Local correlations and hole doping in NiO

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Using a combination of ab initio bandstructure methods and dynamical mean-field theory we study the single-particle spectrum of the prototypical charge-transfer insulator NiO. Good agreement with photoemission and inverse-photoemission spectra is obtained for both stoichiometric and hole-doped systems. In spite of a large Ni-d spectral weight at the top of the valence band the doped holes are found to occupy mainly the ligand p orbitals. Moreover, high hole doping leads to a significant reconstruction of the single-particle spectrum accompanied by a filling of the correlation gap.

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I. INTRODUCTION

Already in 1937, at the outset of modern solid state physics, de Boer and Verwey drew attention to the surprising properties of materials with incompletely filled 3d-bands, such as NiO. This observation prompted Peierls and Mott to discuss the interaction between the electrons. Ever since transition metal oxides (TMOs) were investigated intensively. This interest further increased when it was discovered that TMOs display an amazing multitude of ordering and electron correlation phenomena, including high temperature superconductivity, colossal magnetoresistance and Mott metal-insulator transitions. In the late 1950’s MnO and NiO were taken as the textbook examples of antiferromagnets. However, when the importance of local Coulomb correlations in the transition metal d-shell was realized TMOs were considered candidates for Mott insulators. In the mid 1980’s Zaanan, Sawatzky and Allen (ZSA) introduced their classification of TMOs and related compounds into Mott-Hubbard and charge-transfer (CT) systems. In the early TMOs the ligand p-band is located well below the transition metal d-band and thus plays a minor role in the low energy dynamics. Such a case, called Mott–Hubbard system in the ZSA scheme, is well described by a multi-band Hubbard model. On the other hand, the late TMOs belong to the CT type where the p-band is situated between the interaction split d-bands. A more general Hamiltonian where the p-states are explicitly included is then needed, which can be viewed as a combination of multi-band Hubbard and Anderson lattice models. A major impulse for detailed investigations of CT systems, and especially of their hole doped regime, came with the discovery of high temperature superconductivity in cuprate perovskites. While the standard three-band Hamiltonian for cuprates contains only one d-orbital per lattice site, the description of cubic transition metal oxides, the prominent member of which is NiO, requires the full set of d-orbitals. The latter are of interest not only for fundamental research, but play an important role also in fields such as geophysics. Furthermore, recent progress in high pressure experiments made the insulator-to-metal transition in some TMOs accessible in the laboratory, providing yet another stimulus for theoretical investigations.

We report a computational study of NiO combining ab initio band structure calculations in the local density approximation (LDA) with the dynamical mean-field theory (DMFT), an approach known as LDA+DMFT. By treating the local correlations and the Ni 3d-O 2p hybridization on the same footing we provide a description of the full valence and conduction band spectra of a CT system with strong hybridization. We will show that a good quantitative agreement with photoemission and inverse-photoemission data can be obtained thereby. This provides a solid foundation for the subsequent investigation of hole doping, a question of broader interest mainly in the context of cuprates. It will be shown that the behavior of the doped holes clearly reveals the CT character of NiO.

NiO is a type II anti-ferromagnet \( T_N = 523 \) K with a magnetic moment of almost \( 2 \mu_B \) and a large gap surviving well above \( T_N \). The standard LDA band theory predicts NiO to be a metal, or an antiferromagnetic insulator if spin polarization is allowed. A severe underestimation of the gap and the magnetic moment suggests, however, that the Slater antiferromagnetic state obtained within LDA does not describe the true nature of NiO. On the other hand exact diagonalization studies on small clusters were quite successful in describing the single- and two-particle spectra, showing that the local Coulomb interactions are important. This made it clear that an explicit treatment of Coulomb interactions within the 3d shell is needed, and methods such as LDA+U, self-interaction correction, or GW were introduced. The static, orbitally dependent self-energy of LDA+U enforces a separation of the occupied and unoccupied d-bands and thus opens a gap comparable to experiment. This in turn leads to a significant improvement of the
TABLE I: Orbital occupancies and the local moment on the Ni site for different hole dopings.

| n_h | n_{0\sigma} | n_{1\sigma} | n_p | n_{1d} |
|-----|-------------|-------------|-----|--------|
| 0   | 0.547       | 1.000       | 0.969 | 1.85 |
| 0.6 | 0.531       | 0.994       | 0.885 | 1.61 |
| 1.2 | 0.530       | 0.980       | 0.800 | 1.45 |

description of static properties such as the local moment or the lattice dynamics. However, the LDA+U method is limited to an ordered state and does not yield the electronic excitations and the effect of doping correctly.

A systematic inclusion of dynamical correlations was made possible by dynamical mean-field theory. Since its introduction DMFT proved to be a powerful tool for the investigation of electronic systems with strong local correlations. In connection with band-structure methods, the LDA+DMFT scheme provides access to material specific single-particle spectra as well as more general correlation functions. Applications of LDA+DMFT so far were mostly limited to Mott-Hubbard systems, where the ligand states are integrated out before the correlation problem is solved. Recently, Ren et al. applied this approach to NiO and were able to obtain a realistic gap and the near-gap spectra. However, this approach takes into account only d-electrons, such that the orbital character of the valence and conduction band are bound to be the same, the high frequency incoherent features in the valence band are missing, and the hole doping cannot be described realistically. In this work we go beyond such limitations by working with the ligand p states explicitly.

