Charge Dynamics of 2H-$TaSe_2$ along the Less-Conducting c-Axis

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(Received 11 July 2000)

We present an optical study of 2H-$TaSe_2$ along the less conducting c-axis. This dichalcogenide compound belongs to a large class of conductors called "bad metals" (with a mean free path smaller than the lattice constant along the c-axis), which also includes the superconducting cuprates. The optical response shows the progressive development of a pseudogaplike feature with decreasing temperature. The spectral weight lost by the opening of such a pseudogap goes into the narrow Drude component, developing at low frequency and temperature. There is no violation of the sum rule in 2H-$TaSe_2$ contrary to the cuprates.

DOI: 10.1103/PhysRevLett.86.4136 PACS numbers: 78.20.–e, 71.45.Lr, 74.25.Gz

The two-dimensional (2D) layered transition metal dichalcogenides (e.g., 2H-$TaSe_2$ and 2H-$NbSe_2$) recently received a lot of attention, since they serve as a model material for understanding the still puzzling data of other highly correlated 2D electronic systems, such as the high-T_c superconductors (HTC). They share many physical properties with the HTC cuprates, such as the layered structure and qualitatively similar resistivity and susceptibility [1,2]. 2H-$TaSe_2$ is a relatively simple and nonmagnetic system which exhibits a range of charge-density-wave (CDW) transitions at $T_1^{\mathrm{CDW}} = 122$ K (incommensurate triple CDW) and $T_2^{\mathrm{CDW}} = 90$ K (first-order lock-in transition to a 3×3 commensurate phase) [1]. Our recent optical investigation of 2H-$TaSe_2$ in the (2D) ab plane provides a scenario where the dynamics of the charge excitation spectrum is dominated by two components below about 0.3 eV [3]. There is a Drude term, which narrows progressively with decreasing temperature and with a scattering rate following the transport properties and a mid-infrared (MIR) absorption at all temperatures, which was associated with a pseudogap feature indicating a partial Fermi surface gapping already above T_1^{CDW} [3]. There are strong analogies with the excitation spectra of HTC [4]. Particularly, the pseudogap absorption seems to be a generic feature of 2D layered correlated systems. The similarity in the optical fingerprints of HTC and 2D dichalcogenides is even more striking in the case of 2H-$NbSe_2$, which undergoes a superconducting phase transition at 7.2 K [1]. Indeed, the suppression of the Drude component, because of the development of the superconducting condensate, clearly reveals the MIR absorption of 2H-$NbSe_2$ as in HTC [5].

A full understanding of the optical response and, in a broader perspective, of the intrinsic physics of 2D layered systems can be evinced by the investigation of the anisotropic electrodynamic response along the three crystallographic direction [6]. We suggested [3] that the investigation of the dc transport and charge dynamics along the less conducting c-axis of 2H-$TaSe_2$ would be very relevant. The investigation of the c-axis dc and optical response in the dichalcogenides is of particular importance because we are dealing with a truly two-dimensional system without Cu-O units in its structure. In HTC, the frequency and temperature dependence of the interplane conductivity is still one of the long-standing mysteries. Particular attention has focused on the spectral weight, the integral of the real part of the conductivity over some frequency range, which has been observed to have strong and anomalous temperature dependence in its distribution [7]. In general, it is believed that the c-axis dynamics and its distribution of spectral weight can be used to shed light on the nature of the collective states, either superconducting or CDW, and their peculiar characteristics [8–10]. We report our newest dc and optical results on 2H-$TaSe_2$ along the c-axis. We find a quite similar optical response (i.e., mainly characterized by the pseudogap feature) as in HTC cuprates along the c-axis, but contrary to them the spectral weight is fully conserved and does not present any anomaly, which could be due to the different nature of the pairing channel between superconductors and CDW systems [8].

