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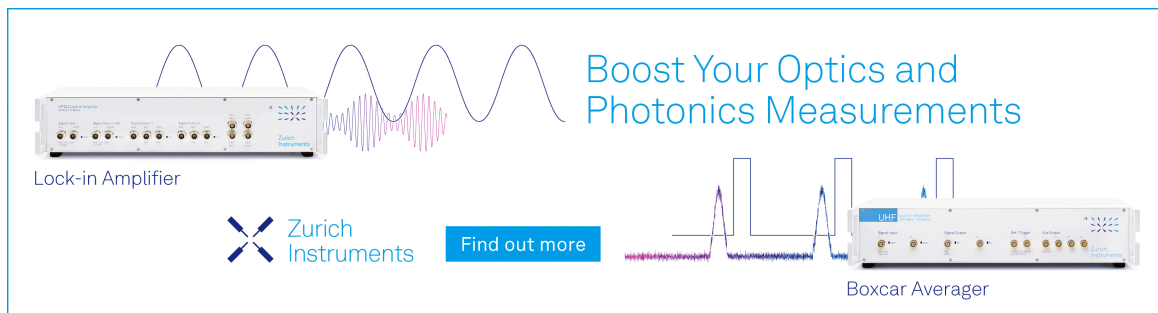
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# Unusual Spin-Peierls Physics in the Layered Quantum Magnet TiOCl

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**Abstract.** We summarize the current knowledge on phases, phase transitions and the electronic structure of the  $S = 1/2$  Mott insulator TiOCl. There are three different phases, with the low-T phase being of the spin-Peierls type. The interesting nature of these phases in conjunction with the different character of the phase transitions still leaves unanswered questions on the dimensionality of the system. Analysis of the electronic structure at room temperature by ARPES reveals pronounced differences between the orthogonal a- and b-axes within the crystal planes. In comparing with the isostructural material TiOBr we find differences in the degree of one-dimensionality, calling for inclusion of frustrated interchain interactions triggered by the underlying triangular lattice into theoretical calculations. Indications of a metallic phase at room temperature induced by pressure are reported, and possible effects of doping are discussed.

**Keywords:** TiOCl, ARPES, electronic structure, Mott insulator, pressure, doping

**PACS:** 71.20.-b, 71.27.+a, 71.30.+h, 79.60.-i

## INTRODUCTION

Searching for interesting many-particle physics in strongly correlated low-dimensional systems the 3d transition metal oxide TiOCl has gained increasing interest in the past years. Beynon and Wilson rediscovered the material in the light of high- $T_c$  superconductivity [1]. Being a Mott insulator, it has been speculated that RVB-like physics might determine the ground state, which upon doping could be eventually driven into this exotic superconducting state. Recently, quasi-one-dimensional electronic and magnetic properties have been confirmed e.g. by magnetic susceptibility measurements and LDA+U calculations [2, 3]. Additionally, a non-canonical spin-Peierls phase was identified [4], making TiOCl only the second inorganic material besides CuGeO<sub>3</sub> with this kind of ordering.

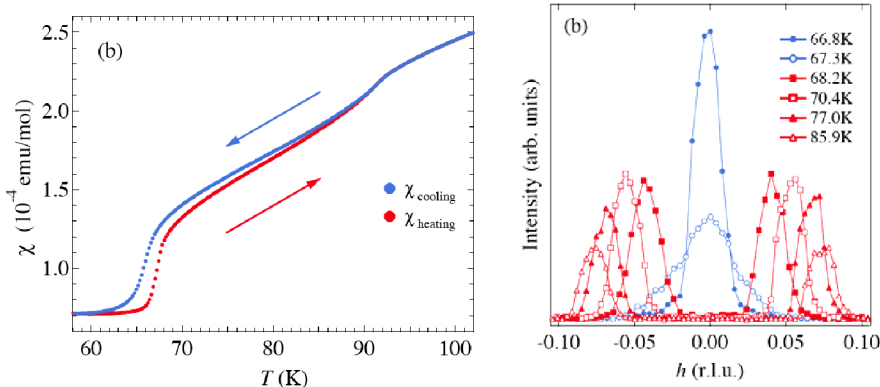
## CRYSTAL STRUCTURE AND PHASE TRANSITIONS

