Dynamics of Correlated Two-Dimensional Materials: The $2H$-$TaSe_2$ Case

V. Vescoli and L. Degiorgi
Laboratorium für Festkörperphysik ETH Zurich, CH-8093 Zurich, Switzerland

H. Berger and L. Forró
Departement de Physique, EPF Lausanne, CH-1015 Lausanne, Switzerland

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We report a study of dc transport properties up to 600 K and of the optical response over a broad spectral range of the two-dimensional (2D) dichalcogenide $2H$-$TaSe_2$. Our findings suggest a dynamics of the charge excitation spectrum dominated by two relevant features: a Drude contribution, which narrows with decreasing temperature, and a broad pseudogaplike feature in the midinfrared range, which is present at all temperatures below 300 K. The implications of these results with respect to the charge-density-wave phase transition at 122 K and more generally for the excitation spectrum of 2D correlated systems, e.g., the high temperature superconducting cuprates, will be addressed. [S0031-9007(98)06527-2]

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The understanding of the physical properties of two-dimensional (2D) correlated systems recently regained a lot of importance, because of the discovery of the high-temperature superconducting cuprates. This is mainly because of the variety of correlations acting and of the instabilities occurring in 2D systems. The 2D layered transition-metal dichalcogenides (like, e.g., $1T$-TaS_2 and $2H$-$TaSe_2$) are relatively simple and nonmagnetic systems which exhibit a range of charge-density-wave (CDW) transitions [1]. The pronounced quasi-2D nature of the crystallographic structure leads to strongly anisotropic physical properties and approximately cylindrical Fermi surfaces. Obviously, the Fermi surface-driven instabilities are generally weaker in 2D than in 1D systems. In this latter case, the instability induced by the Peierls transition [2,3] reflects a strong enhancement of the static electronic susceptibility, which develops at selected wave vectors spanning the Fermi surface (i.e., the so-called Fermi surface nesting at $q = 2k_F$). Nevertheless, under particular nesting conditions, or as a result of saddle-point singularities [4], the electronic susceptibility can be sufficiently enhanced even in 2D for a CDW to develop. At variance with the 1D case, however, 2D materials remain metallic in the presence of the CDW, since energy gaps can open only at discrete points of the Fermi surface. Moreover, quasi-2D systems should not present the peculiar 1D spectroscopic properties (like, e.g., photoemission and optics [5,6]), for which a possible Luttinger liquid (or marginal Fermi liquid) scenario has been suggested [7].

In this Letter, we report our investigation of the dynamics of the charge excitation spectrum as well as of the transport properties of $2H$-$TaSe_2$, which undergoes a second-order transition to an incommensurate triple CDW at $T_1^{\mathrm{CDW}} = 122$ K, followed by a first-order lock-in transition to a 3×3 commensurate phase at $T_2^{\mathrm{CDW}} = 90$ K [1]. First optical investigation performed above the far-infrared (FIR) spectral range (i.e., $0.04 < \omega < 5$ eV) [8] suggested a weak gap structure with threshold near 0.25 eV, indicating moreover that $2H$-$TaSe_2$ retains most of its metallic bands, with gaps opening over a rather restricted region in q space [8].

The main motivation is related to the possibility that $2H$-$TaSe_2$ could serve as a model system for understanding the still puzzling data of other (2D) highly correlated electronic systems, such as the high-T_c superconducting cuprates (HTSC). For this purpose, $2H$-$TaSe_2$ is indeed an excellent material, because it shares many physical properties with HTSC: like the layered-like structure and qualitatively similar resistivity (see below) and susceptibility [1,9]. Our optical data reveal the progressive formation of a narrow Drude-like mode in FIR by lowering T below T_1^{CDW} and a pseudogaplike feature which appears at any temperatures below 300 K, implying that early interpretation [8] of the excitation spectrum must be revisited.

The $2H$-$TaSe_2$ sample was prepared from the elements by a reversible chemical reaction with iodine as a transport agent [10], and has the form of a platelet of approximately 3.5×2.5 mm^2. Figure 1 displays the temperature dependence of the resistivity $\rho(T)$ up to 600 K, which was measured with the conventional four point contacts method and which agrees with previous results [1]. The inset in Fig. 1 shows an enlargement of $\rho(T)$ around T_1^{CDW} and T_2^{CDW}. The major features are the weak change of slope around 300 K and the sudden drop of $\rho(T)$ at the normal-incommensurate CDW phase transition around 120 K, while the incommensurate-commensurate CDW transition at 90 K is barely observable. The absence of a well defined increase of $\rho(T)$ at T^{CDW} would suggest a scenario where the Fermi surface and consequently the charge excitation spectrum are little affected by the transition. Equivalently, the transport data indicate that the scattering rate seems to be