The 2H-$TaSe_2$ sample was prepared from the elements by a reversible chemical reaction with iodine as a transport agent [3]. The sample growth conditions were optimized for making thick single crystals. The sample used in the optical study had ab-plane dimensions of 5×5 mm^2, while in the c-axis direction it was 4 mm long. The crystal was embedded into epoxy in order to polish an optically flat surface. The polishing procedure does not lead to a "contamination" of the c-axis response with in-plane properties. A crystal from the same batch was characterized with dc transport measurement in the ab plane and along the c-axis with a conventional four-probe technique. The data are shown in the 4–400 K range in Fig. 1. The resistivity along the c-axis is qualitatively similar to the one within the ab plane, even though it is about 25 times larger at room temperature, and the anisotropy increases

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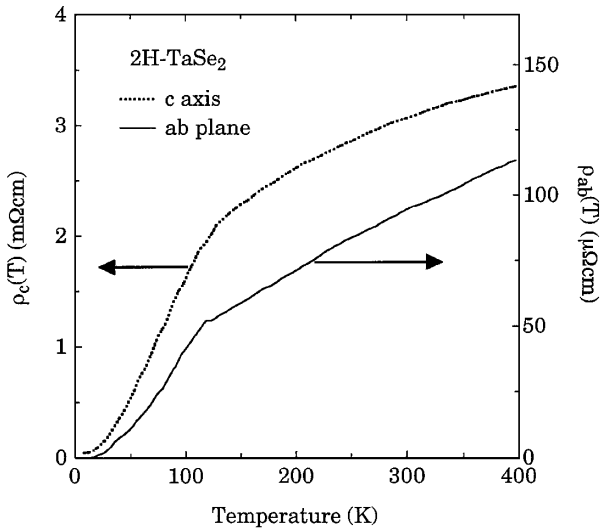

FIG. 1. dc transport of 2H-$TaSe_2$ along the c-axis and in the ab plane [3].

to 50 around 100 K. Above the CDW phase transition around 120 K the c-axis $\rho(T)$ is increasing monotonically, with a tendency to saturation around 400 K, while $\rho(T)$ in the ab plane decreases almost linearly from 400 down to 120 K. In optimally doped good quality HTC single crystals, both the in-plane and out-of-plane resistivities have metalliclike slope. When the samples are underdoped, the in-plane resistivity shows a linear temperature dependence above T^* and goes below the linearity for $T < T^*$ and the out-of-plane resistivity picks up a nonmetallic temperature dependence. It is not clear yet whether this nonmetallic behavior in dc transport is intrinsic to the underdoped state or it is due to the disorder introduced by underdoping. For example, the two-chain $YBa_2Cu_4O_8$ compound "124," which is intrinsically underdoped, has a metalliclike T dependence for the interplane transport and a saturation above 200 K has been seen [11], similar to the dichalcogenides (Fig. 1).

The calculation of the electronic mean free path (l) within a simple Drude model gives $l \sim 1$ Å along the c direction (i.e., much smaller than the lattice constant), while in the ab plane $l \sim 16$ Å (i.e., 5 times the lattice constant) [12]. A mean free path of the order of the lattice constant means also that the out-of-plane dc transport is beyond the Ioffe-Regel limit. Therefore, the resistivity within the Boltzmann theory should not show a metalliclike transport along the c direction. The positive slope of $\rho_c(T)$ (i.e., $d\rho_c/dT > 0$) evokes the same puzzle for this conductor as for a whole class of materials with narrow bands, very often called *bad metals*. Metalliclike transport is observed even for a very high value of the resistivity, as in fullerenes, manganites, and organic conductors [13]. How it is possible to have the metallic conductivity without extended states is a major and yet unresolved problem. The generality of such puzzling transport features is a further motivation for studying how this bad metallicity does manifest itself in the optical response along the c-direction.

The electrodynamic response has been achieved by measuring the reflectivity $R(\omega)$ at different temperatures with light polarized along the c-axis and along the direction parallel to the ab plane, where we reproduced our previous results [3]. The real part $\sigma_1(\omega)$ of the optical conductivity is obtained by Kramers-Kronig transformation of the $R(\omega)$ spectra [3]. Figure 2(a) displays the measured optical reflectivity at various temperatures along the c-axis and, for comparison, $R(\omega)$ within the ab plane at 20 and 300 K [3]. The anisotropy of the optical response is quite evident. The reflectivity spectra for both polarizations and at any temperatures do extrapolate to $\omega = 0$ with the Hagen-Rubens law, $R(\omega) = 1 - 2(\omega/\sigma_{dc})^{1/2}$, using σ_{dc} values in fair agreement with the transport measurements. There are a few interesting features in the temperature dependence of $R(\omega)$ along the c-axis: first, the absorption at 6000 cm^{-1} which gets stronger with decreasing temperature and has a high frequency tail coinciding with the plasma edge of $R(\omega)$ within the ab plane. Around 2000 cm^{-1} we do observe another feature developing with decreasing temperature similarly to the MIR band seen for the ab plane [3]. The temperature dependence at low frequencies is also quite remarkable: the reflectivity above