TiOCl crystallizes in the FeOCl structure, i.e. in buckled bilayers of Ti and O separated by layers of Cl ions. Along the c-axis these structures are coupled to each other only by weak van-der-Waals forces, while chains of one atomic kind are aligned along the b-axis. In the a-b-plane, the underlying Ti mesh resembles a distorted trian-

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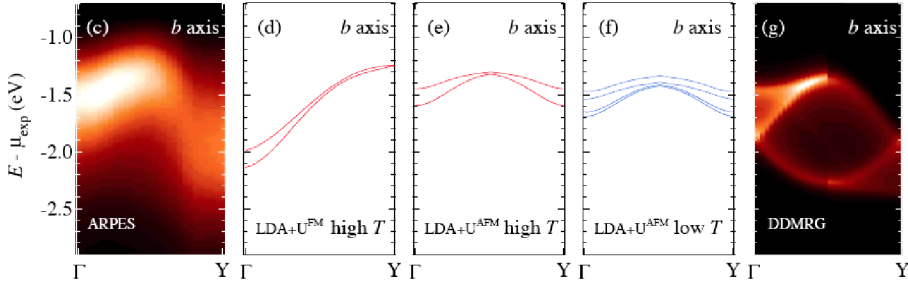
**FIGURE 1.** Left panel: Magnetic susceptibility of TiOCl. At  $T_{c1} = 91$  K a kink is visible due to a second order phase transition. At  $T_{c2} = 67$  K a first order transition can be recognized by the hysteresis between cooling and heating. Right panel: Evolution of the  $(\delta, 1.5, 0)$ -Miller reflection upon crossing the low-T phase transition (from [5]). The appearance of peaks at non-integer  $h$ -values indicates the incommensurate ordering in the intermediate phase.

gular lattice. The local octahedral coordination of  $Ti^{3+}$  by four O and two Cl ions leads to a crystal field splitting into  $e_g$ - and  $t_{2g}$ -states. Distortion of these octahedra further lowers the  $d_{xy}$  orbitals by about 200 meV. It was shown to be the true ground state by LDA+U calculations and polarization-dependent PES experiments [6].

For the high-temperature phase the magnetic susceptibility can be fitted to a Bonner-Fisher curve with  $J \sim 660$  K, thus in the respective temperature range TiOCl resembles a one-dimensional Heisenberg antiferromagnet. In Fig. 1 one sees that at  $T_{c1} = 91$  K a second order phase transition sets in, which however does not yet lead to a (commensurate) spin-Peierls phase. Instead, another phase transition at  $T_{c2} = 67$  K, this time of first order, finally gives this kind of ordering, as is shown by the sudden appearance of a peak at half-integer value of  $k$  in the reciprocal space by x-ray diffraction [5]. This indicates a doubled unit cell which is characteristic for the dimerization into  $S=0$  singlets along the  $b$ -axis, as is expected in a spin-Peierls phase. The accompanying lattice distortion nevertheless is slightly shifted out of the  $b$ -direction towards the ligands (O and Cl), thus minimizing the elastic strain of the structure. By detailed analysis of the reflexes in the  $h$ - $k$ -plane, i.e. at non-integer  $h$ - and  $k$ -values in the reciprocal plane, the intermediate phase could be identified to be incommensurate, finally locking in commensurately into the spin-Peierls order at  $T_{c2}$ . This finding is corroborated by specific heat measurements showing an insufficient release of heat at the phase transitions [7].

