Direct Observation of the Spin-Density-Wave Gap in $(TMTSF)_2PF_6$

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We have measured the optical properties of the linear chain compound bis-(tetramethyltetraselenafulvalene)hexafluorophosphate, $(TMTSF)_2PF_6$, in the spin-density-wave state which develops below $T_{SDW} = 12$ K. In the direction perpendicular to the chains, we observe clear signatures of the spin-density-wave gap and model these features with a formalism similar to the one worked out for the superconducting state but with case I coherence factors. [S0031-9007(96)00257-8]

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The electrodynamics of the superconducting and the charge-density-wave states have been thoroughly explored and are well understood [1,2]. 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 (s wave, BCS) superconducting state, the zero frequency mode is followed, for $T = 0$, by vanishing conductivity up to the gap frequency and then the absorption smoothly rises due to case II coherence effects [1]. At finite temperatures a low frequency tail 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 [3]. The situation is somewhat different for the density-wave state in which case I coherence factors lead to a sharp maximum in the conductivity at the gap. The conductivity spectrum of a charge-density-wave system was first calculated by Lee, Rice, and Anderson [4].

In contrast to these ground states, the electrodynamics of the spin-density-wave state (SDW) is little explored and understood [2,5] because optical evidence for the SDW gap has not been found to date [6]. This is mainly for two reasons. First, experiments on linear chain compounds, where the development of the SDW state leads to the full removal of the Fermi surface, have been performed along the highly conducting axis where the reflectivity is high (and consequently changes induced by the formation of the ground state are difficult to detect); and second, the normal state properties are fundamentally different from those of a simple metal [7,8]. Analysis of early optical measurements [9,10] in the direction parallel to the chains explained a peak around 200 cm^{-1} as evidence of a gap structure. However, this feature exists well above T_{SDW} with little change at the SDW transition temperature itself, and consequently cannot be the single particle gap associated with the SDW ground state [7]. Experiments conducted with the field polarization perpendicular to the chains [10,11] show that below some characteristic frequency the reflectivity drops as the temperature is lowered through T_{SDW}. This occurs at various 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 $(TMTSF)_2PF_6$ crystals gave indications for a SDW gap around 32 cm^{-1} perpendicular to the chains [12]. We believe that this unsatisfactory variety of results is due to the investigation of small crystals and mosaics, which often led to a reflectivity significantly smaller than that observed by us (in some cases exceeding our low frequency values by one order of magnitude). Surface scattering and interference effects due to the aligned needles in the mosaic configuration can lead to spurious results and important alternation of the specular condition.

In order to address the issues mentioned we have conducted optical experiments on the Bechgaard salt $(TMTSF)_2PF_6$ in a wide spectral range. The moderate conductivity perpendicular to the chain direction makes the exploration of the electrodynamics of the SDW state more accessible. For the first time we were able to directly detect and completely analyze the SDW gap.

All the experiments were performed on large single crystals (4×2 mm^2). The wide crystals were slowly grown during a period of 6 months by keeping the solution at low temperature (0 °C). The optical reflectivity was measured in both polarizations parallel ($E \| a$) and perpendicular ($E \| b'$) to the chain direction using five different spectrometers which cover an extremely wide spectral range from 8 to 10^5 cm^{-1} [13]. We have performed a Kramers-Kronig (KK) analysis in order to obtain the components of the optical conductivity.

In Fig. 1 we display the optical reflectivity R of $(TMTSF)_2PF_6$ measured in both polarizations, perpendicular and parallel to the chains at temperatures above and below the SDW transition at $T_{SDW} = 12$ K over a wide spectral range. Perpendicular to the chains [Fig. 1(a)] we find a well-developed plasma edge and a low frequency behavior, which above the transition can be qualitatively described as the response of a Drude metal. There remains a discrepancy between the optical and dc data

