I. INTRODUCTION

Strongly correlated low-dimensional quantum spin-1/2 systems have attracted much attention during the last years since they can serve as a testing ground for theoretical concepts which are believed to play a key role in understanding materials of paramount technological potential like the high-$T_c$ superconductors or the CMR (colossal magnetoresistance) manganites.\textsuperscript{1,2} This applies in particular to one-dimensional systems for which exactly solvable many-body models exist.\textsuperscript{3} In particular to one-dimensional systems for which exact solvable many-body models exist.\textsuperscript{3} Weakly interact through van der Waals forces. In a local dimensional structure of the FeOCl type, where buckled charge, spin, orbitals, and lattice. In this perspective, the electronic properties of TiOCl at room-temperature and slightly above, \textit{i.e.} well above the transition temperatures $T_{c_1}$ and $T_{c_2}$. To this end we performed polarization dependent angle-resolved photoemission measurements (ARPES) which provide momentum-resolved information on the electronic structure. The experiments are complemented by LDA+$U$ and Hubbard model calculations. Our photoemission data confirm the one-dimensionality of the electronic structure and give no evidence for sizable phonon-induced orbital fluctuations as origin for the non-canonical phenomenology of the spin-Peierls transition in this compound. A comparison of the experimental data to our own LDA+$U$ and Hubbard model calculations reveals a striking lack of understanding regarding the quasi-one-dimensional electron dispersions in the normal state of this compound.

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Unusual quasi-one-dimensional electron dispersions in the spin-1/2 quantum magnet TiOCl

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We have studied the electronic structure of the spin-1/2 quantum magnet TiOCl by polarization-dependent momentum-resolution photoelectron spectroscopy. From that, we confirm the quasi-one-dimensional nature of the electronic structure along the crystallographic $b$-axis and find no evidence for sizable phonon-induced orbital fluctuations as for the non-canonical phenomenology of the spin-Peierls transition in this compound. A comparison of the experimental data to our own LDA+$U$ and Hubbard model calculations reveals a striking lack of understanding regarding the quasi-one-dimensional electron dispersions in the normal state of this compound.

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dence for any significant (phonon-induced) admixtures of $d_{xz}$ and $d_{yz}$ orbitals to the ground state, implying that orbital fluctuations play no role for the low-temperature physics of TiOCl. Nevertheless, the detailed comparison of the experimental results to our electronic structure calculations as well as to recent LDA+DMFT calculations show that even the normal state properties of TiOCl are far from being fully understood.

II. TECHNICAL DETAILS

A. Experimental

Single crystals of TiOCl were prepared by chemical vapor transport from TiCl$_3$ and TiO$_2$. The samples were characterized by x-ray diffraction, specific heat, magnetic susceptibility, and electron spin resonance measurements. The high quality of our crystals can be directly inferred from the susceptibility data displayed in Fig. 1, in which a pronounced hysteresis at $T_c$ signals the first-order character of the lower transition.

Photoemission spectroscopy has been performed mainly at our homelab using He I (21.2 eV) and Al K$_\alpha$ (1486.6 eV) radiation and an Omicron EA 125 HR electron energy analyzer. For polarization-dependent measurements we utilized an Omicron AR 65 spectrometer equipped with a He discharge lamp and a rotatable polarizer. Additional polarization experiments with linearly polarized synchrotron light were performed at the SIS beamline of the Swiss Light Source at the Paul-Scherrer-Institute (Villigen, Switzerland) using a Scienta SES 100 analyzer. The energy and angular resolution amounted for the homelab experiments to 60 meV and $\pm 1^\circ$, respectively, and to 80 meV and $\pm 0.2^\circ$ in the SLS experiments. The layered structure of TiOCl facilitates easy surface preparation by in situ crystal cleavage. The resulting surfaces were clean and atomically long-range ordered as evidenced by x-ray induced photoemission (XPS) and low-energy electron diffraction (LEED), respectively. Because TiOCl is an insulator, all photoemission data were taken at room temperature or above in order to minimize sample charging. From systematic temperature-variations we found that the charging is almost negligible at and above $\approx 370$ K. In this situation the maximum of the Ti 3$d$-peak (see below) is located at 1.45 eV below the experimental chemical potential $\mu_{exp}$, which corresponds to the Fermi edge position of a silver foil. Spectra measured at lower temperatures have been aligned accordingly.

