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BRIEF REPORTS

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Density-wave charge dynamics in conducting polypyrrole

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Reflectance spectra of polypyrrole (PPy) doped with PF_6, obtained at 250 K and below, show the formation of a peak in the joint density of states at 110 cm^{-1} and an associated redistribution of oscillator strength. In addition, a Fano-like resonance is observed at 70 cm^{-1}. We discuss the results in terms of a transition to a density-wave ground state characterized by an energy gap ($2\Delta/hc \approx 100\,cm^{-1}$) and a pinned collective mode (at 70 cm^{-1}). Despite the energy gap, PPy-PF_6 remains ''metallic'' at low temperatures; i.e., the gap spans only a part of the Fermi surface.

The possibility of collective states arising from many-body effects in conducting polymers has been discussed for many years. The reduced dimensionality and the importance of electron-electron correlations in the metallic state have stimulated predictions of incommensurate charge-density wave (or spin-density wave) dynamics and superconductivity in this class of materials.[1–3] Although evidence of a spin gap in very-high-conductivity doped polyacetylene has been presented,[4,5] such phenomena have not been realized more generally, in part because the physics of metallic polymers is dominated by severe disorder.

Recently, however, sample quality has been significantly improved, and the metal-insulator (M-I) transition has been studied in detail.[6] In the metallic regime, the electronic states at the Fermi energy are delocalized and the electrical properties are correspondingly enhanced.[6] With these improved materials, one might hope to have an opportunity to observe the onset of density-wave phenomena or superconductivity.

When synthesized electrochemically under rigorous conditions,[7] the transport[7–9] and optical properties[10–12] of polypyrrole (PPy)–PF_6 are indicative of a disordered conductor on the metallic side of the M-I transition. Furthermore, metallic (PPy)-PF_6 exhibits an unusual resistivity decrease (versus temperature T) at low temperatures.[8,9] Recent x-ray structural analysis suggests that PPy-PF_6 is quasi-two-dimensional with good overlap of wave functions both along the polymer chain and in the column direction.[13] This structure resembles that found in the low-dimensional charge-transfer salts, in which charge-density waves (CDW), spin-density waves (SDW), and superconductivity (SC) are well known.[14–17]

We report far-infrared (ir) reflectance results obtained from PPy-PF_6 at low temperatures. Below 250 K, a sharp, asymmetric feature peaked at 110 cm^{-1} and a Fano-like resonance at 70 cm^{-1} are observed. We attribute the 110-cm^{-1} feature to the peak in the joint density of states

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associated with an energy gap ($2\Delta/hc \approx 100\,\mathrm{cm}^{-1}$) in the single-particle excitation spectrum. Despite the existence of the energy gap, however, PPy-PF_6 remains ''metallic'' at low temperatures; i.e., the gap spans only a part of the Fermi surface. The results are discussed in terms of the formation of a density-wave-like ground state.

The frequency-dependent conductivity $\sigma(\omega)$ and dielectric function $\varepsilon(\omega)$ are very sensitive to the details of reflectance, especially in the far-ir. Reflectance measurements suggested the emergence of interesting spectroscopic features in PPy-PF_6 in the far-ir at low temperatures.[18] However, because of poor detector sensitivity for $\omega < 100\,\mathrm{cm}^{-1}$, the detailed features in $\sigma(\omega)$ and $\varepsilon(\omega)$ could not be resolved. We have now extended the measured frequency range down to 8 cm^{-1} and enhanced the accuracy by utilizing higher-sensitivity far-ir spectrometers. The results unambiguously show the development of the gap-edge feature peaked around 110 cm^{-1} and a resonance mode at 70 cm^{-1}.

Free-standing films of metallic PPy-PF_6 were prepared under nitrogen by anodic oxidation in an electrochemical cell containing 0.06M of pyrrole monomer, 0.06M of tetrabutylamonium-hexafluorophosphate, and 1% (by volume) water in propylene carbonate. A glassy-carbon electrode and platinum foil were used as the working electrode and the counterelectrode, respectively. The polymerization was carried out galvanostatically at 0.1–0.3 $\mathrm{mA/cm}^2$ with the cell at $T = -40\,°\mathrm{C}$. Free-standing films with thicknesses typically 10–20 μm were peeled off the electrode. Visual inspection of the sample surfaces indicated that the surface quality was sufficient for specular reflectance measurements without concern for scattering losses.

