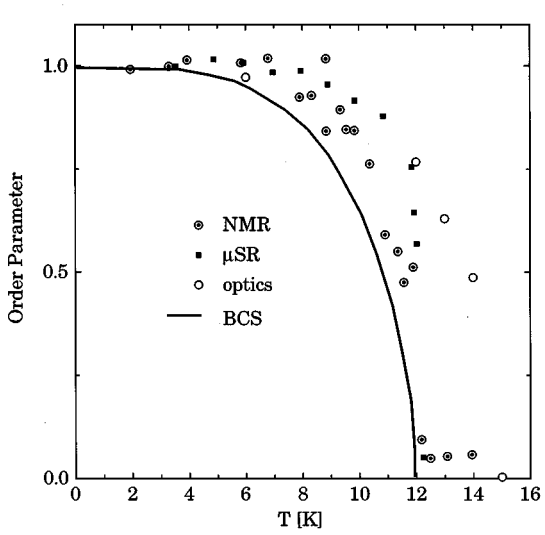

FIG. 4. Temperature dependence of the SDW order parameter as evaluated from optical, NMR, and μ SR experiments, compared to the prediction of the BCS theory (Refs. 3, 34–36).

From the optical spectra perpendicular to the chains one can extract the temperature dependence of the SDW gap [defined by the frequency where $\sigma_1(\omega)$ has a maximum, see Fig. 3(a) in Ref. 21] which corresponds to the amplitude of the SDW order parameter. Figure 4 displays the temperature dependence of the SDW gap normalized by the gap at $T \ll T_{SDW}$ for the $(TMTSF)_2PF_6$ compound, compared with values from other experiments[34–36] and with the prediction of the mean-field BCS theory.[3] For the $(TMTSF)_2ClO_4$ compound the low $T_{SDW} \sim 6$ K and our experimental limitations do not allow for a precise determination of $\Delta(T)$. Even though $\Delta(T)$ roughly follows the BCS trend, there are important differences. First of all, the SDW gap extracted from the optical results is different from zero already at temperatures which are larger by almost 2 K (larger than the temperature inaccuracy of ± 0.5 K) than T_{SDW}. Second, the order parameter displays a sharper onset at T_{SDW} than predicted by BCS, as particularly evidenced by the μSR and optical results. This latter feature, reminiscent of a first order phase transition,[34,36,37] may be ascribed to the low dimensionality of the system and can be reconciled with strong fluctuations of the order parameter at $T > T_{SDW}$.[38] As the temperature decreases, the system crosses over from one to three dimension and long-range static magnetic order appears. Since a fluctuating order parameter exists above the transition temperature, the static magnetic order parameter frozen at T_{SDW} may have a finite value.[36] Nevertheless, transport[22,23] and NMR data[35,37] give little indication for fluctuation effects. Moreover, the μSR experiments[36] pointed out that the temperature dependence of the magnetization $M(T)$ is distinctly different from the temperature dependence of the order parameter identified as the frequency shift $\nu_\mu(T)$ of the zero field muon spin precession, as shown in Fig. 4. While $\nu_\mu(T)$ saturates at low temperatures below about $T_{SDW}/2$, $M(T)$ displays, on the contrary, a remarkable temperature dependence. Within the mean-field BCS theory both the gap and the magnetization should be essentially