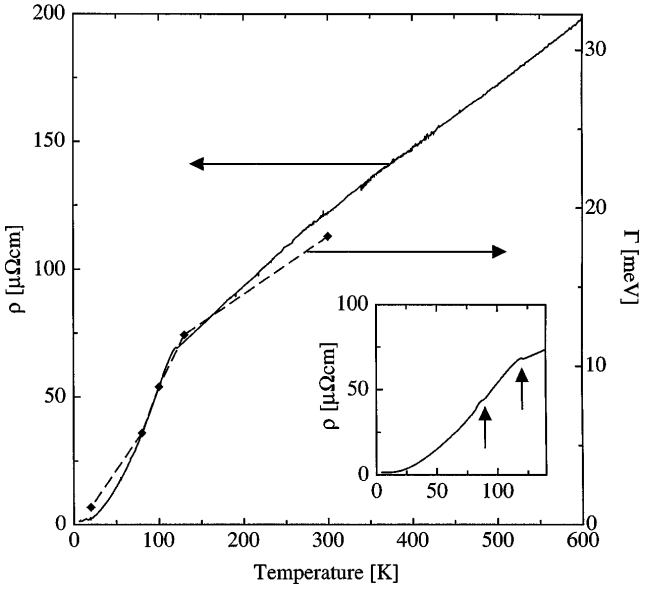

FIG. 1. Temperature dependence of the resistivity $\rho(T)$ of $2H$-$TaSe_2$ up to 600 K, scaled with the temperature dependence of the Drude scattering rate (see text) below 300 K. The inset displays an enlargement of $\rho(T)$ around the two CDW phase transitions (arrows), pointing out the corresponding weak anomalies in the transport properties.

strongly reduced below 120 K, because of the freezing out of scattering channels.

The electrodynamic response has been achieved by measuring the reflectivity $R(\omega)$ along the 2D layer planes as a function of temperature ($10 \leq T \leq 300$ K) over a broad spectral range (2 meV $\leq \omega \leq$ 12 eV) by applying several spectrometers. This considerably extends the previously measured spectral range [8], allowing for a reliable application of the Kramers-Kronig transformation in order to obtain the complex optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ [11].

Figure 2 presents $R(\omega)$ and the real part $\sigma_1(\omega)$ of the optical conductivity at relevant temperatures above and below the corresponding incommensurate and commensurate CDW phase transitions. By lowering the temperature and by crossing the respective phase transitions we do not observe any sharp changes in the optical spectra but rather a continuous evolution which can be summarized as follows. Below the visible spectral range $\sigma_1(\omega)$ is characterized at all temperatures by a broad midinfrared (MIR) absorption overlapped to a low frequency Drude-like contribution (see below). By lowering the temperature from 300 K there is a redistribution of the spectral weight among the two components accompanied by a progressive narrowing of the Drude resonance in the FIR range. The broad maximum of the MIR absorption slightly shifts towards higher frequency (i.e., from approximately 0.07 up to 0.08 eV) between 300 and 80 K and in a somehow more pronounced way [i.e., at about 0.15 eV at 10 K; see inset of Fig. 2(b)] below 80 K. The overall behavior of $\sigma_1(\omega)$ and particular its dc limit (i.e., $\omega \rightarrow 0$) agree with the trend of the transport properties. The onset of the commensurate phase transition at T_2^{CDW} leaves the excitation spectrum as well as the transport and thermodynamic [1] properties almost unaffected.

