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Importance of many-body effects to the spectral function of 1*T*-TiTe$_2$

G. Nicolay, B. Eltner, and S. Hüfner
FR 7.2, Institut für Experimentalphysik, Universität des Saarlandes, Postfach 151150, D-66123 Saarbrücken, Germany

F. Reinert*
Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

U. Probst and E. Bucher
Fachbereich Physik, Universität Konstanz, D-78457 Konstanz, Germany

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We present a line-shape analysis of high-resolution angle-resolved photoemission spectra of the quasi-two-dimensional system 1*T*-TiTe$_2$, measured with an energy resolution of 5 meV and an angular resolution of 0.3°. The analysis is based on the spectral function, containing contributions from electron-phonon and electron-electron scattering and a remaining contribution from electron-impurity interaction. Our results show that the low-temperature spectra near k_F can only be adequately described by taking all three contributions into account. In particular, the electron-phonon interaction has a distinct effect on the shape of the spectral function close to the Fermi level, making the influence of the electron-electron interaction hardly visible for this material. Furthermore, we discuss the importance of the sample quality and the influence of impurities on the photoemission spectra.

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Photoemission spectroscopy (PES) is an important tool to study the electronic structure of solids, molecules, and surfaces.[1] In recent years, the resolution of this technique in both the energy ($\Delta E \lesssim 1$ meV) and momentum ($\Delta\theta \lesssim 1°$) domains has been improved considerably, allowing the investigation of finer details in the electronic structure, as they can be caused, e.g., by many-body effects. The most prominent many-body effects in a solid are based on the interaction of two electrons directly by the Coulomb potential (electron-electron interaction) or by the coupling of two electrons via the elastic excitations of the solid (electron-phonon interaction). These many-body effects make the exact description of the system very complicated. A standard theoretical approach to this problem is Landau's Fermi-liquid concept.[2–4] In this concept one treats the electronic system of a solid as one of independent quasiparticles with renormalized physical properties in comparison to the free electrons. The renormalization gives rise to a finite lifetime of the quasiparticles and a modification of the dispersion curves.

By definition, the spectral function is the imaginary part of the Green's function $G_k(E)=[E-\epsilon_k-\Sigma_k(E)]^{-1}$ of the many-body system; in our context, we are interested in the spectral function of the photohole, which bears the information of the initial state. The self-energy Σ describes the interaction of an electron or hole with the system, in particular with phonons (Σ^{ph}) and or electrons (Σ^{el}); impurities or defects in a real crystal lead to a scattering of the electrons, resulting in an additional contribution Σ^{imp}. These three terms sum up to the total self-energy $\Sigma=\Sigma^{ph}+\Sigma^{el}+\Sigma^{imp}$; without interaction, the spectral function consists of a δ peak at the single-electron energy $\epsilon_{\mathbf{k}}$.

Since the electron-impurity scattering can be regarded as independent of energy and momentum, we approximate for the present analysis this contribution as an imaginary constant[5]

$$\Sigma^{imp}_{\mathbf{k}}(E) = \mathrm{i}\Delta^{imp}. \tag{1}$$

To describe the electron-phonon contribution to the self-energy we use the Debye model in the limit of $T=0$, giving the imaginary part

$$\mathrm{Im}\,\Sigma^{ph}(E) = \frac{\pi\lambda}{3}\left[\frac{E^3}{\omega_D^2}\Theta(\omega_D - E) + \omega_D\Theta(E-\omega_D)\right] \tag{2}$$

(Θ is the Heaviside step function) and the real part

$$\mathrm{Re}\,\Sigma^{ph}(E) = -\frac{\omega_D\lambda}{3}\left[\frac{E}{\omega_D} + \frac{E^3}{\omega_D^3}\ln\left|1-\frac{\omega_D^2}{E^2}\right| + \ln\left|\frac{1+\dfrac{E}{\omega_D}}{1-\dfrac{E}{\omega_D}}\right|\right]. \tag{3}$$

ω_D defines the Debye energy, and λ is the electron-phonon coupling parameter. In the further discussion we will focus on the imaginary part $\mathrm{Im}\,\Sigma$ of the total self-energy, giving the intrinsic linewidth of the spectrum.