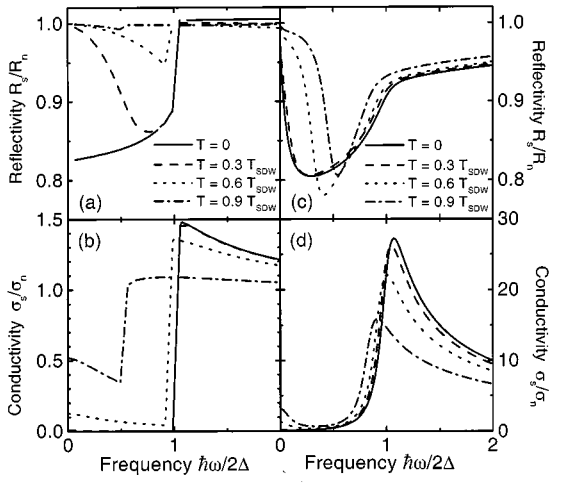

FIG. 5. Reflectivity and real part of the optical conductivity at $T<T_{SDW}$ calculated with the Mattis Bardeen approach with case I BCS coherence factors [(a) and (b)] and compared with the 2D Hubbard model [(c) and (d)] (Refs. 4,41). Both quantities are normalized by the respective normal state (i.e., $T>T_{SDW}$) values.

temperature independent below $T_{SDW}/2$, if determined by single-particle excitations. The variation of $M(T)$ at low temperatures is determined by collective spin-waves rather than by single-particle excitations.[36] However, when discussing the experimental results, one should take into account the different nature of the charge and spin excitations, as probed by different experiments [e.g., $\sigma(\omega)$ or $\rho(T)$, and ESR or Knight shift, respectively].

In our first report,[21] we attempted to reconcile our experimental data on $(TMTSF)_2PF_6$ with the BCS theory, assuming that any contribution from the collective SDW mode is negligible and that the normal state conductivity is independent of frequency in the range of interest (dirty limit). At first glance, there is a rather good agreement between the experimental findings and the Mattis-Bardeen calculation of the BCS electrodynamic response,[4] taking into account the case I coherence factors[21] (case I and II coherence factors are exchanged in going from the superconductor to the SDW state[1]). While the first assumption might be accepted, the second one is too rough, since $\sigma_1(\omega)$ at $T>T_{SDW}$ is very much frequency dependent for both compounds in the range where the SDW gap absorption appears. Thus, we further developed our model so that the normal-state conductivity below the gap feature [e.g., see also Fig. 3(a) in Ref. 21] is described by an *ad hoc* phenomenological Drude behavior with $\Gamma/2\Delta=0.1$ and imposing the conservation of the spectral weight as observed (i.e., what is lost by the gap opening piles up at the gap feature so that the total spectral weight is constant). A situation where $\Gamma/2\Delta<1$ would be more appropriate for a clean limit scenario. In Figs. 5(a) and 5(b) we display the frequency dependences of the normalized reflectivity and conductivity as calculated using the BCS formalism with the case I coherence factor. At $T=0$ a peak in $\sigma_1(\omega)$ and a remarkable suppression of $R(\omega)$ at 2Δ can be recognized. The resulting gaplike feature is qualitatively different from the electrodynamic response of superconductors, as predicted by the BCS approach with case II coherence factors.[3,21] Recent experimental results on the temperature dependent ultrasonic attenuation also indicate the presence of a coherence peak right below T_{SDW}. This can be well described by the BCS formalism with case II coherence factor (for a superconductor the case I prediction would be appropriate for the ultrasonic attenuation).[39] Therefore, there are several experimental indications that within a BCS framework the coherence factors are indeed exchanged between a superconductor and a SDW state, as expected.

However, the application of the Mattis-Bardeen formula with case I coherence factors to the SDW state can only provide a qualitative picture of the contribution from particle-hole excitations across the gap. The BCS formula for $\sigma_1(\omega)$, strictly speaking, is only known for the dirty limit: a limit which is not achieved with our ''*ad hoc*'' condition $\Gamma/2\Delta=0.1$ [Figs. 5(a) and 5(b)]. In this respect, our calculation is a forced application of the BCS theory. However, a similar calculation in a dirty limit condition [i.e., where $\sigma_1(\omega)$ in the normal state is frequency independent in the spectral range of interest] gives similar and qualitatively equivalent results.[21]