B. LDA+U calculations

On the theoretical side, we have determined the electronic structure of TiOCl by performing density functional theory (DFT) calculations in the generalized gradient approximation (GGA) and in the so-called LDA (GGA)+U approximation using the full-potential linearized augmented plane-wave code WIEN2k. Since the LDA+U calculations are performed on a spin-polarized state, we considered a ferromagnetic alignment of the Ti spins (FM) as well as an antiferromagnetic arrangement of the Ti spins along the b direction (AFM). The latter was found to be lower in total energy compared to the FM state. We also performed LDA+U calculations for the low-temperature crystal structure of TiOCl in an antiferromagnetically spin-polarized state. In all calculations we used $R_K$ = 6 and 56 k irreducible points for Brillouin-zone integrations. The values for the onsite Coulomb repulsion $U$ as well as onsite exchange $J_0$ were taken to be 3.3 eV and 1 eV, respectively, which accounts well for the intersite exchange constant derived from the magnetic susceptibility.

C. Dynamical density-matrix renormalisation group calculations

To better account for correlation effects beyond the LDA+U approach we have also determined the one-particle spectral function of the one-dimensional (1D) Hubbard model at half band-filling using the dynamical density-matrix renormalisation group (DDMRG) method. The calculations were performed on 32-site chains with open boundaries and we kept up to 200 density-matrix eigenstates. The broadening of the spectra is $\eta/t = 0.2$.

III. RESULTS AND DISCUSSION

A. Valence density of states

Figure 2 shows angle-integrated photoemission spectra measured with 21.2 eV (UPS) and 1486.6 eV (XPS) photons. Both spectra consist of two well separated regions. The small intensity differences between the UPS
and XPS data are due to different photoemission cross sections. Also shown is the occupied part of the density of states (DOS) obtained from the LDA+U calculation for the room-temperature structure assuming ferromagnetic spin alignment (LDA+U<sup>FM</sup>). From the comparison of theory and experiment we identify the low-binding energy peak as Ti 3<sup>d</sup>-like, whereas the states between −9 eV and −4 eV are predominantly derived from Cl 3<sup>p</sup> and O 2<sup>p</sup> levels. The overall shape of the theoretical DOS and the experimental spectra are rather similar. Note, however, that the LDA+U DOS is shifted to higher binding energy in order to align the theoretical and experimental Ti 3<sup>d</sup> peaks. With this alignment the relative separation between Ti 3<sup>d</sup> and the ligand <sup>p</sup> states still appears ≈0.5 eV too small. The value of 2 eV for the correlation gap as determined from optical spectroscopy is in reasonable agreement with our photoemission data and the LDA+U calculations (not seen here, as the figure displays only the occupied DOS).

In the following we focus on the Ti 3<sup>d</sup> part near the chemical potential, which is shown as a blow-up in Fig. 3. According to the LDA+U calculation, it has exclusively 3<sup>d</sup><sub>xy</sub> orbital character. As seen in the upper panel of Fig. 3 the experimental 3<sup>d</sup> spectrum has a similar asymmetry as the LDA+U<sup>FM</sup> DOS but is much broader. We emphasize that the experimental width is perfectly reproducible and not due to instrumental broadening, which is much smaller. A comparison to the LDA+U DOS for antiferromagnetic spin configuration (which seems the more natural choice considering the Bonner-Fisher-type susceptibility) yields an even stronger disagreement.

We note that LDA+U accounts for the onsite Coulomb interaction only in a mean-field way and is thus effectively still a one-electron theory for static ordered systems. One may thus speculate that the origin for the conflicting 3<sup>d</sup> widths lies in pronounced electronic correlation effects and/or fluctuations of spin-Peierls or orbital nature beyond the scope of LDA+U. Electronic correlation effects can in principle be accounted for by a combination of LDA and dynamical mean field theory (LDA+DMFT) or by suitable many-body models. The lower panel of Fig. 3 shows a comparison of the experimental Ti 3<sup>d</sup> spectrum to two different LDA+DMFT calculations and the DOS of the half-filled 1D single-band Hubbard model calculated using the DDMRG method (using U = 3.3 eV and a transfer integral of t = 0.23 eV, corresponding to the LDA+U calculations). The LDA+DMFT calculations are taken from Refs. 17 and 25 and used different impurity solvers and basis sets. While the LDA+DMFT curves indeed display a broadening much closer to that of the experiment, none of these curves can sufficiently explain the shape of the experimental data. The striking disagreement between the two LDA+DMFT calculations should probably be traced back to the fact that, contrary to the multi-orbital QMC solver, the IPT solver is quite uncertain for anisotropic multi-band problems as it is the case for TiOCl. Also the 1D Hubbard model does not reproduce the bandwidth and the detailed spectral shape of our photoemission data.
B. Dispersions and anisotropy of the electronic structure

We now turn to our angle-resolved photoemission data, which are shown in Fig. 4 in a broad energy range for the two crystallographic directions \(a\) and \(b\). Both data sets are displayed in two alternative ways: as intensity plots \(I(k, E)\), and as energy distribution curves (EDCs). As seen, there is well-pronounced dispersion particularly in the Cl 3\(p\)/O 2\(p\) part of the spectra between \(-9\) eV and \(-4\) eV. This behavior and the clear symmetry of the dispersions with respect to the \(\Gamma\) point is indicative of the good crystal surface quality.

