Doping the unusual spin-Peierls systems TiOX (X=Cl, Br)

TiOCl and the related isostructural oxyhalide TiOBr are low-dimensional Mott insulators with a $3d^1$ configuration (optical gap ca. 2eV) which display unusual magnetic properties. Because the Ti^{3+} ions form topologically a triangular-like lattice, it was speculated early in the nineties that these materials were magnetically highly frustrated and could display resonating valence bond (RVB)-type superconductivity, if driven into a metallic state. However, in case of TiOCl the Bonner-Fisher-type behavior of the susceptibility above T_{c2}=95K and the occurrence of a dimerized spin-Peierls phase below T_{c1}=67K indicate that the magnetic coupling is quasi-one-dimensional. This is supported by LDA+U calculations and angle-resolved photoelectron spectroscopy (ARPES) which find a pronounced electronic anisotropy with small but finite interchain coupling. The latter has been argued to be responsible for the non-canonical spin-Peierls behavior with an incommensurate precursor phase between T_{c1} and T_{c2}, which may bring magnetic frustrations (and hence RVB physics) back into play. While TiOBr exhibits the same phase diagram, its one-dimensional character is less pronounced which makes it an even better candidate for bond dimer fluctuations. Our XPS and ARPES studies on n-doped crystals using alkali metal intercalation show the emergence of additional states in the charge gap concomitant with a transfer of spectral weight from the original lower Hubbard band. Surprisingly, this additional spectral weight is not cut off by the Fermi distribution function at the chemical potential but rather shows a pseudogap-type of behavior. Thus seemingly no metallic phase is observed which might be due to strong electron coupling to phonons or other degrees of freedom (magnons etc.) shifting the spectral weight away from the chemical potential to higher binding energies.