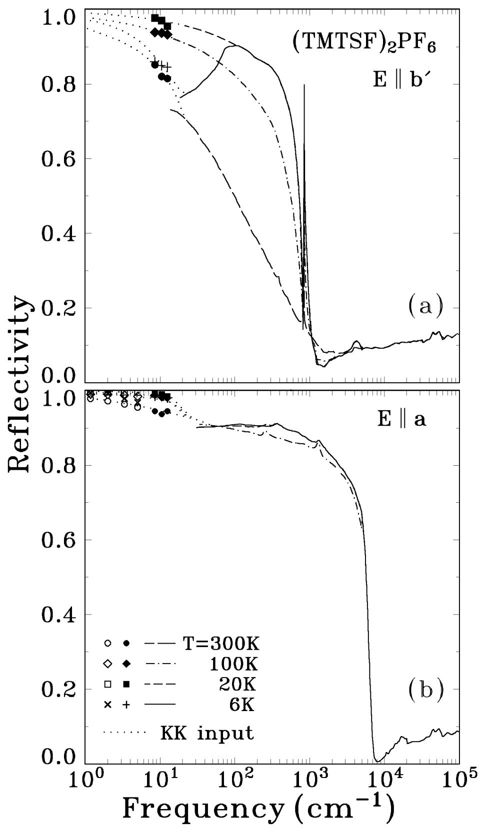

FIG. 1. The optical reflectivity of $(TMTSF)_2PF_6$ measured at various temperatures with polarization (a) perpendicular and (b) parallel to the chain direction. The lines were obtained by standard optical techniques, the solid symbols represent data taken by the submillimeter spectrometer, and the open symbols are results of microwave and millimeter wave measurements from Donovan *et al.* [8]. The dotted lines indicate the extrapolations used for the Kramers-Kronig analysis. At 835 cm^{-1} a phonon mode of the PF_6^- anion is seen.

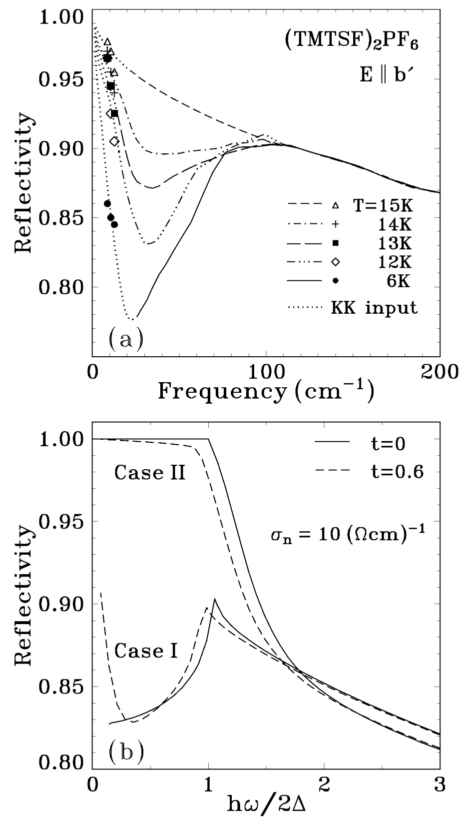

FIG. 2. (a) The low frequency optical reflectivity of $(TMTSF)_2PF_6$ measured perpendicular to the chains ($E\|b'$). The SDW gap opens as the temperature is lowered below 15 K. The solid lines are optical reflectivity data, the symbols indicate the results of the submillimeter wave measurements; the dashed line represents the extrapolation for the Kramers-Kronig analysis. (b) The frequency dependent reflectivity calculated for case I and case II coherence factors for two different temperatures: $T = 0$ (solid lines) and $t = T/T_c = 0.6$ (dashed lines). For the absolute value of the reflectivity a constant conductivity in the normal state $\sigma_n = 10$ $(\Omega\ \mathrm{cm})^{-1}$ was assumed.

which requires further investigation. Parallel to the chains [Fig. 1(b)] the behavior is somewhat more complicated and will be discussed elsewhere [7]. What is important for this discussion of the electrodynamics of the SDW state is that optical measurements conducted parallel to the chains give no clear-cut evidence for the single particle gap nor for a SDW state. The situation is fundamentally different for the polarization perpendicular to the chains ($E\|b'$). As seen more clearly in Fig. 2(a), as the temperature is reduced below 15 K the reflectivity significantly decreases at frequencies below 70 cm^{-1}, which is seen as evidence that a well-defined single particle gap develops. At the low frequency end of our measured spectral range, we see a sharp upturn in reflectivity resulting from the contribution of free, or uncondensed carriers which are thermally excited across the single particle gap; this effect becomes less pronounced at low temperatures. Indications of this feature were seen in Ref. [10]. Because of the absence of low-temperature dc results and data in the microwave range we cannot rule out the development of a finite frequency mode at very low frequencies; however, this does not influence the following analysis. The KK transformation of the reflectivity spectra was done assuming a simple metallic behavior at low frequencies, hence we have used the Hagen-Rubens extrapolation [14] to zero frequency below our lowest measured frequency of 8 cm^{-1}. Figure 3(a) displays the optical conductivity of $(TMTSF)_2PF_6$ for the perpendicular direction at various temperatures. We clearly identify a sharp feature peaked at 70 cm^{-1}, which moves to slightly lower frequencies and decreases in intensity as the temperature increases up to 15 K. The existence of this feature also slightly above the SDW transition temperature of 12 K can most likely be ascribed to fluctuation effects which will be discussed below.