II. COMPUTATIONAL DETAILS

LDA+DMFT proceeds in two steps: (i) construction of the effective Hamiltonian from converged LDA calculation, and (ii) solution of the corresponding DMFT equations. Here we use the projection onto Wannier functions to obtain an eight-band p – d Hamiltonian

\[ H = \sum_{k,\sigma} (h_{k,\alpha\beta}^{dd} d_{k\alpha\sigma}^\dagger d_{k\beta\sigma} + h_{k,\alpha\beta}^{pp} p_{k\alpha\sigma}^\dagger p_{k\beta\sigma} + h_{k,\alpha\gamma}^{dp} d_{k\alpha\sigma}^\dagger p_{k\gamma\sigma} + h_{k,\alpha\gamma}^{dp} p_{k\alpha\sigma}^\dagger d_{k\gamma\sigma} + \sum_{i,\sigma,\sigma'} U_{i\alpha\beta}^{\sigma\sigma'} n_{i\alpha\sigma} n_{i\beta\sigma'}). \]

Here \( d_{k\alpha\sigma} \) and \( p_{k\gamma\sigma} \) are Fourier transforms of \( d_{i\alpha\sigma} \) and \( p_{i\gamma\sigma} \), which annihilate the d or p electron with orbital and spin indices \( \alpha \sigma \) or \( \gamma \sigma \) in the \( i \)th unit cell, and \( n_{i\alpha\sigma} \) is the corresponding occupation number operator. The elements of \( U_{i\alpha\beta}^{\sigma\sigma'} \) matrix are parameterized by \( U \) and \( J \). The constrained LDA calculation yields \( U=8 \) eV and \( J=1 \) eV. To account for the Coulomb interaction already present in LDA we renormalize the \( dd \)-diagonal elements of the LDA Hamiltonian by the double counting correction

\[ h_{k,\alpha\beta}^{dd} = h_{k,\alpha\beta}^{dd} - (N_{\text{orb}} - 1) \delta_{\alpha\beta}. \]

where \( n_{\text{LDA}} \) is the average LDA occupation per orbital and \( N_{\text{orb}}=10 \) is the total number of orbitals within the shell.

Next we iteratively solve the DMFT equations on the Matsubara contour, a key part of which is the auxiliary impurity problem solved by quantum Monte-Carlo (QMC) method. The results reported here were obtained at \( T=1160 \) K. To obtain the single-particle spectral functions analytic continuation to real frequencies is performed using the maximum entropy method. Applying QMC to a gapped system requires careful assessment of ergodicity and autocorrelation issues.

III. RESULTS AND DISCUSSION

A. Single particle spectra

The orbital occupations, shown in Table I and the local moment of 1.85 \( \mu_B \) obtained from the paramagnetic DMFT solution correspond to a \( d^8 \) groundstate of the Ni ion with two ferromagnetically coupled holes of \( e_g \) symmetry. In Fig. I the calculated spectral densities resolved into Ni 3d and O 2p contributions are compared to photoemission and inverse photoemission data. Using the full \( p – d \) Hamiltonian we are able to cover the entire valence and conduction bands spectra. Features corresponding to 4s and 4p bands at 10 eV and 13 eV, respectively, are not included in the theoretical spectrum. As
shown by Eastman and Freeouf, the relative intensity of the 2p contribution increases with decreasing photon energy. Therefore the 120 eV spectrum is dominated by Ni 3d emission, while at 66 eV photon energy the O 2p contribution peaked around -4 eV is resolved (for a detailed orbital decomposition see Ref. 25). The theoretical spectrum very well reproduces the experimental features, including the size of the gap, the d character of the conduction band, the broad d peak at -9 eV, the position of the p-band, and the strong d contribution at the top of the valence band. While the gap and the Hubbard subbands can be described already with the static theory (LDA+U), a dynamical treatment is apparently needed to capture the substantial redistribution of spectral weight between the incoherent (-9 eV) and resonant (-2 eV) features in the d-band. As crude as this approximation may be we believe that the essential physics of p-d weight transfer is captured correctly. In Fig. 2 we show the single-particle spectral density resolved in Fig. 3: (color online) Ni-d and O-p resolved spectral densities for a hole concentration $n_h = 0.6$ (offset for better resolution). The inset shows a comparison of $e_g$ spectral densities for hole concentrations $n_h = 0.6$ and 1.2.

B. Hole doping

Next we discuss hole doping of NiO. An experimental realization can be found in Li$_x$Ni$_{1-x}$O studied in the doping range $x = 0.02-0.4$. Using the Hamiltonian of the undoped system the replacement of $x$ Ni$^{2+}$ ions by Li$^{2+}$ ions introduces on average $n_h = x/(1-x)$ hole per Ni site. As crude as this approximation may be we believe that the essential physics of p-d weight transfer is captured correctly. In Fig. 3 we show the single-particle spectral densities for $n_h = 0.6$ corresponding to $x = 0.38$. There is no significant difference between the $t_{2g}$ spectra in the doped and undoped cases, but the $e_g$ spectral function changes significantly. Most notably the Mott gap is filled, while the Hubbard subbands are preserved as distinct features. This is also observed in experiment, as shown in Fig. 4. A quite different behavior was reported in the single-band Mott insulator, where the gap survives doping while the coherent peak merges with one of the Hubbard subbands. Further hole doping of NiO leads to a spectral weight transfer from both upper- and lower-Hubbard-subbands to the quasiparticle part of the $e_g$ spectrum (see inset of Fig. 3), which can be viewed as an enhancement the itinerant character of the system.
Theoretical Ni-$d$ spectral densities for electron addition and electron removal obtained for $n_h = 0.6$ hole-doped NiO compared to the photoemission and inverse-photoemission spectra of Li$_2$Ni$_3$O (the experimental baseline is offset for better readability).

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