## ELECTRONIC STRUCTURE

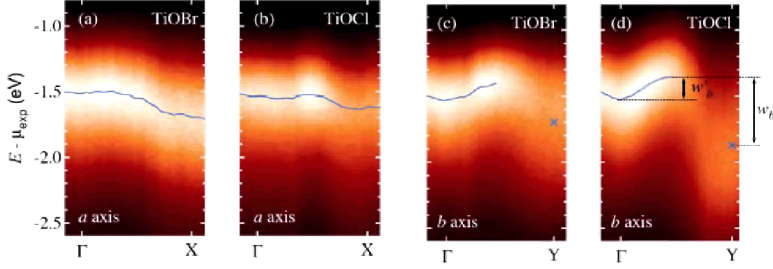
Single-band 1D Hubbard model calculations by DDMRG [6], DFT calculations, e.g. LDA+U [3], and combined methods like LDA+DMFT [8] have been carried out so far, shining light on the room-temperature electronic structure of TiOCl available to photoemission experiments. Early LDA+U correctly identified the energetics of the



**FIGURE 2.** From left to right: Ti 3d-Dispersion along the b-axis from ARPES, LDA+U calculation with ferromagnetic spin alignment, LDA+U with antiferromagnetic alignment for the high-T and low-T phase, and single-band Hubbard calculation (all with dispersions along the b-axis). LDA+U<sup>FM</sup> does not reproduce the downbending towards the outer zone boundary, while LDA+U<sup>AFM</sup> introduces this feature artificially by means of a doubled unit cell. The shadow band in the Hubbard calculation is not reproduced in experiment (which is not due to experimental resolution). (from [6])

valence band, and also succeeded in predicting that the  $d_{xy}$ -orbital is the lowest orbital available for the 3d electron of the Ti atom. This was proven by PES studies using linearly polarized light [6]. Knowing the orientation of the orbital lobes in the crystal and making use of selection rules this procedure allowed to distinct between the respective contributions of  $d_{xy}$  and the other  $t_{2g}$  orbitals. However, the DFT methods fail to reproduce peak shapes and widths extracted from experimental determinations of the band structure, while the Hubbard model calculation, which gives reasonable agreement in this respect, shows distinct features not present in ARPES, namely the shadow band. In Fig. 2 these results are summarized. Recent cluster-DMFT calculations seem to overcome previous shortcomings and show good correspondence of Ti 3d peak shapes with experimental data [9].

We carried out ARPES measurements of the valence band structure, in particular the Ti 3d spectral weight, in the high-T phase on self-grown crystals. Results along the paths X- $\Gamma$ -X (crystallographic a-axis) and Y- $\Gamma$ -Y (b-axis) show a pronounced one-dimensionality in that strong dispersion is only visible in the latter case. Elevated temperatures of about 350 K had to be used in order to minimize sample charging. A comparison of a- and b-axis dispersions in TiOCl and the isostructural material TiOBr is shown in Fig. 3 [10]. Those two compounds differ only slightly in lattice spacing because of larger atomic radii of the bromide, and thus the electronic structures are equal to a large extent. Focussing on TiOCl, it can be seen that the band widths along the a-axis and the b-axis (termed  $w_b$ , as indicated in the picture) differ significantly in magnitude, in contrast to the case of TiOBr, where they are equal within experimental uncertainties. This finding has been verified over a large number of samples and is thus an intrinsic property. It seems that while qualitatively the same features appear in both compounds, TiOCl has more one-dimensional character than TiOBr. However, since the shadow band is missing (in both cases), interchain coupling is assumed to play a major role in determining the electronic structure in TiOCl as well, although the ratio of in-chain over out-of-chain hopping is roughly  $\sim 1/8$ . Additionally, by com-



**FIGURE 3.** Ti 3d spectral weight dispersions (from [13]): along (a) a-axis and (c) b-axis for TiOBr, and along (b) a-axis and (d) b-axis for TiOCl. The blue lines indicate the maxima of the peaks obtained through a fitting procedure described in [10]. It can be seen that while dispersions along the a-axis are of comparable size in both compounds, the situation is significantly different along the b-axis: a much more pronounced downbending towards the zone boundary is visible in TiOCl, which in the case of TiOBr remains closer to the range of the a-axis dispersion.