Coherence factors play an important role in the electrodynamics of the various broken symmetry ground states of metals. For the BCS superconducting state, case II coherence factors are associated with the transitions induced by the electromagnetic wave. This leads to a smooth rise of the conductivity for frequencies $\omega \geq 2\Delta/\hbar$ and to a reflectivity below the gap which is 100% at zero temperature. For density wave states, case I coherence factors appear in the electrodynamic response, leading to a fundamentally different behavior for frequencies around the single particle gap [2]. Both cases are described by the expression [1,3]

$$\frac{\sigma_1(\omega,T)}{\sigma_n} = \frac{2}{\hbar\omega}\int_{\Delta}^{\infty} \frac{[f(\mathcal{E}) - f(\mathcal{E} + \hbar\omega)](\mathcal{E}^2 \pm \Delta^2 + \hbar\omega\mathcal{E})}{(\mathcal{E}^2 - \Delta^2)^{1/2}[(\mathcal{E} + \hbar\omega)^2 - \Delta^2]^{1/2}}\, d\mathcal{E} - \frac{1}{\hbar\omega}\int_{\Delta-\hbar\omega}^{-\Delta} \frac{[1 - 2f(\mathcal{E} + \hbar\omega)](\mathcal{E}^2 \pm \Delta^2 + \hbar\omega\mathcal{E})}{(\mathcal{E}^2 - \Delta^2)^{1/2}[(\mathcal{E} + \hbar\omega)^2 - \Delta^2]^{1/2}}\, d\mathcal{E}. \tag{1}$$

Here $2\Delta(T)$ describes the temperature dependent single particle gap, and $f(\mathcal{E},T) = [1 + \exp\{\mathcal{E}/k_BT\}]^{-1}$ the Fermi-Dirac distribution. The positive sign in Eq. (1) is appropriate for case II, the negative sign is appropriate for case I coherence factors. In Fig. 3(b) the optical conductivity calculated for both case I and case II coherence factors is displayed. At zero temperature $\sigma_1 = 0$ below the single particle gap, and we obtain a smooth rise of $\sigma_1(\omega)$ for the superconducting case and a characteristic square root singularity at the gap frequency for the case of the SDW ground state. At finite temperatures, the contribution of the thermally excited electrons leads to a low frequency tail, with progressively increasing spectral weight with increasing temperature. The imaginary part of the conductivity $\sigma_2(\omega,T)$ can be either calculated in a similar way [1] or obtained by a KK transformation of $\sigma_1(\omega,T)$. While parallel to the chains the system is in the clean limit [8], for the perpendicular direction it is in the dirty limit [7]. From both components of the conductivity, the frequency dependent reflectivity was calculated and is displayed in Fig. 2(b). For the sake of simplicity, we assumed for both cases that the normal state conductivity $\sigma_n = 10\ (\Omega\ \mathrm{cm})^{-1}$ is independent of frequency in the range of interest. Experimentally this is not the case for $(TMTSF)_2PF_6$, as Fig. 3 clearly demonstrates. A temperature and frequency dependent normal state conductivity can be included in the evaluation but at this point we are interested more in overall qualitative features than in a detailed comparison between theory and experiment. In the analysis, we also neglect the contribution coming from the low frequency collective SDW mode. The reason for this is that experiments along the chain direction give clear evidence for a collective, pinned phason mode [8] but in the perpendicular direction no indications for this mode are available to date. For both the superconducting and the SDW case, sharp changes in the reflectivity occur at the gap frequency. Well above the gap, the reflectivity is not sensitive to the development of the broken symmetry ground state. At zero temperature, the reflectivity below the gap is 100% for the superconducting case, while for the SDW ground state the reflectivity decreases and approaches a constant value as $\omega \to 0$. Spectral weight arguments play an important role for the superconducting state [1] and they are also important for the SDW ground state. As the collective mode is probably absent or insignificant in the direction perpendicular to the chains (and therefore does not contribute to the spectral weight), all the spectral weight of the Drude response found above T_{SDW} is removed from the gap region and located in the single particle response at 70 cm^{-1} as the temperature is lowered below the transition.