The electron-electron interaction can be approximated for states close to the Fermi surface by a Taylor expansion[6] as

$$\Sigma^{el}(E,T) = \alpha E + \mathrm{i}\beta[E^2 + (\pi k_B T)^2]. \tag{4}$$

A photoemission spectrum contains contributions from both the photohole and photoelectron final state. Therefore, it is usually difficult to determine directly the desired spectral function of the photohole. This can be illustrated by the relative weight of the hole and electron contribution to measured photoemission linewidth Γ_m at normal emission, which is given by $\Gamma_m=(v_{f\perp}/v_{i\perp})\Gamma_i+\Gamma_f$,[7] with the photoelectron contribution Γ_f, determined by the scattering processes of the excited photoelectron in the photoemission final state and the photohole contribution Γ_i which is equal to 2 Im Σ from the definition above. $v_{f\perp}$ and $v_{i\perp}$ are the group velocities of photoelectron and hole perpendicular to the surface. In strictly two-dimensional systems, the final-state contributions from the photoelectron are suppressed, because $\hbar v_{i\perp} = \partial E_k / \partial k_\perp = 0$. Thus, in order to study the spectral function of the photohole—i.e., the properties of the "initial" system—one needs a two-dimensional system. Therefore such investigations by photoemission spectroscopy have been performed particularly on surface states[8–12] or on layered compounds.[13,14]

The first detailed study on the spectral function of a Fermi-liquid system was performed on 1T-TiTe$_2$.[13] This work was followed up by a number of other investigations, establishing TiTe$_2$ as a Fermi-liquid reference system, but also suggesting problems with impurities and the finite three dimensionality.[13,15–17] In all these investigations the low-temperature spectra were fitted by taking Σ^{el}, Σ^{imp}, the resolution broadening, and three-dimensional broadening effects into account. In no case there was an explicit consideration of Σ^{ph} to describe the spectral function.

In all these previous photoemission studies on TiTe$_2$, the electron-electron interaction was considered to be the relevant term of the quasiparticle self-energy. The largest value for the electron-electron parameter β obtained so far is 314 eV^{-1},[18] and the smallest one is 0.5 eV^{-1}.[15] Even the most recent results, obtained with an energy resolution of 8 meV on samples with 2 $\mu\Omega$ cm residual resistivity, have to assume an additional impurity-induced photoemission linewidth of $\Delta^{imp} = 17$ meV,[15] which may obscure intrinsic many-body effects—namely, the electron-electron and electron-phonon contributions.

In this paper we present high-resolution photoemission data measured with an energy resolution of 5 meV and an angular resolution of ±0.15°. Using the same electron-phonon coupling constant as obtained from the temperature-dependent line broadening,[15] we show that even this weak electron-phonon coupling ($\lambda = 0.2$) is important for the interpretation of the photoemission spectra. As a matter of fact, a good fit to the measured spectra can only be obtained by incorporating Σ^{ph} into the spectral function. On the other hand, the value of β plays no significant role for the line shape of the spectra close to the Fermi level. If one includes electron-phonon or impurity scattering terms, the electron-electron coupling influences the spectra only at higher binding energies—e.g., as an increased background intensity. However, the remaining impurity contribution ($\Delta^{imp} = 14$ meV) is still by far the most important one for the calculation of the linewidth of the spectral function, although it is smaller than in all previous investigations.

