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Coexisting one-dimensional and three-dimensional spectral signatures in $TaTe_4$

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Using angle-resolved photoemission spectroscopy, we probe the electronic band structure of $TaTe_4$ single crystal samples. Resistivity and optical measurements were also performed on the same samples. The experimental data indicate a combination of quasi-one-dimensional and three-dimensional electronic properties. We observe a finite spectral intensity, but no dispersing quasiparticle states near the chemical potential. [S0163-1829(99)06611-4]

I. INTRODUCTION

The electronic properties of the compound $TaTe_4$ present some puzzling aspects. Like other transition-metal chalcogenides, $TaTe_4$ exhibits a charge-density-wave (CDW) instability, and a related periodic lattice distorsion (PLD), typical of quasi-one-dimensional (1D) systems. The tendency toward this ordered state is strong, and the system is in a CDW phase over the entire temperature range where it is chemically stable. At the same time, the transport and optical properties are those of an almost isotropic three-dimensional metal. In this paper we present angle-resolved photoemission spectroscopy (ARPES) data showing that an unusual coexistence of 1D and 3D features characterizes the spectral properties of $TaTe_4$.

Normal three-dimensional metallic systems are described as Fermi liquids. In such systems, ARPES reveals dispersing coherent states, which cross the Fermi level, thereby establishing the Fermi surface.[1] The leading edge of the spectral function exhibits an energy-resolution-limited cutoff at the chemical potential due to the Fermi-Dirac distribution function. The spectral properties of metallic one-dimensional systems are remarkably different. No dispersing coherent states crossing the Fermi level have been observed by ARPES so far. The spectral function leading edge is not resolution limited, and does not exhibit a Fermi-Dirac cutoff. Instead, the intensity at the chemical potential is strongly reduced, and a pseudogap is observed.[2–7] The origin of this unusual spectral behavior is still debated. Various models of correlated electrons in one dimension predict strong spectral weight suppression near the chemical potential.[8–11]

The crystal structure and superstructure of $TaTe_4$ is important for interpreting the photoemission data.[12–19] The average structure, corresponding to the normal phase, has a tetragonal unit cell and two chemical units per cell ($a=6.513$ Å, $c=6.812$ Å). In the structure one can identify chains of Ta atoms running along the (001) direction. Each Ta atom is surrounded by eight Te atoms in a square antiprismatic coordination. The interchain Te-Te distance is shorter than the intrachain distance, so that ${Te_2}^{2-}$ dimers are formed between adjacent chains.

Below 450 K, $TaTe_4$ is in a distorted CDW phase with a commensurate superstructure ($2a\times 2a\times 3c$), which implies a Fermi wave vector $k_F=1/3c^*$ (c^* is the reciprocal-lattice vector parallel to the chain). The Ta-Ta distance is modulated, so that Ta_3 clusters form along the chain, with a phase difference of $2/3\pi$ between adjacent chains. The conduction band derived from the metal atoms has mainly d_{z^2} character. However, there is a significant overlap of metal d and Te p orbitals. Simple chemistry considerations suggest that this band is half filled (d^1 configuration), but 1/3 filling has also been claimed to explain the observed CDW periodicity.[20]

As we show below, the resistivity indicates a three-dimensional metallic system. Similarly, optical conductivity data indicate a three-dimensional metal with almost *free* carriers. Shubnikov–de Haas[21] measurements reveal a three-dimensional Fermi surface. Structurally, however, as mentioned above, the tetrachalcogenide family has a tendency toward quasi-one-dimensional behavior due to the presence of oriented Ta-Ta chains in the structure. Unlike the 1D $(TaSe_4)_2I$ system, which has a similar structure,[22,23] the optical conductivity of $TaTe_4$ exhibits a Drude peak both perpendicular and parallel to the Ta-Ta chains, consistent with the metallic and nearly isotropic character of the material in the CDW phase.

Our ARPES data reveal a strong suppression of quasiparticle states near the chemical potential, which is a characteristic feature of 1D systems. However, we also observe a nearly k-independent intensity at E_F, a feature which is typical of normal 2D or 3D metals. Therefore the spectral properties of $TaTe_4$ exhibit a rather unique coexistence of 1D and 3D spectral signatures.