Figure 5 shows an enlargement of the Ti 3\(d\) ARPES spectra. From a comparison of the bare EDCs one can easily see that the spectral changes along the \(b\)-axis are considerably stronger than along the \(a\)-axis. This observation confirms the quasi-one-dimensional electronic (and magnetic) nature of TiOCl and corroborates the LDA+U prediction\(^5\) that 1D chains are formed by direct hopping via Ti 3\(d\)_{xy} orbitals along the \(b\) direction. We note, however, that the dispersion along the \(a\)-axis is still finite as seen from a closer inspection of the \(k\)-dependence of the peak maximum, which moves to slightly higher binding energy from \(\Gamma\) to \(X\). The size of the \(a\)-axis dispersion is directly related to the interchain coupling, which may play an important role for the complex spin-Peierls transition behavior\(^6\). A comparison of the experimental \(a\)-axis dispersion to that of the LDA+U\(^{FM}\) calculation is displayed in Fig. 6 and yields qualitative agreement concerning size and direction of the dispersion. Note again, however, that the LDA+U bands had to be shifted in energy to give a good match to the ARPES data.

The spectral changes in the \(b\)-axis ARPES data are somewhat more complex (right panel of Fig. 5). They start out at \(\Gamma\) with a single peak at \(\approx 1.5\) eV below the chemical potential. With increasing momentum the peak shifts clearly towards \(\mu_{\exp}\) and reaches its smallest binding energy about halfway between \(\Gamma\) and the zone edge. For even larger momentum the peak rapidly drops in intensity and seems to move back to slightly higher binding energy. At the same time a new feature appears at \(\approx -2.5\) eV until at the zone boundary (\(Y\)) the spectral shape has evolved into a broad hump. This behavior and...
been reproducibly observed on many different samples and is hence to be taken as intrinsic.

Figure 7 shows the experimental b-axis dispersion as ARPES intensity plot in comparison with various theoretical calculations. Starting with the theoretical LDA+U dispersion calculated for the high-temperature (non-dimerized) structure we find pronounced disagreement with the experiment, particularly in the second half of the ΓY direction where the theoretical bands continue to disperse upwards, whereas the experimental dispersion turns over and bends downwards until at the Y-point the spectral weight distribution is strongly broadened and seems to reach even higher binding energy than at Γ. Using antiferromagnetic spin alignment in the LDA+U approach doubles the unit cell and hence results in a dispersion symmetric about 1/2ΓY (center panel of Fig. 7). Although LDA+U dispersion thus reproduces the dispersion maximum halfway along ΓY, it does clearly not account for the asymmetric experimental behavior and the strong broadening towards the Y-point. Motivated by speculations that the unusual high-temperature behavior of TiOCl could be caused by fluctuations of the spin-Peierls order parameter, Fig. 7 shows LDA+UAFM dispersions for the dimerized low-temperature phase.15 We note that such fluctuation effects have been observed in charge Peierls systems well above the actual transition temperature.22 However, as is evident from the figure, the effect of (fluctuating) dimerization results in band doubling but is otherwise rather small and hence cannot explain the phenomenology of the ARPES data.

The right panel of Fig. 7 finally displays the momentum-resolved spectral weight distribution of the 1D single-band Hubbard model, calculated within DDMRG for the U and t parameters of the LDA+U calculations. We note that in this case the spectra are entirely of incoherent nature and correspond to momentum-dependent continua, which are structured in intensity due to the phase space available for decomposition of a real (photo-)hole into separate collective spinon and holon excitations. As a consequence a number of different dispersive structures appear, whose detailed (non-quasiparticle) nature are discussed in, e.g., Refs. 23 and 26. Comparing the DDMRG result with our ARPES data we find several corresponding features such as the initial upward dispersion (due to spin and charge branches in the Hubbard model22), the dispersion maximum at 1/2Γ, and the asymmetric shift of weight to larger binding energy towards the Y-point. Also the overall energy width of the spectral weight distribution is greater than in the LDA+U calculations. On the other hand, the experiment does not show the pronounced spin-charge splitting between Γ and 1/2Γ predicted by DDMRG, nor the holon “shadow band” which in the Hubbard model spectrum disperses downwards from Γ.

In addition, we calculated the spectral functions of two closely related Hubbard-type models in the Mott-insulating phase: The extended Hubbard model which includes a next-neighbor Coulomb repulsion V and the t-t'-U model which takes into account a next-neighbor hopping t'. The resulting spectral functions (not shown) for V/t < 2 and t'/t < 0.5, respectively, display no qualitative differences compared to the simple Hubbard model spectral function. However, the spectral weight of the spin branch in the t-t'-U model is significantly reduced for appropriate parameters (U/t = 15.7, t'/t = 0.14). This may indicate why the spin-charge splitting is not resolved experimentally.