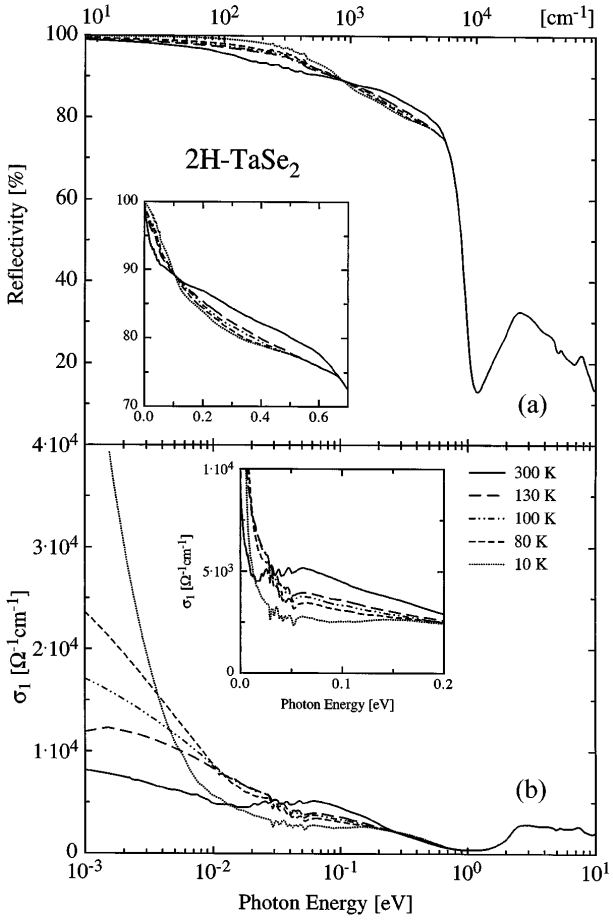

FIG. 2. (a) Reflectivity and (b) real part of the optical conductivity of $2H$-$TaSe_2$ at relevant temperatures below and above the CDW phase transitions at T_1^{CDW} and T_2^{CDW}, respectively. The insets display an enlargement of the frequency range below 0.7 and 0.2 eV for $R(\omega)$ and $\sigma_1(\omega)$, respectively.

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 this material. First of all, from the width of the narrow Drude-like mode at low frequencies one can estimate the scattering rate (Γ) of the free charge carriers effectively involved in the metallic contribution of $\sigma_1(\omega)$. This could be also obtained by applying the phenomenological Lorentz-Drude model [12]. Details of the fit procedure will be presented elsewhere. The temperature dependence of Γ below 300 K, normalized to $\rho(T)$, is shown in Fig. 1, which highlights the sudden decrease of the (Drude) scattering rate below T_1^{CDW}. The immediate conclusion is that both the transport and optical properties are the consequence of the freezing out of the scattering

channels. Second, our optical results do not display any clear signature of a CDW-gap feature, developing in coincidence with the onset of the CDW phase transition. This is in clear contrast with respect to the conclusion arrived at by Barker *et al.* [8]. With an *ad hoc* interpolation procedure, they were able to artificially subtract the high temperature optical conductivity (considered here as background) from the low temperature one (i.e., at $T < T_2^{\mathrm{CDW}}$). Such an analysis led to a gaplike absorption (i.e., a CDW Peierls gap) peaked at approximately 0.3 eV (an order of magnitude larger, however, than the value of $3.52k_{\mathrm{B}}T^{\mathrm{CDW}}$ estimated within the mean-field BCS theory). Around 0.3 eV our spectra are temperature independent and do not give evidence for any gaplike feature. Instead, there is a slight shift of spectral weight from energies around 0.07 to about 0.15 eV upon lowering the temperature. Nevertheless, the mode strength of the MIR absorption remains constant. Basically, it is the high frequency tail of the Drude response which shifts to lower frequencies because of its narrowing. Moreover, the MIR absorption in our spectra persists up to temperature larger than T_1^{CDW}. It is worth noting that the data of Barker *et al.* did not extend below the midinfrared range. Therefore, we might speculate that the disagreement between ours and Barker's data, as far as the gap is concerned, could be ascribed to the limited frequency range investigated in Ref. [8].

Several other experiments addressed the problem of possible evidence for the Peierls gap due to the formation of the CDW condensate but contrasting estimates have been presented. Here, we quote a few photoemission results [13,14]. Both Dardel *et al.*'s and Liu *et al.*'s work, the latter one with enhanced angle resolution, suggest that the Fermi surface is gapped by the CDW phase transitions, yet such a gapping occurs only over a small fraction of the Fermi surface [13,14]. Similar to optics and transport properties, these data are not affected by the incommensurate-commensurate CDW transition at 90 K. An estimation of the gap from the measured spectral function is quite difficult and possibly beyond the resolution of the photoemission technique. Nevertheless, it was found that spectral intensity is lost at 20 K at about 0.5 of the Γ-K direction in the Brillouin zone, which is accompanied by a transfer of the removed spectral intensity at higher energies. A gap of about 160 meV was inferred [13]. The most recent photoemission data further confirm that in the normal state two Fermi surface crossings along Γ-K occur and that a saddle band lies very close to Fermi level E_{F} for an extended region along Γ-K. In the CDW state, the energy gap is found to be near zero at the first Fermi surface crossing and large in the saddle band region, in agreement with prediction from the "saddle-point" CDW mechanism by Rice and Scott [4,14]. The small fraction of the Fermi surface involved in the gapping and consequently the small fraction of free charge carriers, which condense in the CDW, are also confirmed by the temperature independent spectral weight of the low frequency Drude-like metallic contribution in $\sigma_1(\omega)$.

Barker *et al.* anticipated that a narrow Drude with an anomalously low and very temperature dependent scattering should develop at low frequencies (i.e., at $\omega <$ 0.01 eV, below the measured spectral range in Ref. [8]), because their spectra did not extrapolate towards the measured dc value [8]; a guess which is now confirmed by our measurement in FIR [Fig. 2(b)]. Barker *et al.* also envisaged the interesting possibility that the low frequency (Drude) spectral weight is associated with a sliding-CDW mode [8]. On the contrary, we believe that the scaling between Γ and $\rho(T)$ (Fig. 1) indicates the suppression of the scattering channels associated to q vectors of the Fermi surface's pockets involved in the CDW condensate.