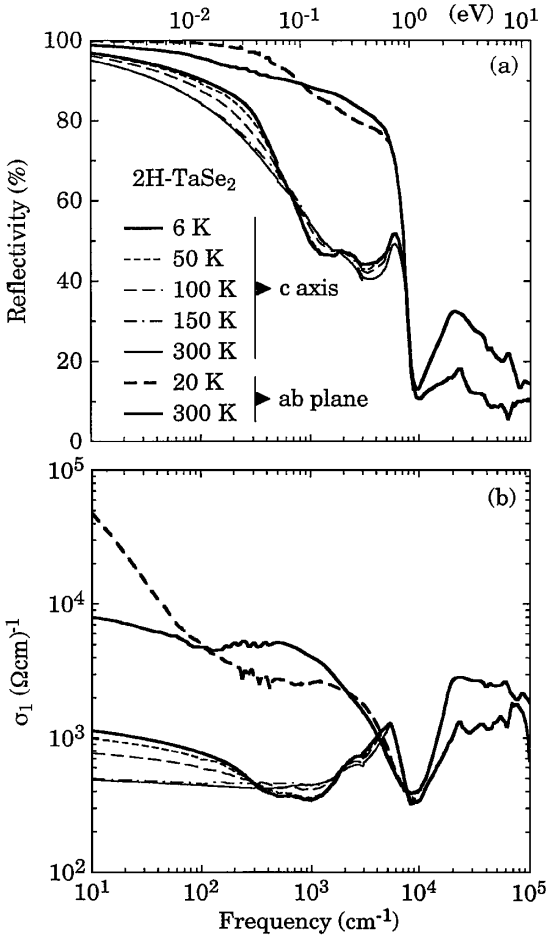

FIG. 2. (a) Optical reflectivity and (b) real part $\sigma_1(\omega)$ of the optical conductivity of 2H-$TaSe_2$ along the c-axis and within the ab plane.

120 K displays an over-damped-like plasma edge below 1000 cm^{-1}. Below 120 K, this plasma edge gets sharper with decreasing temperature.

In Fig. 2(b), we compare the corresponding optical conductivities (using a log-log scale), while Fig. 3 emphasizes the temperature dependence of $\sigma_1(\omega)$ along the c-axis below 5000 cm^{-1}. Again we can recognize a few fingerprints associated to the features already mentioned in Fig. 2(a) for light polarized along the c-axis. Particularly, one can notice the Drude component at low frequency (i.e., $\omega < 300$ cm^{-1}), which narrows with decreasing temperature signaling the suppression of scattering channels. This also means that the scattering rate, coinciding with the width of the Drude component, decreases remarkably below 100 K. It is worthwhile to remark that at 300 and 150 K $\sigma_1(\omega)$ along the c-axis is flat and slightly increases with increasing frequency. While the finite $\sigma_1(\omega \to 0)$ value implies a Drude-weight background, the overall shape of $\sigma_1(\omega)$ in far infrared is not the one expected for a good metal. Combined with an unphysically short mean free path extracted above from $\rho_c(T)$ it would suggest again a "bad metal" behavior at high temperatures, more compatible with a disordered and incoherentlike transport. The sharpening of the low frequency plasma edge in $R(\omega)$ and the narrowing of the Drude component in $\sigma_1(\omega)$ along the c-axis at low temperatures indicate the onset of coherent transport and dynamics. In the range 300–1000 cm^{-1}, there is a suppression of spectral weight with decreasing temperature suggesting the opening of a pseudogap below 2000 cm^{-1} (Fig. 3). The optical conductivity is then dominated by the strong absorption at about 6000 cm^{-1}, where spectral weight is redistributed from the high frequency tail to the low frequency tail of the absorption with decreasing temperature. As a reminder of the discussion on the data within the ab plane, performed in Ref. [3], we just recall the narrowing of the Drude component, as well as the shift of the MIR absorption from 700 to 2000 cm^{-1} with decreasing temperature [Fig. 2(b)].