Overall, the agreement is much better for our Hubbard model calculations than for the LDA+U band dispersions, suggesting that the experimental spectra are indeed dominated by electronic correlation effects. We note, however, that we cannot really expect the 1D single-band Hubbard model to account fully for our spectra, as it completely ignores the orbital degrees of freedom.
hence virtual excitations into these states will be even more important than the double occupations on the same site (with energy scale $U = 3.3$ eV) already contained in the single-band model. Therefore, it would be highly desirable to compare our ARPES spectra to that of a suitable multi-orbital 1D Hubbard model which however is still out of reach for the DDMRG.

C. Polarization-dependent photoemission

As already discussed in the introduction, the high-temperature phase of TiOCl is characterized by anomalous broadening of the phonon lines in Raman and infrared spectroscopy. This indicates strong coupling of the lattice to the electronic (spin or orbital) degrees of freedom. Indeed, LDA+U calculations for frozen lattice distortions corresponding to the relevant phonon modes have shown that the orbital ground state may switch from $3d_{xy}$ to $3d_{x^2-y^2}$ for sufficiently large amplitude. Such a dynamical Jahn-Teller effect would lead to an orbitally mixed character of the time-averaged ground state.

Experimental information on orbital symmetry can be obtained from polarization-dependent ARPES, making use of selection rules realized for special experimental geometries. Assume the direction of the incident linearly polarized light and the emission direction of the photoelectrons lie within the same crystal mirror plane. Then with the polarization vector within and perpendicular to the mirror plane the ejected electrons can stem only from states with well-defined even or odd parity with respect to this plane, respectively. If we choose the experimental setup as sketched in Fig. 8 the $d_{xy}$-derived band states of TiOCl are even with respect to the $(b,c)$ mirror plane while the $d_{xz,yz}$ states are odd. With the $(b,c)$-plane lying horizontally, photoemission from the $d_{xy}$ states is hence dipole-allowed only for horizontal light polarization, whereas $d_{xz,yz}$-emission can be observed for vertical polarization only.

In the main panel of Fig. 8 we display the results of such an ARPES experiment obtained with 21.2 eV photons at room temperature. The spectra were recorded at normal emission (i.e., at the $\Gamma$ point) with horizontal (blue) and vertical (red) polarization, respectively. Since a laboratory He lamp with a rotatable polarizer was used, the photon flux is not changed by switching the polarization and the spectra can be normalized to equal integration times per channel. At first glance, one can see that the intensity distribution over the whole valence band indeed is strongly affected by polarization effects. Focussing on the Ti 3$d$ states reaching down to about 3.5 eV below $\mu_{\text{exp}}$ their spectral weight is significantly reduced but not completely suppressed upon switching the polarization from horizontal to vertical, indicating the dominance of $d_{xy}$ emission. The residual 1 : 4.8 weight for vertical polarization can be quantitatively accounted for by the finite degree of light polarization ($\approx 85\%$), possible small sample misalignment and the effect of thermally activated symmetry-breaking phonons. Similar data for the Ti 3$d$ derived part of the electronic structure using polarized synchrotron radiation is depicted in the inset of Fig. 8. These spectra were recorded at a photon energy of 110 eV and a temperature $T = 365$ K and normalized to equal photon flux. Due to the higher polarization degree of the synchrotron radiation the residual relative weight for vertical polarization is even further reduced. We note that this contribution does not vary down to room temperature within experimental accuracy again indicating that phonon-induced orbital fluctuations are not important in this temperature range.

Hence we have direct experimental evidence that there is no sizable dynamical Jahn-Teller admixture of $d_{xz}$ and $d_{yz}$ states to the $d_{xy}$ ground state at room temperature. This is in line with the reasoning based on recent cluster calculations combined with polarization-dependent optical data, although such an effect cannot be excluded for far higher temperatures.

IV. CONCLUSIONS

In summary, we have investigated the electronic structure of TiOCl by means of angle-resolved photoelectron spectroscopy at and slightly above room temperature. From those measurements we confirm the predicted quasi-one-dimensional nature of the low-lying energy excitations. However, the electron dispersions along the one-dimensional axis cannot be explained by LDA+U or DDMRG calculations of the one-dimensional single-band
Hubbard model. From the specific polarization dependence of the Ti 3d spectral weight close to the chemical potential sizeable phonon-induced admixtures of $d_{xz}$ and $d_{yz}$ derived states to the $d_{xy}$ ground state can be ruled out. Thus a scenario where the non-canonical behavior of the spin-Peierls transition in this compound is traced back to orbital fluctuations within a dynamical Jahn-Teller scenario does not seem plausible.

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