The optical conductivity of several quasi-one-dimensional systems, like, e.g., $K_{0.3}MoO_3$ with $T_{\mathrm{CDW}} \sim 180$ K, is characterized at $T > T_{\mathrm{CDW}}$ by a pseudogaplike feature at about 0.2 eV, which develops in a true CDW gap below T_{CDW}, and by a narrow (Drude-like) mode centered at zero frequency [15]. This was suggested to be the consequence of fluctuation effects where the formation of short range CDW segments leads to a partial gapping of the Fermi surface and to the so-called low frequency (i.e., narrow Drude term) paraconductivity contribution above T_{CDW} [15]. Such (1D) fluctuation effects are supposed to develop in the temperature range between the mean-field temperature T_{MF} ($\sim$600 K for $K_{0.3}MoO_3$) and T_{CDW}, the critical temperature for the 3D Peierls transition. Also the 1D organic Bechgaard salts present an excitation spectrum, deviating quite remarkably from a conventional Drude behavior [6,11]. Besides a low frequency narrow mode centered at zero frequency, $\sigma_1(\omega)$ above the spin density wave (SDW) phase transition temperature T_{SDW} is dominated by a FIR mode which develops with decreasing temperature. It has been ascribed to a charge (Mott) correlation gap, consistent with the prediction of models associated to a Tomonaga-Luttinger liquid approach [11].

There are many common features in the normal state $\sigma_1(\omega)$ of 1D and 2D CDW systems, even though their origin could be different. On the one hand, we can expect that 2D fluctuation effects associated with short range CDW segments are also present in $2H$-$TaSe_2$ and lead to the pseudogap at about 0.07 eV already below 300 K, which merges in a partial CDW gap at about 0.15 eV below 80 K. This would agree with the photoemission estimation. The crossover to a long range ordered CDW below T_1^{CDW} in $2H$-$TaSe_2$ and its lock-in state at T_2^{CDW} further suppress the scattering channels, causing the sharp drop in the resistivity and Drude scattering rate (Fig. 1). On the other hand, the short range CDW segments above 120 K might be considered as objects strongly scattering the free charge carriers. This could suggest a scenario where the low frequency (i.e., long wavelength limit) excitation spectrum is characterized by a free (Drude-like)

charge carriers contribution, while at high frequency (i.e., short wavelength limit) a local bound state like excitation identified with the MIR absorption can develop. The transport would then be dominated by strong electron-electron scattering, and when the phase space is reduced by the CDW long range ordering, the scattering channels are less effective. The strength of the scattering can be seen in the fact that although we lose some part of the Fermi surface, the resistivity decreases by 2 orders of magnitude from 120 down to 4 K.

Finally, it is worthwhile to qualitatively compare $2H$-$TaSe_2$ with the situation encountered in some HTSC. There is mounting evidence that the normal state of underdoped HTSC is also dominated by a pseudogap. A number of physical probes, as, for instance, optics [16,17], show that below a characteristic temperature T^*, which can be well above the superconducting transition temperature T_c, the physical response of HTSC materials can be interpreted in terms of the formation of a partial gap or a pseudogap (corresponding to a broad MIR absorption peaked around 0.1 eV), by which a suppression of the density of low-energy excitations is understood. This gap, which is overlapped to a Drude component in the normal phase, persists in the superconducting state. While the optical spectra of $2H$-$TaSe_2$ and HTSC have rather similar common features, particularly with respect to the two components in $\sigma_1(\omega)$ (i.e., Drude term and broad MIR pseudogaplike absorption), the physics of both systems may be quite different. In HTSC, T^* defines the opening of a gap in the spin excitation spectrum leading to a suppression of scattering channels. From the above discussion, T_1^{CDW} for $2H$-$TaSe_2$ could be identified with T^* and T_{MF} with the temperature where short range antiferromagnetic correlations start to build up in HTSC. Our measurements set room temperature as the lower bound for T_{MF}.

In summary, the optical response of $2H$-$TaSe_2$ provides a scenario where the dynamics of the charge excitation spectrum is dominated by two components below about 0.3 eV. There is a Drude term which narrows progressively with decreasing temperature with a scattering rate following the transport properties, and a MIR absorption at all temperatures, which might be associated with a pseudogap feature indicating a partial Fermi surface gapping already above T_1^{CDW}. There are strong analogies with the excitation spectra of 1D systems and even HTSC. Particularly the pseudogap absorption seems to be a generic feature of 1D as well as 2D layered-like correlated systems. As a future outlook, it appears of importance to optically investigate $2H$-$TaSe_2$ along the less conducting axis (i.e., equivalent to the c axis in HTSC) and of intentionally and controlled doped materials, since defects and possibly interlayer coupling are supposed to have a strong influence on the 2D electronic properties.

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