Therefore, we want to expand the analysis of our data by elaborating a mean-field approach which aims directly at the SDW phase transition in strongly anisotropic compounds, following a suggestion by Maki.[40,41] It is worth noting that the mean-field (i.e., BCS-like) SDW scenario was found to provide a useful framework for understanding the electronic properties of the half-filled insulating state of the Hubbard model, as shown by Bulut *et al.* with quantum Monte Carlo calculations.[42] Virosztek and Maki studied the magnetotransport of field-induced spin-density waves within the two-dimensional Hubbard model.[41] The complex magnetoconductivity parallel $\sigma^{\|}(\omega)$ and perpendicular $\sigma^{\perp}(\omega)$ to the chain direction was derived in mean-field theory in the clean limit, taking into account the pinning of the collective phase mode in the chain direction and the anisotropy in the hopping matrix elements $t_{\perp}/t_{\|}<0.1$.[41] In our case of a conventional SDW in zero external magnetic field the complex conductivity perpendicular to the chain direction reads[43]

$$\sigma^{\perp}(\omega)=-\frac{ne^2}{m}\alpha^2\frac{1}{i\omega-\Gamma}[1-f_0(\omega+i\Gamma)] \tag{1}$$

and

$$f_0(z)=\int_{\Delta}^{\infty}dE\,\frac{\Delta^2}{\sqrt{E^2-\Delta^2}}\,\frac{\tanh(E/2k_BT)}{E^2-(z/2)^2},\quad z=\omega+i\Gamma. \tag{2}$$

Note, ω is an energy ($\hbar=1$), and $\alpha=(t_{\perp}b'/t_{\|}2a)$ depends on the anisotropy, where $t_{\|}$ and $t_{\perp}$ are the transfer integrals, and a and b' the intermolecular distances along the a and b' direction, respectively. n and m are the charge carriers concentration and mass, which cancel out in the ratio (Fig. 3). Γ phenomenologically accounts for impurity scattering and quasiparticle damping. Equations (1) and (2) represent the inclusion of the effect of scattering in the collisionless result[41] by the substitution $\omega\rightarrow\omega+i\Gamma$. From the optical response at temperatures above and below T_{SDW} we estimate $\Gamma/2\Delta\sim0.08$ (i.e., an effective clean limit scenario). In Figs. 5(c) and 5(d) we present the calculated reflectivity and the real part $\sigma_1^{\perp}(\omega)$ of the optical conductivity perpendicular to

the chain at $T<T_{SDW}$ normalized by the corresponding quantities at $T>T_{SDW}$. The prefactor α in Eq. (1) has been adjusted such that the reflectivity shows the plasma edge at the measured frequency visible in Fig. 1. For the temperature dependence of the gap $\Delta(T)$ we used the measured amplitude of the SDW order parameter from various experiments (see Fig. 4).

The calculated conductivity $\sigma_1^{\perp}(\omega)$ at $T<T_{SDW}$ consists of two parts: a low frequency part from electron-hole pairs which are not condensed (i.e., thermally excited across the gap), and a quasi-particle contribution from broken particle-hole pairs at $\omega \geqslant 2\Delta$. The theory predicts no contribution from the collective mode in the SDW state. While the theoretical low frequency behavior (i.e., $\omega \ll 2\Delta$) is directly ascribed to the response of thermally activated carriers, our measurements indicate that the situation is not that simple, as we discuss elsewhere.[31] Moreover, the phase of the complex SDW order parameter propagates in the direction of the SDW-ordering wave vector, which points approximately in chain direction. Thus, the contribution of this ''phason'' to the current perpendicular to the chains is supposed to be negligibly small[41,44] and does not appear in Eq. (1), leaving all available spectral weight to the excitations across the gap. The collective contribution of the phason mode in the chain direction is routinely attributed to the gapped Fermi sea dragged along in the direction of the electric field. In an open Fermi surface situation applicable to quasi-one-dimensional systems this shift cannot result in a net current in the perpendicular direction due to the Brillouin zone periodicity.