The transport and optical properties of PPy-PF_6 are very sensitive to the details of the preparation conditions.[9–12] The resistivity ratio, $\rho_r = \sigma(1.4\,\mathrm{K})/\sigma(300\,\mathrm{K})$, and the reduced activation energy, $W = -d(\ln\rho)/d(\ln T)$, have proven to be useful for characterizing the relative disorder in the samples.[7] Therefore, we carried out complete transport measurements on a series of samples and selected the most metallic samples for reflectance measurements ($\rho_r \approx 1.7$, $W < 0$ with $\sigma_{\mathrm{dc}} \approx 350\,\mathrm{S/cm}$ at 300 K). These samples also showed the resistivity maximum around 13 K, below which $d\rho/dT > 0$.

The reflectance $R(\omega)$ was measured from 8 cm^{-1} to $5 \times 10^4\,\mathrm{cm}^{-1}$ using four different spectrometers. In the submillimeter-wave spectral range (8–13 cm^{-1}), a coherent source spectrometer based on backward wave oscillators was used. For $15 < \omega < 300\,\mathrm{cm}^{-1}$, a Bruker 113v ir interferometer equipped with a He-cooled Si bolometer was used. A Nicolet Magna-750 Fourier-transform (fr) spectrometer covered the spectral range between 100 and 9000 cm^{-1}. The agreement in the overlap spectral range between different instruments was excellent. Since even a few percent error in $R(\omega)$ is crucial to the Kramers-Kronig (KK) analysis, extra care was taken in all procedures for obtaining absolute values of $R(\omega)$.

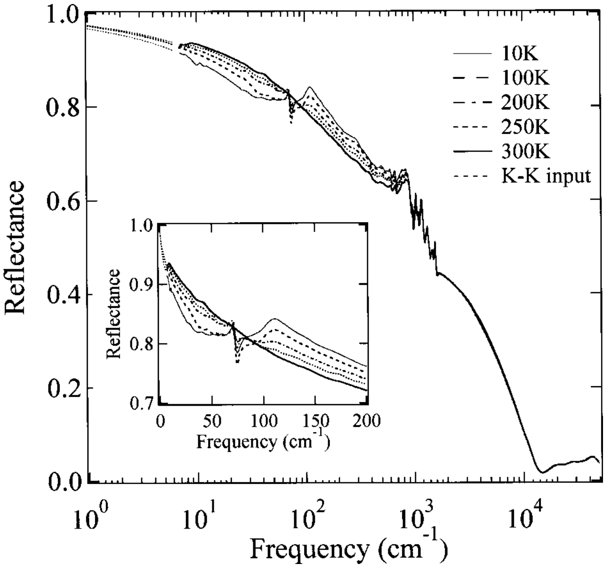

FIG. 1. Reflectance spectra $R(\omega)$ of PPy-PF_6 measured at various temperatures from 10 to 300 K. The dotted lines below 8 cm^{-1} indicate the extrapolation by the Hagen-Rubens formula used for the Kramers-Kronig analysis. The inset shows $R(\omega)$ below 200 cm^{-1} on a linear scale.

Figure 1 shows $R(\omega)$ of metallic PPy-PF_6 at various temperatures between 10 and 300 K. For 300 K, the reflectance spectrum is typical of metallic polymers; a well-defined plasma edge around $1.5 \times 10^4\,\mathrm{cm}^{-1}$ (1.8 eV) with $R(\omega)$ increasing toward unity at lower frequencies ($R > 90\%$ for $\omega < 20\,\mathrm{cm}^{-1}$). In the far-ir region below 100 cm^{-1}, the Hagen-Rubens (HR) approximation provides an excellent fit to $R(\omega)$ as indicated in detail in the inset.[12] Previous analysis demonstrated that $R(\omega)$ and the optical constants obtained at 300 K can be accurately described by the localization-modified Drude model (except for the obvious phonon features around 400–1000 cm^{-1}).[10,12]