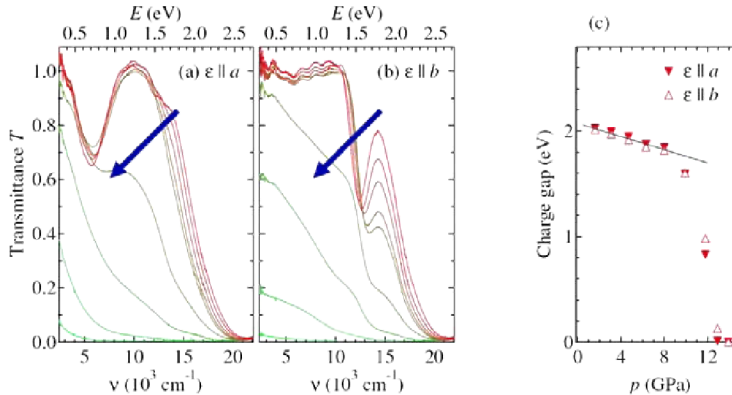
**TABLE 1. Comparison of TiOBr and TiOCl**

	TiOBr	TiOCl	$\Delta x/x$
$w'_b$	0.13 eV	0.17 eV	-23%
$w_b$	0.26 eV	0.47 eV	
J from magnetic susceptibility	32 meV	58 meV	-45%
$t = 0.5\sqrt{JU}$	0.16 eV	0.22 eV	-26%
t from LDA+U	0.17 eV	0.21 eV	-19%

paring bandwidths quantitatively as is summarized in Tab. 1, we found that they obviously scale with  $t \sim \sqrt{J}$  and not with  $J$ , which can be seen from the fact that the relative differences  $\Delta x/x$  between TiOCl and TiOBr are almost equal when comparing  $w'_b$  with the obtained hopping integrals  $t$ , in contrast to the extracted  $J$ 's. This suggests that electronic dispersions have their origin in charge excitations rather than in spin excitations.

## METALLIZATION AND DOPING

In order to retain any chance of reaching a superconducting phase instead of the spin-Peierls phase at low temperatures, it is imperative to first show that it is possible to drive the Mott-insulating system into a metallic state. For TiOCl, there is strong evidence from a recent study of optical transmittance and reflectance under pressure that this can be achieved [11]. Figs. 4(a) and (b) show transmittance along the two different axes a and b for different pressures. The features around  $6000 \text{ cm}^{-1}$  and  $13000 \text{ cm}^{-1}$ , respectively, are on-site excitations into  $t_{2g}$  orbitals, which are not degenerate anymore due to the distortion of the octahedral coordination of Ti atoms. For pressures above roughly 12 GPa however, the transmittance is suppressed over almost the entire studied frequency range. In Fig. 4(c) one can see how the charge gap of initially about 2 eV closes rather abruptly at those pressures.



**FIGURE 4.** (a),(b): Transmittance spectra of TiOCl for light polarization  $\epsilon$  along the a- and b-axis, respectively. Arrows indicate the direction of increasing pressure. The most drastic changes appear between 10 and 12 GPa. (c) Closing of the charge gap at around 12 GPa. (from [11])

In isostructural materials of the XNCl-type ( $X = \text{Hf}, \text{Zr}$ ) it has been shown that a superconducting state at rather high transition temperatures ( $T_c = 25.5 \text{ K}$ ) can be reached by suitably doping the crystals [12]. This route seems very promising for TiOCl as well and preliminary photoemission results show the appearance of new states within the gap region, but a detailed qualitative and quantitative analysis is still under way.

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