The photoemission experiments have been performed with a SCIENTA SES200 spectrometer equipped with a monochromatized GAMMADATA VUV lamp using a photon energy of $h\nu = 21.2$ eV (He I).[11] The base pressure in the system was $\approx 5 \times 10^{-11}$ mbar, increasing to $\approx 1 \times 10^{-9}$ mbar during the measurement because of the He-gas leakage from the differentially pumped discharge lamp. The energy resolution and the position of the Fermi energy were determined from the Fermi edge of a cooled noble-metal sample. The energy resolution for the spectra presented here amounts to about 5 meV, the angular resolution to ±0.15°; all spectra were measured at $T = 10$ K. The TiTe$_2$ samples were grown by iodine-vapor transport and oriented using Laue or low-energy electron diffraction (LEED) measurements. The surface of the TiTe$_2$ was prepared by *in situ* cleaving with a cleavage post at low temperatures. Note that at low temperatures the spectra showed a time-dependent increase of the linewidth due to a surface deterioration, also observed on surface states.[19] Although momentum-dependent data have been obtained, we show here only data at the Fermi surface (k_F spectra), because the spectra display the smallest linewidth and the Taylor approximation for the electron-electron interaction is valid only close to the Fermi level. To simulate the experimental data, we calculated the spectral function according to the Eqs. (1)–(4) given above, including the finite-energy resolution by a convolution in energy with a Gaussian of $\Delta E = 5$ meV [full width at half maximum (FWHM)]. The finite angular resolution was considered by an integration over modeled spectra with different ϵ_k within a Gaussian window with a FWHM of 3 meV. This value can be estimated from the known angle resolution and the measured band dispersion of the analyzed band, $(\partial E_k / \partial k)\Delta k$.

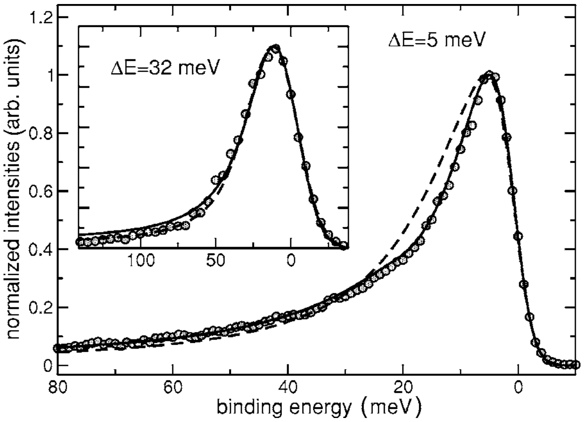

FIG. 1. High-resolution ARUPS data on TiTe$_2$ (He I) with a line-shape fit including electron-phonon, electron-electron, and electron-impurity interactions; the dashed line gives the model function without the electron-phonon contribution [$\lambda = 0.2$, $\beta = 0.005$ eV^{-1}, $\Delta^{imp} = 14$ meV (FWHM), $\omega_D = 20$ meV]. The inset shows the same model functions broadened by a Gaussian with FWHM 32 meV, in comparison with the data from Ref. 13 (normalized to the same maximum height).

Figure 1 shows a high-resolution k_F spectrum of TiTe$_2$ at a temperature of $T = 10$ K. A detailed look at the line shape reveals a slight kink around a binding energy of 20 meV, which is not described adequately by a scenario using only the electron-electron interaction—neither in the largely simplified form of Eq. (4) (Taylor expansion) nor in more elaborated theories[20]—and the electron impurity scattering term. As is obvious from Fig. 2 this is an immediate consequence of Σ^{ph}. The numerical fit of the data is considerably improved if the electron-phonon interaction is taken into account as well, which was done in none of the previous investigations of 1T-TiTe$_2$. With Debye model parameters from the literature ($\lambda = 0.2$ and $\omega_D = 20$ meV; see Refs. 15 and 21 and references therein) yielding Σ^{ph} we get the solid

