The question how the electronic structure of a Mott insulator develops upon doping is a long-standing problem in condensed matter physics. Marked additional attention is lent to this issue by the fact that the cuprate high-temperature superconductors are doped Mott (or charge-transfer) insulators as well. In Mott insulators, short-range electron correlations induce for partially occupied bands with integer filling a charge gap in the single-particle excitation spectrum, while band theory predicts a metal. For transition-metal oxides, the local (onsite) Coulomb energy U can be defined as the energy difference for removing and adding an electron to a site in the initial d\textsuperscript{\textit{d}} configuration, i.e. with \textit{n} electrons in the d shell. The single-particle excitation energies give rise to the incoherent spectral weight of the lower (LHB) and upper Hubbard bands (UHB), respectively. At room temperature, TiOCl is a prototypical low-dimensional Mott insulator with a 3\textit{d}\textsuperscript{5} configuration. In this respect it represents the electron analogue to the almost full 3\textit{d} shell with one single hole in the insulating parent compounds of the cuprates. Beyond the interest in this compound as a Mott insulator — and particularly the possibility to metallize it by the exertion of pressure — also the intriguing spin-Peierls scenario involving two successive phase transitions to incommensurate and commensurate order as well as its triangular lattice with frustrated interactions have attracted much attention recently.

We have electron-doped TiOCl by alkali-metal evaporation and monitored the electron-removal spectrum as a function of doping by photoemission spectroscopy (PES). A prime example is found for what is known under the notion of spectral weight transfer (SWT), which is a characteristic many-body effect expected in the case of a band-filling controlled Mott insulator-metal transition. However, intriguingly, we do not detect a metallic phase at any doping concentration up to \textit{z} \approx 0.5, which is at variance with theoretical expectations within usual one- or multi-orbital Mott-Hubbard scenarios.

We argue that a single-particle alloy effect prevents the insulator-to-metal transition in alkali-metal intercalated TiOCl which thereby is identified as a realization of an alloy Mott insulator.

TiOCl crystallizes in a two-dimensional (2D) structure, where Ti-O bilayers are stacked along the crystallographic c-axis and only weakly interact through van-der-Waals forces, which leaves space in between for intercalation with dopants. With the Ti ions centered in a distorted octahedron of O and Cl ligands, the degeneracy of the 3\textit{d}\textsuperscript{2\textsubscript{g}} orbitals is lifted such that the lowest d orbitals are split by about 0.3eV. Single crystals were grown by chemical vapor transport as described elsewhere. Clean surfaces were exposed by \textit{in situ} cleavage and dosed by alkali-metal vapor from SAEST\textsuperscript{TM} dispensers. Data was recorded with a SPECS PHOIBOS 100 analyzer at a total energy resolution of 700meV and 70meV using Al K\textsubscript{\textalpha} (1486.6eV) and He I\textsubscript{\textalpha} (21.22eV) radiation for core-level (XPS) and valence-band (UPS) spectroscopy, respectively. To minimize charging effects and to ease atomic diffusion the samples were held at elevated temperatures (\approx 360K) during dosing and measurements. Preservation of symmetry and atomic long-range order at the surface were monitored by low-energy electron
diffraction (LEED). The chemical stability of the oxygen was inferred from the unchanged O 1s core-level spectra and a stoichiometric analysis of the Ti : O ratio.

That dosing the TiOCl crystals by alkali-metal vapor (Na and K; within the scope of this study, Na and K are interchangeable) essentially leads to both intercalation of the alkali-metal atoms into the van-der-Waals gaps and the donation of electrons to the Ti sites — as is known from the structurally identical TiNCl [12] — is demonstrated in Fig. 4. In the left panel, the Na 1s core-level spectrum is displayed for normal emission (NE) and an emission angle of 70° with respect to the surface normal. If the alkali-metal atoms only built an overlayer without intercalating into the TiOCl structure, one would expect a small and a huge Na 1s signal at NE and 70°, representing bulk and surface sensitive spectra, respectively. However, both signals are of comparable intensity. Actually, the moderately higher intensity at 70° can be quantitatively understood if one simulates the PES signal [13] due to the discrete vertical distribution of the Na ions, taking into account the stronger exponential damping of photoelectrons emitted deeper from the solid. A direct spectroscopic proof for successful electron doping can be inferred from the Ti 2p core-level spectra in the right panel of Fig. 4. The spectral weight at the lower binding energy sides of the Ti²⁺ related main doublet, which increases with dosing time, can be attributed to emission from the 2p level of Ti²⁺ as evidenced by its chemical shift of 2.7 eV and thus is a direct manifestation of extra electrons at the Ti sites. Moreover, from a standard fitting procedure using two Voigt profiles for each Ti valency to the Ti 2p spectra (cf. Fig. 4) a rather accurate determination of the electron doping concentration can be obtained through $x = A(2^+)/[A(2^+)+A(3^+)]$, where $A$ denotes the area of the Voigt profiles for each valency.