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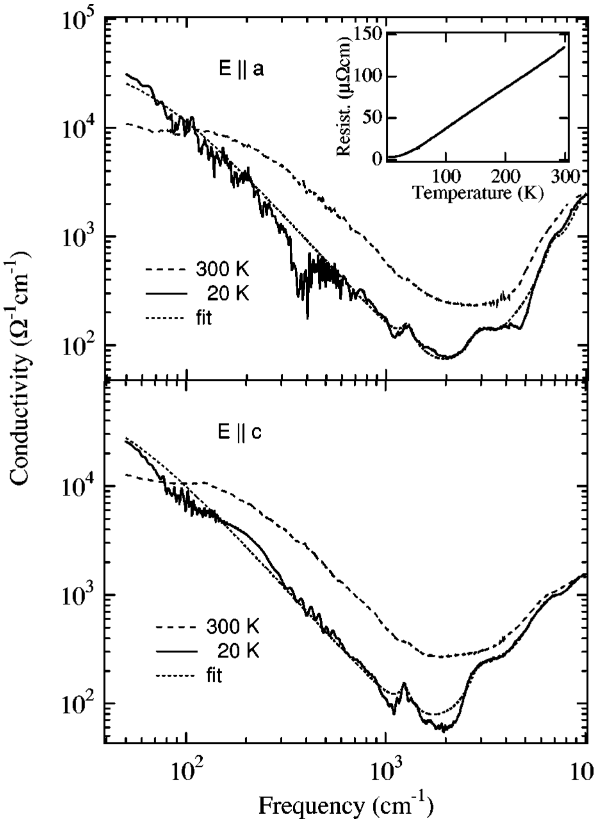

FIG. 1. Optical conductivity of TaTe$_4$ for 15 and 300 K with the electric field perpendicular and parallel to the Ta-Ta chain. (Inset) Resistivity vs temperature data measured parallel to the Ta-Ta chains.

II. EXPERIMENT AND RESULTS

Single crystals of TaTe$_4$ and NbTe$_4$ were grown in sealed quartz tubes using the vapor transport method, with tellurium chloride as the transport agent.[24] This method produced high-quality single crystals of several millimeters size, with a needlelike substructure along the crystallographic *c* axis. The crystals were characterized by x-ray crystallography and transport measurements. We show only the resistivity, optics, and photoemission data taken for TaTe$_4$; the data taken for NbTe$_4$ are similar.

Resistivity measurements were performed parallel and perpendicular to the chains by use of a four-probe configuration. Polarized reflectance measurements were made at temperatures from 15 K to room temperature. A Bruker 113 V Fourier spectrometer was used in the 40–4000-cm^{-1}(5 meV–0.5 eV) range, a Perkin Elmer grating monochromator was used in the 2000–13 000-cm^{-1}(0.25–1.6 eV) range, and a Zeiss microscope spectrometer was used for the 12 000–30 000-cm^{-1}(1.5–3.7 eV) range. The optical conductivity and other optical constants were determined by a Kramers-Kronig analysis of the reflectance, using standard extrapolations.

The inset of Fig. 1 illustrates the resistivity data, measured parallel to the Ta-Ta chains. The resistivity exhibits a metalliclike behavior down to the lowest temperature measured. Data for the perpendicular directions (not shown) indicate that the resistivity is isotropic within the experimental uncertainty, in good agreement with previous data[20]. Figure 1 illustrates the optical conductivity at 15 and 300 K both perpendicular (upper panel) and parallel (lower panel) to the chain direction, with Drude-Lorentz fits for the low temperature data. A Drude peak is evident in both directions, indicating that *free* carriers are present even in the CDW phase. The dc extrapolations for both temperatures are in reasonable agreement with the dc resistivity. The fit parameters for the Drude parts are as follows: For the perpendicular direction, the oscillator strength is $12\,400 \pm 200$ cm^{-1}, with a scattering rate of 58 ± 10 cm^{-1}. The parallel direction gives an oscillator strength of $13\,000 \pm 200$ cm^{-1} with a scattering rate of 40 ± 10 cm^{-1}. The low-temperature data show a feature near 3000 cm^{-1}(0.37 eV), which we take to be the CDW gap. Calculations of the effective number of electrons from the optical conductivity and the fits to the reflectance indicate that 20–30 % of the carriers are involved in the CDW transition. There is also an absorption in both directions at 1270 ± 20 cm^{-1} which has an oscillator strength of 800 ± 75 cm^{-1}, an order of magnitude lower than that of the CDW. We do not know its origin with certainty.[25]

The ARPES measurements were carried out in Lausanne and in Wisconsin at the synchrotron radiation center (SRC). In Lausanne we used a He discharge lamp ($h\nu = 21.2$ eV) and a Scienta ESCA-300 spectrometer. At the SRC we used linearly polarized light in the range of 15–30 eV from the NIM4 beamline, and a VSW HA 50 electrostatic analyzer mounted on a two-axis goniometer. We performed ARPES measurements at temperatures between 40 and 120 K. The thermally limited energy resolutions were 15 and 80 meV. The angular resolution was $\pm 1°$. Single-crystal samples oriented by Laue x-ray diffraction were cleaved *in situ* at a pressure of 2×10^{-10} torr to expose the (010) surface.