Our previous discussion on the ab-plane spectra in 2H-$TaSe_2$ [3] pointed out the similarity with the optical response of HTC, which is mainly characterized by a pseudogap feature developing below the characteristic temperature T^* (with $T^* > T_c$ for the underdoped and $T^* \approx T_c$ for the optimally and overdoped cuprates [4]). While in HTC the pseudogap opens in the spin excitation spectrum, in 2H-$TaSe_2$ the MIR absorption in the ab plane is the consequence of the partial gapping of the Fermi surface due to the formation of short range order CDW segments [3]. In the CDW ground state (i.e., $T < T_2^{\mathrm{CDW}}$) the CDW segments undergo a long range ordering, making the scattering channel less effective and inducing the narrowing of the Drude components [3]. A similarly interesting comparison can be performed also with respect to the c-axis spectra. The suppression of scattering leads to the narrowing of the Drude component in $\sigma_1(\omega)$ [Figs. 2(b) and 3] or alternatively to the sharpening of the low frequency (i.e., below 1000 cm^{-1}) plasma edge in $R(\omega)$ [Fig. 2(a)]. This latter feature is very much compatible with the behavior of $R(\omega)$ in HTC along the c-axis [7]. It is worth noticing that in (disordered) underdoped HTC the overdamped behavior is more pronounced because of the semiconductinglike resistivity at high temperature (in contrast to the decreasing resistivity with decreasing temperature in the dichalcogenides). Moreover because of superconductivity, the $R(\omega)$ spectra of HTC are quite similar to those expected for the London limit and the almost total reflectivity at low temperature [7] indicates a scattering rate tending to zero. In the optical conductivity spectra this implies a delta function at $\omega = 0$ [7]. For 2H-$TaSe_2$, the small but finite scattering rate leads to the narrow Drude component even at T much smaller than T_2^{CDW}. Along the c-axis, the pseudogap feature in 2H-$TaSe_2$ is seen by the decreasing $\sigma_1(\omega)$ in the spectral range between 300 and 2000 cm^{-1} and can be well recognized at $T < 90$ K, i.e., below T_2^{CDW}. Indeed, at 300 and 150 K $\sigma_1(\omega)$ is rather flat in that range while at 100 K one can observe an incipient suppression of $\sigma_1(\omega)$ which is pronounced at 50 and 6 K (Fig. 3).

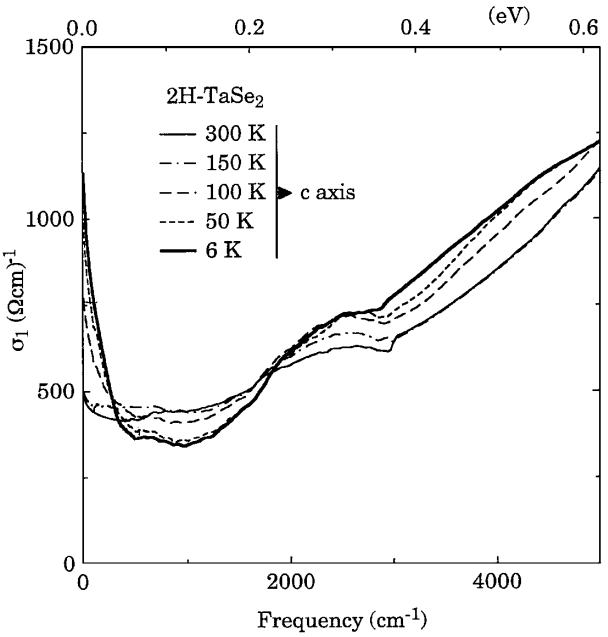

FIG. 3. Temperature dependence of $\sigma_1(\omega)$ of 2H-$TaSe_2$ in the spectral range below 5000 cm^{-1}.