We note here that a recent calculation[45] of the effect of impurity forward scattering and backscattering on the conductivity of density waves using many-body techniques does confirm the qualitative features of the result given by Eqs. (1) and (2). The low frequency peak centered at $\omega=0$ does indeed freeze out exponentially as the temperature is lowered. However, the frequency dependence of this peak at low temperatures is not Drude-like. In the frequency range $T \ll \omega \ll \Delta$ the conductivity falls off as $\omega^{-1/2}$. It remains to be seen whether a focused measurement can confirm the validity of this unconventional power law in density waves.

The qualitative agreement of our calculated reflectivity and optical conductivity [see Fig. 5(c) and 5(d), respectively] with the measured ones shown in Figs. 2(a) and 3(a) is quite satisfactory (such as e.g., the broad gap feature with a remarkable low-frequency tail, as well as the low frequency part associated with the thermally excited particles). Such a calculation further confirms the trends already achieved by our first reasoning, which pointed out the importance of coherence factors in the application of BCS theory. According to our present discussion this is to be expected for the off-chain direction, where the collective ''phason'' mode is not visible. As pointed out above, our model is based on quite rough assumptions and is not intended to reproduce all details of our experimental results. Nevertheless, the suggested approach within the two-dimensional Hubbard model treatment of Virosztek and Maki provides an understanding for the similarity with results within the BCS framework, as well as an improved resemblance to the experimental data. There is, however, a significant disagreement in the absolute value of the calculated conductivity [Fig. 5(d)] compared to the experimental one [Fig. 3(a)]. This can be improved, if we take into account an incomplete suppression of spectral weight in the gap region due to fluctuations. The amplitude in Fig. 5(d) can be further reduced by assuming a broad backgroundlike contribution to the conductivity, induced by many-particle effects not included in our mean-field theory. Since this involves additional fit parameters, we present here results for the simplest model only.

IV. SUMMARY AND OUTLOOK

We have explored the electrodynamics of the SDW ground state perpendicular to the chain direction, where the collective mode contribution is negligible. The form of the optical conductivity in the spectral range, where the SDW gap appears, suggests a single well-defined gaplike absorption at $T<T_{SDW}$. Whether this also suggests a good nesting remains to be seen.[46,47]

Several features of our findings are also of importance with regard to recent experiments and thoughts about the nature of the effect of correlations and reduced dimensionality in these materials. The magnitude of the gap $2\Delta = 70\,\mathrm{cm}^{-1}$ is somewhat larger than predicted by the weak coupling theory, and it is the same for both compounds despite the factor of 2 difference in T_{SDW}. Also, the tranport gap $2\Delta_\rho$ seems to be a little dependent on T_{SDW}. In the weak-coupling limit we expect, on the basis of the measured transition temperature T_{SDW}, a value of $2\Delta = 3.52 k_B T_{SDW} = 15\,\mathrm{cm}^{-1}$ for $(TMTSF)_2ClO_4$, and $30\ \mathrm{cm}^{-1}$ for $(TMTSF)_2PF_6$. Our large gap values are also in contrast to the conclusion reached on the basis of dc resistivity measurements and acoustic experiments.[6,39] The reason for this, we believe, is related to the consequences of the dispersion of the energy bands in the broken symmetry states of highly anisotropic metals. Such dispersion becomes important with increasing deviations from perfect nesting, and was shown by Mihaly *et al.*, using straightforward band theory with simple assumptions, to lead to differences between the gaps as sampled by transport and optical measurements.[48] It turns out that, because of the band dispersion, the transport (thermal) gap can be significantly smaller than the optical one. Such a thermal gap is the difference between the lower edge of the upper band and the upper edge of the lower band and, contrary to the optical excitation, the momentum conservation is relaxed.[48] Within an anisotropic nearest neighbor tight-binding model a ratio between the thermal and optical gap of about 0.5 can be predicted for the quarter filled band $(TMTSF)_2PF_6$ compound,[48] which is in good agreement with the experimental data. Figure 6 schematically represents the density of states relevant for the Bechgaard salts in the SDW ground state. A first gap $2\Delta_\rho$ is mainly due to indirect (therefore momentum nonconserving) transitions, which can be probed by inelastic scattering processes such as the dc transport. A second higher gap $2\Delta_{opt}$ follows from direct (momentum conserving) and therefore optically active transitions.