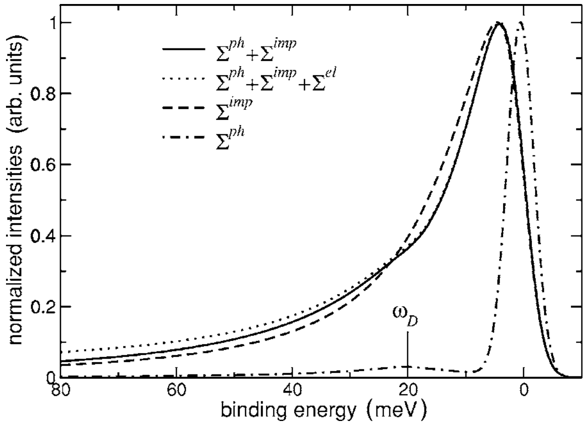

FIG. 2. Normalized model spectra with the different contributions switched on and off. The parameters are identical to the ones used for Fig. 1. To increase the influence of the electron-electron coupling we used $\beta = 1.0\ \text{meV}^{-1}$ here (dotted curve); still the spectral change is small. Σ^{el} alone would make a cause a δ peak at E_F, broadened by the experimental resolution (identical with the dot-dashed curve without the hump at ω_D).

curve in Fig. 1 which fits the data distinctly better than the result without the electron-phonon contribution (dashed line).

We have also measured a large amount of momentum-dependent spectra to investigate the band dispersion $E(k)$. The spectra, however, broaden rapidly when going away from k_F. Since in this work we are interested in the shape of the spectral function, we discuss here only the most narrow data: namely, the k_F spectra measured at low temperatures. Our analysis has shown that the spectra away from k_F give no additional information with respect to the importance of the individual many-body contributions and the Fermi-liquid aspect. In the presented energy range, the model results change only slightly by changing the electron-electron parameter β, because the energy change of the total self-energy is dominated by the energy dependence of the electron-phonon contribution Σ^{ph}. For spectra at $k \approx k_F$, an increase of β mainly increases the background intensity at higher binding energies. The inset in Fig. 1 shows the comparison of a data set measured with an energy resolution of 32 meV,[13] in comparison with two normalized model curves with the same parameters as in the high-resolution plot, except for an increased Gaussian broadening of $\Delta E = 32$ meV to take into account the larger experimental linewidth. One can observe that the presence of the electron-phonon contribution does not significantly alter the result, except in the apparent background (as a result of the normalization to the same maximum height). Therefore, only high-resolution data allow a quantitative analysis of the individual contributions.

In order to demonstrate the importance of the electron-impurity scattering even in the best available experimental data (Fig. 1), we show in Fig. 2 the influence of the individual contributions to the spectral line shape. It is evident that Σ^{ph} and Σ^{el} alone contribute only a small fraction to the width of the spectral function and that the important contribution comes still from the residual part Σ^{imp}, probably mainly from defects in the crystal.

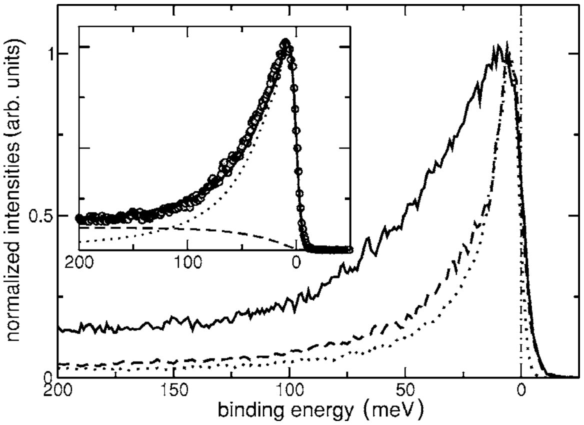

FIG. 3. Equivalent k_F spectra (near the $\bar{M}$ point) on $TiTe_2$ samples of different quality. The dotted curve represents the spectrum in Fig. 1. The inset shows the broadest spectrum in the main figure together with a model spectrum (solid line) including a Shirley background. The parameters are identical to parameters of the fit in Fig. 1, except for the larger impurity contribution $\Delta^{imp} = 36$ meV and a temperature of $T = 25$ K (dashed line, Shirley background; dotted line, calculated spectrum without background).