At 250 K and below, the low-frequency $R(\omega)$ changes dramatically. Between 800 and 100 cm^{-1}, the reflectivity monotonically increases relative to $R(\omega)$ at 300 K. For $\omega < 110\,\mathrm{cm}^{-1}$, the reflectivity monotonically decreases relative to $R(\omega)$ at 300 K; e.g., at 10 K, $R(\omega)$ remains well below that obtained at 300 K for $\omega < 80\,\mathrm{cm}^{-1}$. In the extreme far-ir below $30\,\mathrm{cm}^{-1}$,$R(\omega)$ recovers the ''metallic'' behavior; the $R(\omega)$ curves for all temperatures approach the 300-K curve and increase toward unity as $\omega \rightarrow 0$. The inset to Fig. 1 shows the long-wavelength data on an expanded scale. At and below 250 K, there are two features: the peak at 110 cm^{-1} and a Fano-like resonance at 70 cm^{-1}. These two spectral features sharpen and become more well defined (but do not shift) as the temperature is lowered to 10 K. For $\omega > 800\,\mathrm{cm}^{-1}$, $R(\omega)$ is independent of temperature.

Since such spectral features in $R(\omega)$ are unprecedented in metallic polymers, we carefully checked the reproducibility of the spectra, especially the data in the far-ir region below 300 cm^{-1}. In the range 70–600 cm^{-1}, measurements were carried out at low temperature on ten different samples with nearly identical transport properties. In the range from 20 to 300 cm^{-1}, measurements were carried out at low temperature on four different samples, again with nearly identical transport properties. All aspects of the far-ir data were reproduced. Thus, the data shown in Fig. 1 are typical of the highest quality PPy-PF_6 with transport properties that place them on the metallic side of the M-I transition ($\rho_r < 2$ and $W < 0$). In contrast, however, the new spectral features described in the previous paragraph and shown in Fig. 1 are not observed for samples on the insulating side of the M-I transition ($\rho_r > 10$ and $W > 0$).

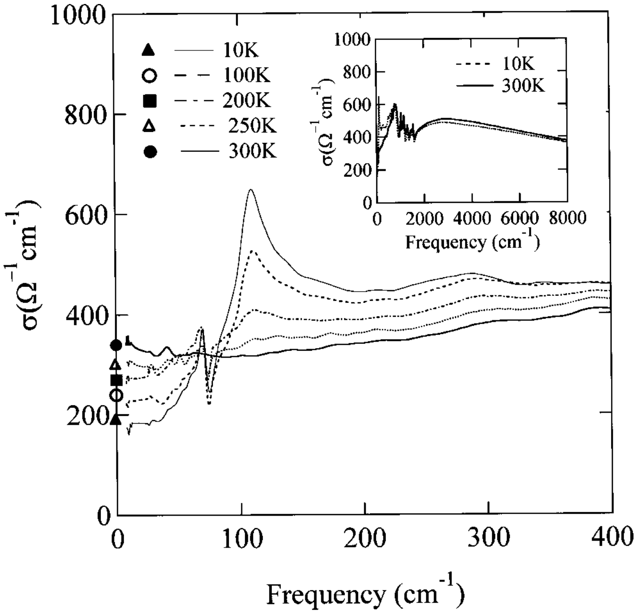

FIG. 2. Optical conductivity $\sigma(\omega)$ of PPy-PF$_6$ below $\omega = 400\,\mathrm{cm}^{-1}$, as obtained from Kramers-Kronig analysis of $R(\omega)$. The inset compares $\sigma(\omega)$ for 10 K (dotted line) and 300 K (solid line) in the ir region for $\omega \leqslant 8000\,\mathrm{cm}^{-1}$. Note the 1:1 correspondence between the dc conductivity (σ_{dc}), shown as the symbols at $\omega = 0$, and $\sigma(\omega \rightarrow 0)$ at each temperature.

