NiO: Correlated Bandstructure of a Charge-Transfer Insulator

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The bandstructure of the prototypical charge-transfer insulator NiO is computed by using a combination of an ab initio bandstructure method and the dynamical mean-field theory with a quantum Monte-Carlo impurity solver. Employing a Hamiltonian which includes both Ni-d and O-p orbitals we find excellent agreement with the energy bands determined from angle-resolved photoemission spectroscopy. This solves a long-standing problem in solid state theory. Most notably we obtain the low-energy Zhang-Rice bands with strongly k-dependent orbital character discussed previously in the context of low-energy model theories.

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The quantitative explanation of the electronic structure of transition metal oxides (TMOs) and other materials with correlated electrons has been a long-standing challenge in condensed matter physics. While the basic concept explaining why materials such as NiO are insulators was formulated by Mott already a long time ago [1], the development of an appropriate, material-specific computational scheme proved to be a formidable task. The electronic structure of the late TMOs, including the related compound NiO: Correlated Bandstructure of a Charge-T ransfer Insulator

The application of the standard bandstructure theory to NiO is marked by a failure of LDA to produce an insulating groundstate [14]. The antiferromagnetic order within LDA [15], despite rendering NiO an insulator, does not present much of an improvement since (i) the band gap is severely underestimated, (ii) the experimentally observed lower Hubbard band is completely missing, and (iii) static quantities such as the local magnetic moment do not agree well with experiment. Moreover, the ARPES data of Tjernberg et al. [16] measured across the Néel temperature \( T_N = 525 \) K show that the NiO bandstructure is rather insensitive to the magnetic order. The first attempt to include the strong on-site correlations into the first-principles bandstructure methods was the LDA+U theory of Anisimov et al. [17]. The static, orbitally dependent self-energy of LDA+U enforces a separation of the occupied and unoccupied \( d \)-bands and thus opens a gap of the experimentally observed size. This in turn leads to a significant improvement in the description of groundstate properties such as the local moment or the lattice constant [18]. Despite this success LDA+U does not provide a good description of the photoemission spectra since it places almost all of the valence \( d \) spectral weight into the lower Hubbard band. Exact diagonalization studies of Fujimori et al. [12] on small clusters [12] provide strong evidence that the dynamical correlations are necessary to capture properly the distribution of the \( d \) spectral weight within the valence band.

A systematic inclusion of local dynamical correlations into lattice models was made possible by the dynamical mean-field theory (DMFT) [5, 6, 7]. The connection of DMFT with bandstructure methods, usually re-
We start the discussion of our results by considering the limit of vanishing $p-d$ hybridization, in which case the entire $d$-spectral weight is located in more or less featureless Hubbard bands located below the $p$-band manifold [21] and the holes in the uncorrelated $p$-bands have infinite lifetimes. The $p-d$ hybridization changes this picture qualitatively. In particular, two additional bands of mixed character appear at -2 and -4 eV of Fig. 1. These bands contain about half of the valence $d$-spectral weight as can be seen from the $k$-integrated spectral functions, which is formally an $8 \times 8$ matrix with the only non-zero elements on the diagonal of $dd$ block, is obtained by solving the equation

$$G_{dd}(\omega^+) = \sum_k (\omega^+ + \mu - h_k - \Sigma(\omega^+))^{-1}.$$  \hspace{1cm} (1)$$

simultaneously for $e_g$ and $t_{2g}$ symmetry. Here the $G_{dd}$ is the diagonal element of the Green function corresponding to either $e_g$ or $t_{2g}$ symmetry, $h_k$ is the $8 \times 8$ Hamiltonian matrix on a mesh of $k$-points and $\mu$ is the self-consistently determined chemical potential. The equation is solved approximately on the contour $3\omega^+ = 0.05\text{eV}$ subject to the constraints $3\Sigma(\omega^+) \leq 0$ and Kramers-Kronig relations, which are, however, satisfied automatically for good quality QMC data.

In Figs. 1 we compare the theoretical bands, represented by the $k$-dependent spectral density $A(k, \omega)$, along the $\Gamma - X$ and $\Gamma - K$ lines in the Brillouin zone with ARPES data of Ref. 4. Both theory and experiment exhibit two relatively flat bands at -2 and -4 eV followed by several dispersive bands in the -4 to -8 eV range and a broad incoherent peak around -10 eV. Overall we find an excellent agreement. The deviations around the $\Gamma$ point in the lower panel of Fig. 1 are due to the inaccuracy in the location of the $\Gamma$ point in off-normal-emission experiment 4. The crosses near the $\Gamma$ point mark a weak band which was interpreted as a consequence of AFM order 4 and is therefore not expected to be found in the paramagnetic phase investigated here. In Fig. 2 we show the orbital decomposition $A_{\omega}(k, \omega)$ of the spectral density visualized as a shape-preserving function $A_{\omega}^{-1}(\omega^+)$, in order to capture both sharp and broader features in a single plot.

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FIG. 2: (color online) The orbitally decomposed spectral function $A_{\nu \nu}(\mathbf{k}, \omega)$ along the Γ-X (left column) and Γ-K (right column) lines in the Brillouin zone plotted as $C + A_{\nu \nu}(\mathbf{k}, \omega)$. The panels from top to bottom show the O-p, Ni-d $e_g$ and Ni-d $t_{2g}$ contributions. Here $C = 1.5, 2$ for the $p$ and $d$ projections, respectively. Detail of the uppermost valence band marked by the dotted lines is shown in Fig. 3.

Special considerations, especially in the case of high temperature cuprate superconductors, have been subject of numerous theoretical investigations. This was initiated by Zhang and Rice [11] who constructed an effective $t - J$ Hamiltonian for holes doped to the copper-oxygen plane and who introduced the notion of a bound state between the $p$-hole and $d$-spin known as Zhang-Rice singlet. Using a canonical transformation of the Hubbard model onto the spin-fermion model Eroles et al. [24] found a strong $k$-dependence in the orbital composition of the Zhang-Rice band. Bala et al. [25, 26] applied a generalized spin-fermion model to a 2D slab of NiO and obtained qualitative agreement with the corresponding part of the ARPES spectrum. They found very strong $k$-dependence of the spectral weight in the uppermost valence band. To a good approximation the latter corresponds to the $p$-spectral weight of the original multi-band Hubbard model [24] and is thus directly comparable to the results of the present study. Unlike model theories, which are restricted to a special part of the Hilbert space, the LDA+DMFT scheme provides a unified picture of all energy scales and avoids

\[ \text{\textsuperscript{1}} \text{ Compare to the symmetric upper and lower Hubbard bands of } e_g \text{ symmetry in Fig. 3 of Ref. 10 where } p - d \text{ hybridization was not included.} \]
any adjustable parameters. The good agreement with the experimental data and the low-energy model theory found in this work demonstrates the capability of DMFT to adequately describe charge-transfer systems and puts the earlier model results on a solid foundation.

In conclusion, by employing dynamical mean-field theory combined with LDA electronic structure calculation we presented the solution to a long-standing problem, the computation of the full valence bandstructure of a charge-transfer insulator. We obtained a very good agreement with the ARPES data of Shen et al. [3, 4] without any adjustable parameters. We found well-separated Zhang-Rice bands at the top valence manifold with strongly k-dependent orbital composition. Our results clearly demonstrate the capability of DMFT to treat, upon explicit inclusion of p–d hybridization, the late transition-metal oxides and charge-transfer systems in general.

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