This point can be emphasized by presenting—in addition to the spectrum from Fig. 1—two arbitrarily selected spectra taken from crystals from different batches under the same experimental conditions (Fig. 3). The apparent linewidth and background in these spectra are very different, indicating the importance of defects for an analysis of the spectral function in this material. A model spectrum for the broad spectrum (solid line) can be derived from the fit for the high-quality spectrum just by increasing the impurity parameters to $\Delta^{imp} = 36$ meV and adding an appropriate Shirley background (see inset). However, it cannot be ruled out that our extracted value for Δ^{imp} from the high-quality sample includes a contribution from the finite photoelectron lifetime broadening, which exists due to the small-$k_\perp$ dependence of the electronic states in $TiTe_2$ as a consequence of its deviation from a perfect two-dimensional system. Estimates of the size of this effect have been given in Ref. 15; the resulting values are consistent with the residual broadening in our analysis, given by Δ^{imp}.

The sample quality is particularly important if one takes the background intensity into consideration. The high-resolution spectra presented here have only a very low background intensity and have not been background corrected. As demonstrated above, both the sample quality and the electron-electron scattering do influence the background significantly. Thus in order to analyze Σ^{ph}, and Σ^{el} in more detail one has to make sure that the impurity scattering is reduced as far as possible.

In order to convey a feeling for the field we have collected a number of results on β, λ, ω_D, and Δ^{imp} as obtained from photoelectron spectroscopy. The most important finding is that—except for the surface state in Cu(111)—the residual, probably defect-induced linewidth is very much larger than the standard resolution in high-resolution photoemission experiments of 3–5 meV. This emphasizes the point of sample quality in a line-shape analysis (see Table I). As we have

TABLE I. Comparison of the line-shape analysis results of various surface (Be, Mo, Bi, and Cu) and bulk systems (LSCO, 2212, TiTe_2) from the literature; $*$ indicates the result of this work.

System	β [eV^{-1}]	λ	ω_D [meV]	Δ^{imp} [meV]	Ref.
Be(0001)	0.063	1.18	70	75	8 and 9
Be(0001)		0.7–0.9			5
Be(0001)		0.7			22
Mo(110)	0.14	0.35–0.52	80	26	10
$\text{Bi}_{1-x}\text{Sb}_x$		0.007/0.54		28	23
Cu(111)	0.02	0.137	27	5	12
LSCO		0.9	72		14
2212		0.5	50		24
TiTe_2	40			35	13
TiTe_2	0.7	0.22	20	17	15
TiTe_2	$\lesssim$0.005	0.2	20	14	$*$

shown above, the electron-electron coupling parameter influences the spectral function for spectra close to E_F only weakly when also other contributions are considered and is thus difficult to determine from the photoemission spectra. With respect to electron-phonon coupling, the parameter λ determined from the line-shape analysis is certainly not the most accurate one and it seems preferable to use the value obtained from tunneling experiments or from the temperature dependence of the photoemission linewidth.

To conclude, we have presented high-resolution (ΔE =5 meV) photoemission data on $1T\text{-TiTe}_2$ near k_f and an analysis of the line shape including contributions from electron-phonon, electron-electron, and electron-impurity scattering. In contrast to earlier results, we have shown that the electron-phonon contribution is mandatory for the line-shape analysis of the spectra close to k_F; the influence from electron-electron scattering is marginal in the considered energy range close to the Fermi level, and therefore only an upper limit for the parameter β can be presented. However, it was demonstrated that there exists still a considerable residual broadening due to impurity scattering and the finite three-dimensional character of the system, which represents—even in high-resolution spectra on high-quality samples—the dominant contribution in the photoemission linewidth.