Figure 2 shows angle-resolved valence-band spectra along three different high-symmetry directions, including (a) the Γ-Z(c axis) chain direction, which lies in the cleavage plane; (b) the in-plane direction perpendicular to (a); and (c) the sample surface normal. The data exhibit dispersing features in Fig. 2(a). Considering the states closest to the Fermi level, there is a state that disperses along Γ-Z from 1.0-eV binding energy at Γ to 0.4 eV at $k = 0.35 \pm 0.05c^*$. This electronic state becomes unobservable for $k > 0.35c^*$. For higher wave vectors we measure a second band dispersing toward lower binding energy. This second band also reaches a minimum binding energy of 0.4 eV at $k = 0.73 \pm 0.05c^*$. We notice a very high intensity in the spectral function at Γ at 1-eV binding energy. In contrast to the two dispersing features along the Γ-Z direction, the data of Figs. 2(b) and 2(c) exhibit essentially no dispersion along both equivalent Γ-X directions. This indicates that the dispersing states are of one-dimensional character. In both directions perpendicular to the Ta–Ta chains an almost nondispersing state is visible at ≈ 0.5-eV binding energy. We cannot report on its dispersion along the Γ-Z direction, because we observe this state only near Γ.

A resonant enhancement of the Ta *d* states is expected when the photon energy is varied across the Ta 4*f* thresholds at 21 and 23 eV [Fig. 2(c)]. Conversely, the data show no resonant behavior, and at most a weak enhancement. The absence of a resonance may be the result of a strong

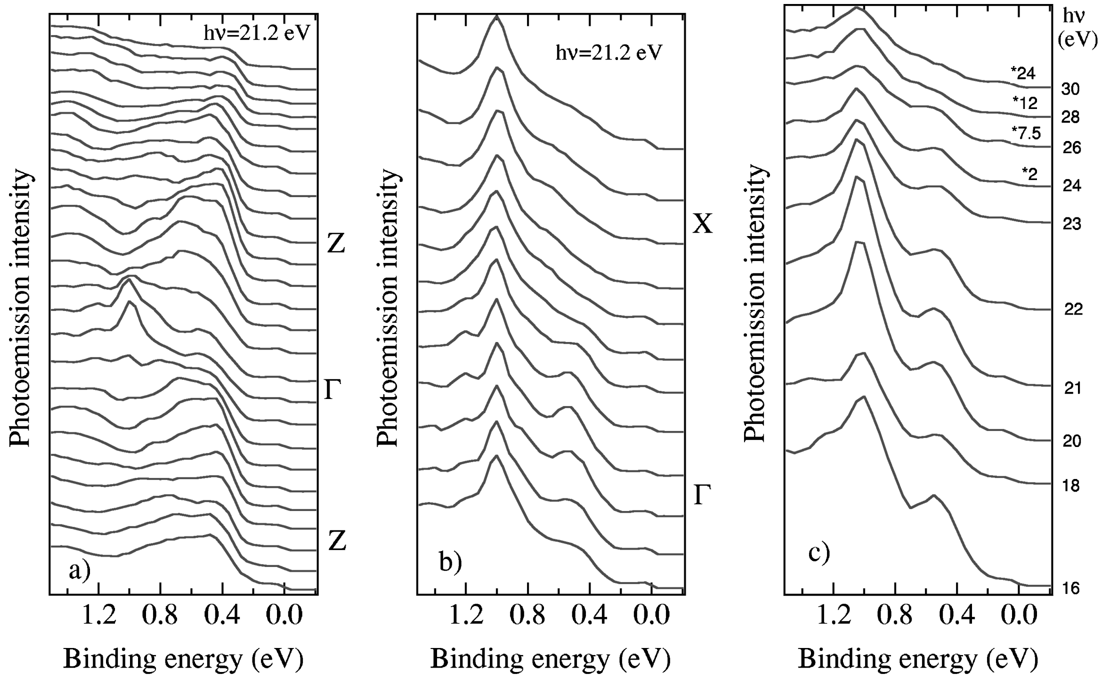

FIG. 2. (a) ARPES spectra along the Ta-Ta chains (Γ-Z) at $T=80$ K. (b) ARPES spectra along Γ-X (in the a-c plane) at $T=80$ K. (c) Normal-emission spectra for different photon energies at $T=120$ K.