In the angle-integrated UPS spectra of the valence band (see Fig. 4 spectra corresponding to those of Fig. 1 right panel), the successful electron doping manifests itself in additional spectral weight, piling up with increasing doping concentration $x$ near the chemical potential $E_{\text{chem}}$ [14]. Already after a tiny amount of dosing the whole spectrum shifts by about 0.6 eV to higher binding energies. In the most simple picture of a Mott insulator the abrupt shift corresponds to a jump of the chemical potential from the midgap position to the lower edge of the UHB [8]. Note that the observed value of 0.6 eV is much smaller than half the optical gap of undoped TiOCl, which is ≈ 2 eV. In addition, with further doping one would expect the formation of a coherent quasiparticle peak at the chemical potential concomitant with a decrease of the LHB (and UHB) spectral weight, indicating a strongly correlated metallic state [15]. Instead, the doping-induced spectral weight develops in a broad hump, partly overlapping with the original spectral weight of the LHB.

If one normalizes the integral $3d$ part of the spectra to $1 + x$ in accordance with the conservation of spectral weight, one finds that the doping-induced weight apparently grows at the expense of the LHB. A quantitative analysis by fitting two Gaussian to the spectra after subtraction of a Shirley background (cf. Fig. 4) reveals that indeed the LHB spectral weight decreases as $1 - x$ while the weight of the additional band increases as $2x$ (see Fig. 4(a) for K intercalation). This SWT is exactly what one would expect in a local picture ($t = 0$), i.e. when no quasiparticle is present, for the LHB and UHB of a Mott insulator [16]. For each additional electron donated to the Ti 3d states, one possibility to remove an electron from a singly occupied Ti site at an orbital energy $\varepsilon$ is discarded in favor of two possibilities to remove an electron from a doubly occupied site at an energy $\varepsilon + U$. While thus it is manifest that a simple Hubbard model picture provides the correct basis to explain the SWT as the most salient feature of our data, it obviously has to be elaborated to account for the other observations, in

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**FIG. 2:** (Color online) Evolution of the overall valence band spectra (left) and the Ti 3d spectral weight near the chemical potential (right) as a function of electron doping $x$.

**FIG. 3:** (Color online) Decomposition of Ti 2p (left) and Ti 3d (right) spectra by fitting to determine the relative amounts of doping-induced spectral weight. For details see text.
particular the insulating behavior at all doping levels.

At this stage, a steer in the right direction might come from drawing a parallel to the cobaltate Na$_3$CoO$_2$, which also exhibits a 2D structure with the alkali-metal ions between the oxide layers. This material has recently attracted much interest because, when hydrated, it becomes superconducting for $x = 1/3$ at $\approx 4.5$ K [17]. At variance with TiOCl, for a wide range of doping concentrations it remains metallic. Only for $x = 0.5$ an insulating phase is observed, accompanied by correlation-induced charge-order [18]. For Na concentrations around $x \approx 0.8$, it was pointed out from neutron scattering that Na ordering occurs driven by inter-ion Coulomb interaction [19]. This patterning in turn influences the electronic structure through the associated periodic Coulomb potential. A similar mechanism might be important in our case. Indeed, recent molecular dynamics studies combined with density functional calculations identified such patterning in the case of Na-intercalation for TiOCl [20].

Taking these observations as a starting point we seek to include one-particle effects of that kind on top of a simple Hubbard model description. Such variants are known under the terms binary alloy or ionic Hubbard model [21–25]. As conventional Hubbard models, these are tight-binding models with a hopping integral $t$ and a local Coulomb repulsion $U$ between electrons at the same lattice site. In addition, the energies at random or alternating sites of a bipartite lattice are lowered by a potential $\Delta$. Depending on the relative sizes of $\Delta, U, t$, and the fraction of alloy sites $\rho$, band and Mott insulating states can follow each other at certain discrete (not necessarily commensurate) band-filling numbers $n$, while away from these filling numbers Anderson insulating or metallic phases occur [24]. E.g. for $\rho < 1$ and in the limiting case $t \ll 1$, all alloy sites, giving rise to an alloy band (AB), are singly occupied for $n = 1 + \rho$ and the system is an alloy Mott insulator. Increasing $n$ further, the electrons prefer to doubly occupy the alloys sites first if $\Delta > U$, and the system becomes an alloy band insulator for $n = 2 + \rho$. Eventually, at $n = 1 + \rho$ all alloy sites are doubly occupied while the remaining sites host one electron and the system is again a Mott insulator. We emphasize that starting from whatsoever insulating state, additional electrons will always induce a metallic or at least Anderson insulating state both of them with finite spectral weight at the chemical potential.