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*Corresponding author. Electronic address: reinert@physik.uni-wuerzburg.de

[1] S. Hüfner, *Photoelectron Spectroscopy. Principles and Applications*, 3rd ed. (Springer-Verlag, Berlin, 2003).

[2] L. D. Landau, Sov. Phys. JETP **3**, 920 (1957).

[3] D. Pines and P. Nozières, *The Theory of Quantum Liquids–Normal Fermi Liquids* (Addison-Weseley, New York, 1966), Vol. 1.

[4] L. Hedin and S. Lundqvist, *Effects of Electron-Electron and Electron-Phonon Interactions on the On-Electron States of Solids*, Vol. 23 of Solid State Physics (Academic Press, New York, 1970).

[5] S. LaShell, E. Jensen, and T. Balasubramanian, Phys. Rev. B **61**, 2371 (2000).

[6] J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).

[7] N. V. Smith, P. Thiry, and Y. Petroff, Phys. Rev. B **47**, 15476 (1993).

[8] M. Hengsberger, D. Purdie, P. Segovia, M. Garnier, and Y. Baer, Phys. Rev. Lett. **83**, 592 (1999).

[9] M. Hengsberger, R. Frésard, D. Purdie, P. Segovia, and Y. Baer, Phys. Rev. B **60**, 10796 (1999).

[10] T. Valla, A. V. Fedorov, P. D. Johnson, and S. L. Hulbert, Phys. Rev. Lett. **83**, 2085 (1999).

[11] F. Reinert, G. Nicolay, S. Schmidt, D. Ehm, and S. Hüfner, Phys. Rev. B **63**, 115415 (2001).

[12] F. Reinert, B. Eltner, G. Nicolay, F. Forster, S. Schmidt, and S. Hüfner, Physica B **351**, 229 (2004).

[13] R. Claessen, R. O. Anderson, J. W. Allen, C. G. Olson, C. Janowitz, W. P. Ellis, S. Harm, M. Kalning, R. Manzke, and M. Skibowski, Phys. Rev. Lett. **69**, 808 (1992).

[14] A. Damascelli, Z. Hussain, and Z. Shen, Rev. Mod. Phys. **75**, 473 (2003).

[15] L. Perfetti, C. Rojas, A. Reginelli, L. Gavioli, H. Berger, G. Margaritondo, M. Grioni, R. Gaál, L. Forró, and F. Rullier Albenque, Phys. Rev. B **64**, 115102 (2001).

[16] L. Kipp, K. Rossnagel, C. Solterbeck, T. Strasser, J. W. Schattke, and M. Skibowski, Phys. Rev. Lett. **83**, 5551 (1999).

[17] K. Rossnagel, L. Kipp, M. Skibowski, C. Solterbeck, T. Strasser,

W. Schattke, D. Voß, P. Krüger, A. Mazur, and J. Pollmann, Phys. Rev. B **63**, 125104 (2001).

[18] S. Hüfner, T. Finteis, S. Schmidt, G. Nicolay, F. Reinert, Z. Hussain, X. J. Zhou, S. A. Kellar, and Z.-X. Shen (unpublished).

[19] G. Nicolay, F. Reinert, F. Forster, D. Ehm, S. Schmidt, B. Eltner, and S. Hüfner, Surf. Sci. **543**, 47 (2003).

[20] K. Matho, Physica B **199&200**, 382 (1994).

[21] M. Hangyo, S. Nakashima, and A. Mitsuishi, Ferroelectrics **52**, 151 (1983).

[22] J. Shi *et al.*, Phys. Rev. Lett. **92**, 186401 (2004).

[23] H. Höchst and S. A. Gorovikov, J. Electron Spectrosc. Relat. Phenom. **144**, 351 (2005).

[24] P. D. Johnson *et al.*, Phys. Rev. Lett. **87**, 177007 (2001).