Ta $5d$–Te $5p$ hybridization, suggested by band-structure calculations.[26,27]

Figure 3 illustrates an intensity plot of the data of Fig. 2(a). We can clearly identify bands that disperse symmetrically around the Γ point. The minimum binding energy of the first band occurs at $k=\pm(0.35\pm0.05)c^*$. This result is in good agreement with the value of the Fermi wave vector, $k_F=1/3c^*$, determined by x-ray and electron diffraction.[14] According to band-structure calculations,[26,27] the d_{z^2} band crosses the chemical potential at $k_F\approx1/3c^*$. The same calculations further predict electron pockets around the zone boundary Z. Both aspects are in qualitative disagreement with our data. In agreement with the calculation, this band does not disperse perpendicularly to the Ta-Ta chains [Figs. 2(b) and 2(c)].

The second band, with a minimum binding energy at wave vector $k=0.73c^*$ has no counterpart in existing calculations, although bands of Te $5p$ character are expected below ≈0.5 eV. We also notice that this band does not exhibit the structural periodicity (umklapp at $c^*/2$). We emphasize that the published calculations refer to the undistorted structure, whereas our measurements were necessarily carried out in the CDW phase.

None of the observed dispersing spectral features cross the chemical potential as would occur in a normal metal, and the intensity is strongly suppressed within ≈0.2 eV of the chemical potential. Nevertheless, as illustrated by the high-resolution spectra of Fig. 4, there is a small but finite spectral intensity up to the chemical potential, and the leading edge indicates a resolution-limited Fermi-Dirac cutoff of the spectral function. To make a direct comparison, we deposited polycrystalline silver films on the sample and found that both leading edges are the same in position and width. The spectral intensity at the chemical potential exhibits only small intensity changes with wave vector, which we were unable to relate to either the lattice or the CDW periodicity. The photon energy dependence of the intensity of this feature indicates a similar orbital symmetry as the main part of the valence band. At the same time, we do not observe any indication of a real CDW-induced Peierls gap. We notice, however, that $\Delta\approx0.2$ eV, the energy range of the strongly suppressed spectral weight, compares well with $2\Delta=0.37$ eV, the gap feature in the optical conductivity.

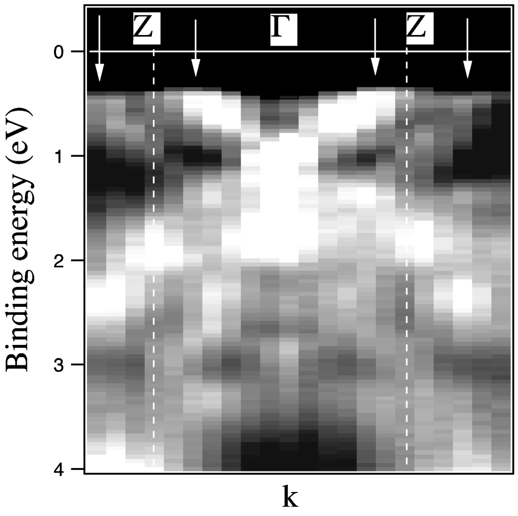

FIG. 3. Intensity plot of the data shown in Fig. 2(a). White arrows indicate the k values where the bands are closest to the Fermi level. Γ and X label the Brillouin-zone center and boundary, respectively.

III. DISCUSSION

The absence of any dispersing feature crossing the chemical potential is certainly surprising. Despite different data

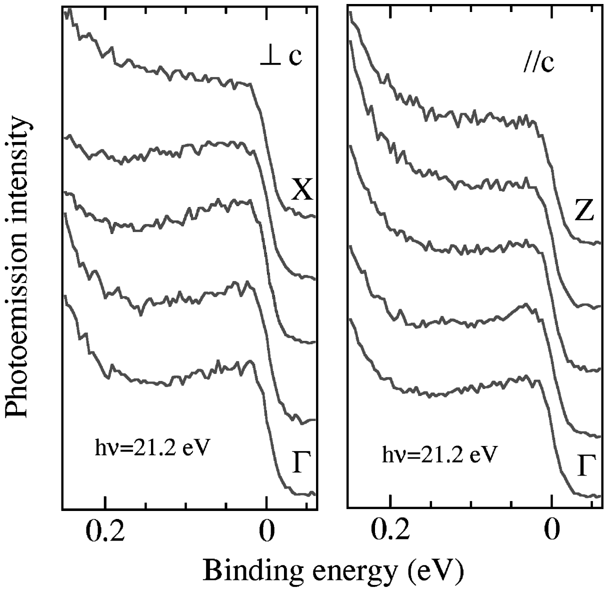

FIG. 4. High-resolution ARPES spectra along Γ-Z and Γ-X. The sample temperature was 55 K. Note the absence of dispersing quasiparticle states. The leading edge corresponds to the Fermi function at this temperature, as proven by evaporating Ag on top of the sample.