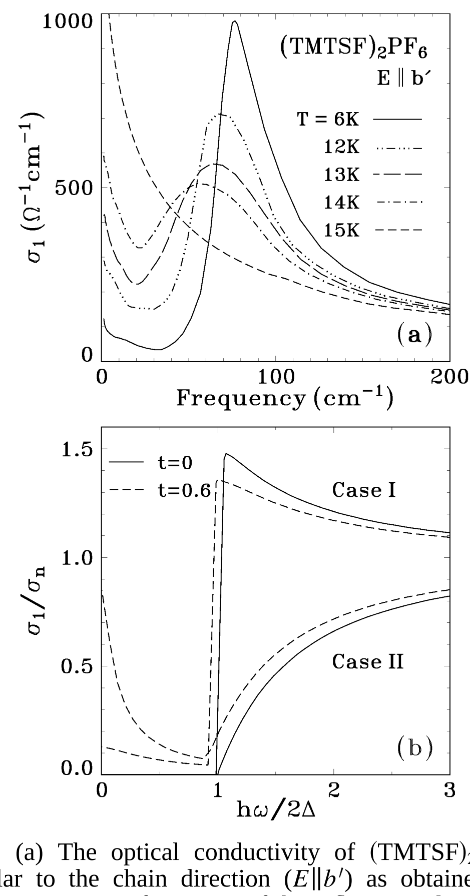

FIG. 3. (a) The optical conductivity of $(TMTSF)_2PF_6$ perpendicular to the chain direction ($E \| b'$) as obtained by the Kramers-Kronig transformation of the reflectivity data. (b) The frequency dependent conductivity calculated by Eq. (1) for case I and case II coherence factors for two different temperatures: $T = 0$ (solid lines) and $t = T/T_c = 0.6$ (dashed lines).

All the signatures calculated for case I coherence factors are observed by experiment; thus we conclude that the electrodynamics of the SDW ground state is qualitatively understood, for the case where the collective mode contribution is negligible. The form of the conductivity near the gap suggests a single well-defined SDW gap, whether this suggests also good nesting remains to be seen [15]. 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 $2\Delta/hc = 70\ \mathrm{cm}^{-1}$ is significantly larger than what the weak coupling theory predicts. In this limit we expect, on the basis of the measured transition temperature $T_{\mathrm{SDW}} = 12$ K, a value of $2\Delta/hc = 3.53k_BT_c/hc = 30\ \mathrm{cm}^{-1}$. Our large gap value also is in contrast to the conclusion reached on the basis of dc resistivity measurements [5]. The reason for this, we believe, is that the dc resistivity is heavily influenced by a small number of states in the gap, leading to a serious underestimation of the magnitude of the gap. The large gap found here may be understood in terms of low-dimensional fluctuation effects [16] and then these are expected to be important below the mean field transition temperature which we estimate as approximately $T_{\mathrm{MF}} = 20$ K. Evidence for such fluctuation effects, however, has not been found by muon spin relaxation measurements [17]. Recent magnetoresistance measurements [15] show dramatic effects well above the SDW transition and they may well be the consequence of one-dimensional fluctuation effects. Our experiments also point to the development of a pseudogap and consequently to the importance of fluctuation effects somewhat above the transition, as the gap feature remains evident even at temperatures above $T_{\mathrm{SDW}} = 12$ K. The Ginzburg criterion leads to the following expression of 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 [18] give $\Delta T = 1$ K. Consequently, the onset of the pseudogap at temperatures approximately 2 K above T_{SDW} may well be due the three-dimensional fluctuation effects associated with the short coherence length. Although we have analyzed our experiments in terms of a spin-density-wave ground state, the Hubbard model leads to the same features which we observe [19].

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