Kramers-Kronig (KK) analysis of $R(\omega)$ yields $\sigma(\omega)$ and $\varepsilon(\omega)$. Extrapolation beyond the measured range (e.g., below 8 cm^{-1} and above $5 \times 10^4\,\mathrm{cm}^{-1}$) are explained in detail elsewhere.[10,12] For $\omega < 8$ cm^{-1}, the HR relation was used to extrapolate to $\omega \rightarrow 0$, as shown in the inset of Fig. 1.

Figure 2 displays $\sigma(\omega)$ at various temperatures. At 300 K, $\sigma(\omega)$ is typical of a disordered metal; $\sigma(\omega)$ decreases with decreasing ω below 2500 cm^{-1} and accurately approaches the measured $\sigma_{\mathrm{dc}}(300\,\mathrm{K})$ value, consistent with previous reports.[10,12] In the far-ir region below 300 cm^{-1}, $\sigma(\omega)$ is featureless and frequency independent at 300 K, consistent with the excellent fit to $R(\omega)$ obtained from the HR approximation in this frequency range. For lower temperatures, however, $\sigma(\omega)$ develops unusual spectral features in the far-ir region. An asymmetric structure peaked at 110 cm^{-1} grows at the expense of the oscillator strength below $\omega < 80\,\mathrm{cm}^{-1}$; thus, $\sigma(\omega)$ decreases for $\omega < 60\,\mathrm{cm}^{-1}$ as the temperature is lowered. In addition, a sharp Fano-like feature (absent at 300 K) appears at 70 cm^{-1}. The peak positions of these two features are nearly temperature independent below 250 K.

The excellent agreement between optically measured $\sigma(\omega \rightarrow 0)$ and σ_{dc} at each temperature is explicitly demonstrated in Fig. 2. This remarkable agreement provides confidence in the accuracy and precision of the $R(\omega)$ measurements.

At frequencies below the gap, $\sigma(\omega)$ does not approach zero. This implies that there are parts of the Fermi surface with no gap (a semimetal), that disorder introduces states within the gap, or that the sample is inhomogeneous with the energy gap in only a fraction (of order half) of the volume. The Fano-like shape of the 70-cm^{-1} mode indicates that this sharp resonance is coupled to the broad electronic background. Thus, there is no large-scale spatial separation (inhomogeneity) of metallic and semiconducting regions.

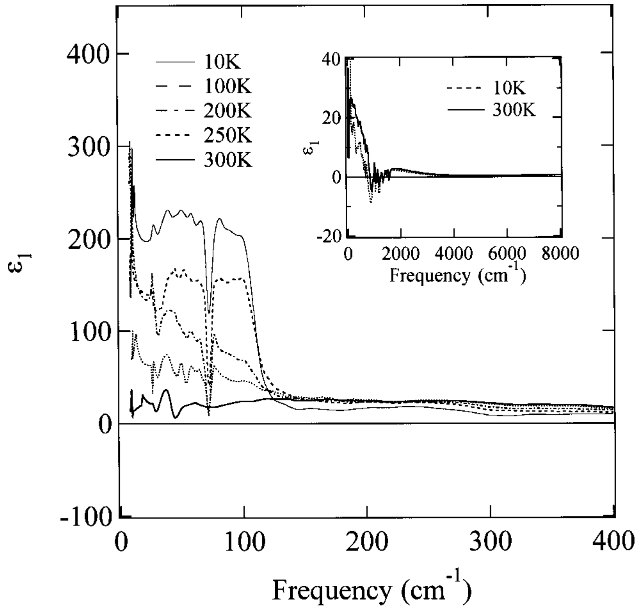

FIG. 3. Real part of the dielectric constant, $\varepsilon_1(\omega)$, for PPy-PF$_6$ for $\omega \leqslant 400\,\mathrm{cm}^{-1}$ as obtained from the Kramers-Kronig analysis of $R(\omega)$. The inset compares $\varepsilon_1(\omega)$ for 10 K (dotted line) and 300 K (solid line) for $\omega \leqslant 8000\,\mathrm{cm}^{-1}$.