Regarding TiOCl, this seeming contradiction can be naturally resolved: in n-doped TiOCl the energy at Ti sites with an alkali-metal ion next to them will be lowered due to its associated Coulomb potential. It is thus the alkali-metal ions themselves that create the alloy sites to which they donate their outer electrons (hence we call these second kind of Ti sites electrostatically induced alloy sites). Consequently, the number of alloy sites is dynamic, not static, as in the aforementioned models. We thus have $\rho = x$, and, for the alloy band to appear in midgap position, $\Delta < U$ (as we will explicate below in a quantitative analysis $U$ has to be replaced by the appropriate effective onsite interaction energy for our case). Starting doping at $n = 1$, for any $x$ this gives $n = 1 + x = 1 + \rho$ and the system is an alloy Mott insulator for all $x$. Note that no doping into the UHB is achieved and hence it remains above the chemical potential, being invisible in photoemission. The spectral weight distribution for both the doped and undoped case is sketched in Fig. 4 (b). Each feature (LHB, UHB, AB) is labelled with the corresponding single-particle excitation by denoting the $d$ configurations of the initial and final states. In this picture the SWT now occurs from the LHB to the AB which as being due to doubly occupied sites takes over the role of the UHB in a clean (and local) Mott-Hubbard picture.

Our arguments can be corroborated quantitatively. In a simple multi-orbital Hubbard model in the atomic limit, i.e., $t = 0$, and with degenerate orbital energies and only one sort of sites an extra electron will be hosted due to the gain in intraatomic exchange energy in a second orbital with parallel spin. Hence, the separation of the LHB and UHB is given by $U - 3J$, where $J$ is the Hund’s rule coupling [26, 27]. Taking a small difference $\delta$ in orbital energies into account ($\delta \ll J$), the separation is given by $U - 3J + \delta$ (cf. upper half of Fig. 4 (b)). From optical absorption [7] it is known that the charge gap is about 2 eV. In the doped case, the position of the LHB and UHB remain essentially unchanged, since the alkali-metal ions hardly affect the orbital energies of remote Ti sites. Instead, the AB emerges within the original charge gap below the chemical potential owing to the lowered orbital energies at Ti sites next to the alkali-metal ions. From the PES data, its energy separation from the LHB amounts to $\sim 1$ eV. Note that in addition to the electrostatic term $\Delta$ also the crystal-field splitting between the ground state orbital and the next higher orbital is slightly lowered from $\sim 0.3$ eV to $\sim 0.1$ eV according to the density-functional calculations in Ref. [24]. Hence, in
The atomic limit, the separation between LHB and AB may be expressed as $U - 3J + \delta^2 \approx \Delta$. From the sketched qualitative picture the chemical potential lies in midgap position between AB and UHB. With the 1 eV splitting between LHB and AB it follows that the chemical potential in the doped case will jump by about 0.5 eV with respect to the undoped case in agreement with the PES data. Moreover, with reasonable assumptions for $U - 3J$ of 2.5 - 3.5 eV \cite{20,26,28}, one can estimate the potential $\Delta$ at the alloy sites to be $\approx$ 2 eV. This value can be understood in a simple point charge model. With the relaxed crystal structure from Ref. \cite{20} for one Na atom per four unit cells, the Na ion induced Coulomb potential at the next Ti site is about 2 eV, taking screening by a dielectric constant around 3.5 \cite{5} into account, and thus well compares with the value derived from our model.

Above, the lifted degeneracy of the two lowest $d$ orbitals in TiOCl was only taken into account for the sake of formal correctness. It adds only a negligible inaccuracy to an estimation of the model parameter $\Delta$. This splitting in the orbital energies of $\approx$ 0.1 eV according to theory \cite{20} apparently cannot be resolved in the AB related feature of the PES spectra in Fig. \ref{fig:2} due to its intrinsic broadness. However, one can exploit the different symmetry of these two orbitals with respect to the $(b,c)$ crystal mirror plane to switch between them in PES by changing the polarization of the incoming photons from horizontal to vertical using the geometry sketched in Fig. \ref{fig:3} \cite{28}. From the different orbital symmetries, one would expect to be able to switch between the LHB and one component of the AB at lower energy and another component of the AB at $\approx 0.1$ eV higher energy, which then would reveal the multi-orbital character of this “band”. It is important to understand that this multi-orbital effect is due to the fact that — in the language of PES — after removing an electron from a doubly occupied alloy site the remaining electron might occupy the one or the other orbital (all other orbital degrees of freedom are quenched) with different energies. It must not be thought of in terms of single-particle states which are occupied in the initial ground state.

The result of this experiment is depicted in Fig. \ref{fig:5}. Shown are the curves resulting from an independent component analysis, since due to the finite degree of polarization, a possible small misalignment of the sample, and symmetry-breaking phonons, for one polarization also a certain fraction of the spectrum for the other is monitored and vice versa. The unspoilt spectra indeed show the expected behavior and allow to infer an energy splitting of the orbitals contributing to the AB of about 0.15 eV.

In summary, we have investigated by photoelectron spectroscopy a prime example for the spectral weight transfer upon doping in a prototypical Mott insulator, which is a fingerprint of many-body physics. To understand why surprisingly no metallic state is induced, one has to take into account single-particle effects in terms of modified site energies due to electrostatic alloying. The multi-orbital nature we demonstrate by polarization-dependent measurements.

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