Alternatively, one could argue that the large gap found here may be due to low-dimensional fluctuation effects.[49] These are expected to be important below the mean field transition temperature (T_{MF}) which we estimate to be approximately between 20 and 30 K. Our experiments indicate the development of a pseudogap, as the gap feature persists even at temperatures above T_{SDW} [see, e.g., $(TMTSF)_2PF_6$ in

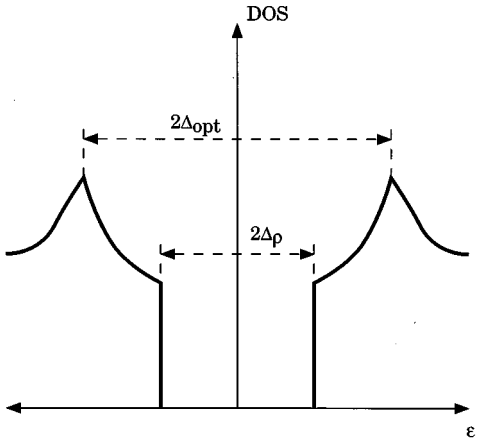

FIG. 6. Schematic density of states (DOS) in the SDW ground state after Ref. 48. The transport and optical SDW gap are marked by Δ_ρ and Δ_{opt}.

Figs. 3(a) and 4]. Recent magnetoresistance measurements[46] also show dramatic effects well above the SDW transition and they may well be the consequence of one-dimensional fluctuations. The Ginzburg criterion leads to the following expression for the fluctuation region above the transition: $\Delta T = T_{\mathrm{SDW}}(\xi_a \xi_b \xi_c \Delta C)^{-2}$, where ξ_x are the coherence lengths in the different crystallographic directions and ΔC is the magnitude of the specific heat anomaly. Estimations based on thermodynamic measurements[50] give $\Delta T = 1$ K. Consequently, the onset of the pseudogap at temperatures approximately 2 K above T_{SDW} [at least for the $(\mathrm{TMTSF})_2\mathrm{PF}_6$ compound, see also Fig. 3(a) and 4] may well be due to the three-dimensional fluctuation effects associated with the short coherence length, even though ΔT is too small with respect to T_{MF} ($\sim$20–30 K) inferred from the experimental data. Nevertheless, there is not so far any indication for a pseudogap feature or even evidence for fluctuation effects either in the susceptibility or in electron-spin-resonance and muon spin relaxation experiments.[25,36]

Finally, we address the issue about the shape of the SDW gap feature. The broad low frequency tail of the SDW gap absorption was already pointed out. A similar behavior was also observed in CDW systems and was ascribed to thermal lattice fluctuations.[51] This latter scenario might be less probable for a SDW condensate, where a priori the lattice should be very weakly or not at all involved in the SDW phase transition. However, the coupling to the lattice and its relevance to the SDW phase transition are still matter of debate and are not completely solved, as shown by recent ultrasonic investigations.[39] While the SDW gap peak itself is reminiscent of the effects due to the coherence factors, its remarkable broadening (larger than the characteristic thermal broadening of the order of $k_B T$) might have different origins: anisotropy of the gap, finite lifetime of quasiparticle excitations, and magnetic (impurities) effects.[52] All these effects are known to induce changes in the density of states and consequently in its manifestation through the optical gap feature. This is indeed very well documented in various type of superconductors (e.g., cuprates and fullerenes).[52] The issues addressed above together with the role played by the low dimensionality (i.e., crystallographic anisotropy), particularly with respect to the electrodynamics in the low frequency spectral range below the SDW gap, remain open and call for further experimental and theoretical work.

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