The existence of an energy gap for $T \leqslant 250\,\mathrm{K}$ is evident from the $\varepsilon_1(\omega)$ spectra shown in Fig. 3. At 300 K, $\varepsilon_1(\omega)$ is small, positive, and featureless. Since PPy-PF$_6$ is a disordered metal close to the M-I transition,[12] $\varepsilon_1(\omega)$ does not cross zero at the plasma frequency ($\omega_p \approx 1.5 \times 10^4\,\mathrm{cm}^{-1}$; see Fig. 1) because the plasma oscillation is overdamped. At 10 K, $\varepsilon_1(\omega)$ increases below 110 cm^{-1}, to $\varepsilon_1(\omega) \approx 200$. The $\varepsilon_1(\omega)$ data in Fig. 3 are characteristic of a system with an energy gap with $2\Delta/hc \approx 100\,\mathrm{cm}^{-1}$. The oscillator strength (Ω_p^2), which is shifted from below 2Δ to above 2Δ (see Fig. 2), can be estimated from the increase in the low-frequency dielectric function at frequencies below the gap,

$$\Delta\varepsilon_1(\omega \rightarrow 0) \approx 1 + (\Omega_p^2/4\Delta^2).$$

Taking $\Delta\varepsilon_1(\omega \rightarrow 0) \approx 200$, we estimate that approximately 1% of the total π-electron oscillator strength is redistributed ($\Omega_p^2/\omega_p^2 \approx 10^{-2}$).

The peak in $\sigma(\omega)$ and the associated redistribution of oscillator strength are indicative of the formation of a gap in the excitation spectrum similar to that observed in low-dimensional conductors and attributed to the formation of a CDW or SDW ground state.[14–17] Below the critical temperature for formation of the broken-symmetry state, the periodicity of the CDW or SDW introduces an energy gap in the single-particle excitation spectrum. As a result, $\sigma(\omega)$ is expected to decrease at frequencies within the gap (to zero in one-dimensional systems), and the corresponding oscillator strength is shifted to frequencies above the gap. In addition, in the density-wave state there is a collective mode that can be described as a sliding CDW (or SDW).[14–17]

The spectral features in the data shown in Figs. 1–3 resemble those expected for a density-wave state, for example, as in (TMTSF)$_2$PF$_6$, where a SDW gap is formed at around

100 cm^{-1} in the direction perpendicular to the chains.[19] With this interpretation, the resonance at 70 cm^{-1} would be identified with the pinned collective mode. The spectral weight within the 70-cm^{-1} resonance corresponds to approximately 10% of the oscillator strength Ω_p^2, which was redistributed from below 2Δ to above 2Δ.

Typically, however, the transition to a density-wave state is described as a second-order transition in which the energy gap goes smoothly to zero at the critical temperature. In contrast, the temperature independence of the gap feature observed in Figs. 1 and 2 suggests a first-order transition. Moreover, within the density-wave picture, the sliding mode is pinned at a finite frequency by higher-order commensurability or by defects and disorder.[15,16] Since PPy-PF$_6$ is a disordered metal near the M-I transition, one would expect disorder pinning to be locally random. Thus the 70-cm^{-1} resonance, which appears only at 250 K and below, might be alternatively described as an infrared-active vibrational mode (IRAV) or a phase phonon rather than a pinned collective mode[20,21]. However, the 70-cm^{-1} resonance is well below the principal IRAV modes of the PPy chain (which appear in the mid-ir region at all temperatures; see Figs. 1 and 2). Therefore, we interpret the 70-cm^{-1} resonance as the lowest-frequency IRAV mode, the pinned collective mode, in the ordered density-wave state with $2\Delta/hc \approx 100\,\mathrm{cm}^{-1}$.

Alternatively, since the gap spans only a part of the Fermi surface, the results reported here can be interpreted in the context of the correlation induced semimetallic state recently proposed by Vescoli *et al.*[22]

In summary, below 250 K, the reflectance data indicate the formation of an energy gap ($2\Delta/hc \approx 100\,\mathrm{cm}^{-1}$). Despite the energy gap, PPy-PF$_6$ remains metallic at low temperatures, implying that the gap spans only a part of the Fermi surface. The results are discussed in terms of the formation of a density-wave ground state. The need for still higher-quality samples with longer mean free path in the metallic state is evident. Nevertheless, the results reported here indicate that the rich physics of low-dimensional conductors can be observed and explored in conducting polymers.

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