analysis methods, we found no trace of a dispersing quasiparticle feature within ≈ 0.2 eV of the chemical potential in any high-symmetry direction. We also varied the photon energy from 15 to 30 eV, to see whether small matrix elements or final-state effects are responsible for the low spectral intensity. This behavior is similar to what has been reported for quasi-one-dimensional materials such as $(TaSe_4)_2I$.[2–4] In marked contrast to a quasi-one-dimensional metal, however, there is a finite spectral weight and a resolution-limited cutoff to the spectral function at the chemical potential. A k-independent spectral weight near the chemical potential is often observed even in angle-resolved spectra of 3D, but not 1D, metals. This density of states-like feature has been attributed to elastic scattering by surface defects.[28,29] In our case, this 3D signal must be associated with the nearly isotropic transport properties and the Drude peak in the optical conductivity (Fig. 1). Paradoxically, the presence of a Drude peak suggests that the charge carriers near the chemical potential are *free*, whereas the ARPES data show no indication of free-electron states. The absence of coherent states near the chemical potential is naturally associated with disorder, and incoherent (hopping) transport mechanism.[30] However, the residual resistivity ratio is equal to 50 and the low residual resistivity of less than $5\,\mu\Omega$ cm together with the scattering parameters deduced from the data illustrated in Fig. 1 suggest a rather pure sample, so that disorder effects do not play an important role.

In a quasi-one-dimensional CDW system like $(TaSe_4)_2I$, where the spectral function vanishes at the chemical potential, no Drude peak is observed in the CDW phase, since the conduction electrons are in the gapped CDW state.[22,23] The oscillator strength is observed at a finite frequency due to a CDW collective mode. In the case of $TaTe_4$, however, a Drude peak is observed in the CDW phase, suggesting that not all conduction electrons near the chemical potential are lost due to the CDW formation. As mentioned above, we infer from our optical data that only 20%–30% of the conduction electrons are involved in the CDW phase. Therefore, in addition to the gapped portions of the Fermi surface involved in the CDW instability, a three-dimensional Fermi surface must also be present, as a result of the stronger interchain interactions in $TaTe_4$.[26]

We can only speculate why this prominent part of the Fermi surface does not clearly appear in the ARPES spectra. There is the possibility that the small intensity variations of the spectral weight at the chemical potential reflect a nearly flatband just above the Fermi level. Recent calculations indeed seem to indicate a dense group of bands near E_F in the reduced zone.[31] A multiband situation is also suggested by measurements of the thermal conductivity, which changes sign with temperature.[20] In this case only the tails of these overlapping bands could be observed by ARPES, smeared by the finite angular acceptance of $\pm 1°$. This corresponds to $\approx 10\%$ of the undistorted Brillouin zone, but 30% of the reduced zone for this material. However, we cannot exclude the fact that the small and k-independent signal reflects an intrinsic spectral property of the correlated unpaired electrons moving in the CDW background.

IV. CONCLUSION

In summary, we investigated the electronic properties of $TaTe_4$, and observed quasi-one-dimensional electronic states near the chemical potential and a three-dimensional k-independent spectral intensity at the chemical potential. The coexistence of 1D and 3D spectral signatures is quite unusual, and we associate it with the stronger interchain interaction compared to the similar, but typically 1D compound $(TaSe_4)_2I$. A crucial point which remains to be clarified is whether the Fermi surface can be decoupled into clearly distinct one- and three-dimensional portions, or if the same Fermi surface is responsible for the CDW instability and the 3D transport properties. We hope that our results will stimulate calculations of the electronic structure for the distorted structure.

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[25] We speculate that this may be a phase mode of the CDW, caused by Coulomb interaction of adjacent chains. The CDW unit cell contains four chains and thus should have three optical-phonon modes in each polarization. Our speculation is that the 1270 cm^{-1} feature may be an optical phase mode, at high frequency because of strong Coulombic forces between antiphase CDW's on adjacent chains.

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