In view of the comparison with the HTC optical response, it is very instructive to discuss the temperature dependence of the spectral weight along the c-axis [Figs. 2(b), 3, and 4]. There are two relevant ranges: the first one above 2000 cm^{-1} up to 10^4 cm^{-1} and the second one below 2000 cm^{-1}. In the first range there is a redistribution of spectral weight with decreasing temperature from high to low energies around the absorption at 6000 cm^{-1} [14]. Below 2000 cm^{-1}, we found that the spectral weight lost by the pseudogap opening is shifted to the narrow Drude component. Indeed, Fig. 4 shows that the spectral weight at low frequency is fully recovered up

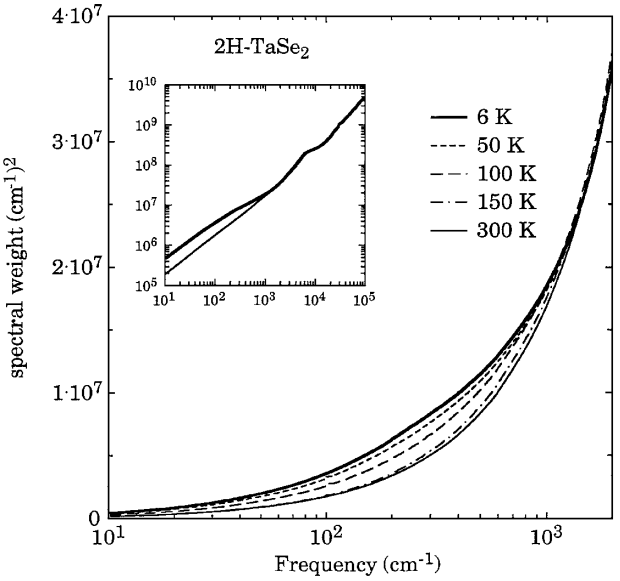

FIG. 4. Temperature dependence of the spectral weight of 2H-$TaSe_2$ below 2000 cm^{-1}. Inset: the spectral weight at 300 and 6 K over the whole measured spectral range.

to 2000 cm^{-1}. Alternatively we can say that by increasing the temperature the broadening of the Drude component shifts the spectral weight to higher frequencies and fills in the pseudogap (see also Fig. 3). This is actually quite different from the situation in HTC [7]. Specifically for the underdoped cuprates, about 50% of the spectral weight of the condensate associated with the Josephson-like collective mode is distributed over a broad spectral range, extending through the mid-IR and even higher [7]. The sum rule violation, in the studied frequency range, in HTC was recently addressed within a variety of theoretical approaches [6,8–10]. Anderson interprets the c-axis optical response on the basis that the entire condensation energy comes from the interlayer Josephson coupling [6]. Kim and Carbotte discussed the influence of coherent and incoherent c-axis coupling [9] while Hirsch and Marsiglio framed the c-axis spectral weight problem within the so-called hole-superconductivity model [10]. Ioffe and Millis [8] attributed such a peculiar behavior of the sum rule to the natural consequence of the superconducting pairing without long range phase coherence. This leads to the famous factor of 2 (i.e., 50% missing weight) [8]. In HTC neither model [8–10] is fully consistent with the experimental findings [7]. In view of our comparison between HTC and 2H-$TaSe_2$, we mention only that the violation of the c-axis sum rule is not expected for short range spin or charge density wave order, as suggested in Ref. [8]. The full recovery of spectral weight within the spectral range of the pseudogap in 2H-$TaSe_2$ is a convincing demonstration of the different nature of the relevant correlations involved in the CDW ground state (i.e., particle-hole pairing with $q = 2k_F$, k_F being the Fermi wave vector) of 2H-$TaSe_2$ with respect to those in the superconducting state (i.e., particle-particle pairing with $q = 0$) of the cuprates.

In conclusion, we have investigated the c-axis optical response of 2H-$TaSe_2$, which presents similar features as the c-axis electrodynamic response in HTC. Nonetheless, the spectral weight distribution is substantially different for the two classes of compounds, in accordance with the different intrinsic nature of the superconducting or charge-density-wave ground states. The conservation or violation of the sum rule can then be used in order to discriminate among different pairing channels. The obvious future development consists in the measurement of the c-axis optical response of a truly two-dimensional superconducting system without Cu-O unit, like 2H-$NbSe_2$ for which experiments are in progress. This will provide further useful experimental information towards a unified microscopic picture of CDW and superconducting phases and might illuminate the way for the understanding of complex physics in transition metal systems [15].

The authors thank D. Basov, A. H. Castro-Neto, M. Grioni, G. Gruner, and A. J. Millis for stimulating discussions and G. Beney for the sample preparation. The financial support by the Swiss National Science Foundation is acknowledged.

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