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Quasiparticle Band Structure of NiO: The Mott-Hubbard Picture Regained

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We demonstrate that the Hubbard correlation among Ni $3d$ electrons is able to reproduce the insulating character of NiO, the correct value of the gap, the orbital character of the valence band edge, and the presence of satellite structures. We have determined the quasiparticle spectra starting from the complex single particle band structure of NiO and including the on-site Hubbard repulsion according to a recently developed three-body scattering theory which allows us to treat highly correlated and highly hybridized systems. The calculated quasiparticle band structure is in excellent agreement with photoemission data.

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NiO is the prototype of transition metal oxides which exhibit a radical breakdown of conventional band theory. According to standard single particle approaches NiO is predicted to be a metal or at most a small gap insulator, while from electrical, optical, and combined direct-inverse photoemission it is known to be an insulator with a gap of few electron volts [1]. During the last decades various and controversial interpretations of the nature of the insulating gap of NiO have been proposed which emphasize (a) the role of electron-electron correlation [2], (b) the covalency of the chemical bond with oxygen [3,4], (c) the importance of antiferromagnetic order [5], and (d) of self-interaction [6,7] or U-corrected [8] energy functionals. The problem is far from being solved: Theories (c) and (d), which interpret NiO as a band insulator, either underestimate the gap or poorly reproduce the observed spectra; Mott-Hubbard theory (a) in its simplest form fails in reproducing the observed orbital character of the gap edges [4,9]; finally theories (b), which describe NiO as a charge transfer insulator, rely on a rather crude description of the band structure.

The breakdown of the single particle description in NiO is evident also from the presence of well-defined satellite features in the excitation spectra [10,11], a clear signal of strong electron-electron correlation. A satisfactory description of the electronic structure of NiO, inclusive of many-body effects, must therefore reproduce quantitatively both the insulating gap and the detailed satellite structure. We demonstrate that this can be achieved in the Mott-Hubbard picture, provided that the complexity of the band structure is fully included.

The Hubbard Hamiltonian has often been used to modify single particle eigenvalues, the implicit assumption being that among the various many-body terms responsible for e-e correlation, the Coulomb repulsion U between electrons sitting on the same atom is the one which is worst treated by band theories based on mean field approaches such as local density functional approximation (LDA). Most of the studies on the Hubbard Hamiltonian are based, however, either on a simplified description of the single particle states or on perturbative approaches to treat the electron-electron correlation. None of these approximations are adequate for NiO where nickel d electrons are highly hybridized with p electrons of the ligand and where the value of the Hubbard parameter U is known to be much larger than the d-band width [12].

We have recently developed a method which allows us to treat correlation effects through an approximate nonperturbative solution of the Hubbard Hamiltonian [13]. This approximation consists of a configuration-interaction expansion of the many-body states of the interacting system where the various configurations differ for the number of electron-hole pairs. The method has a rather wide range of validity since it is not limited to particular band filling and can be applied for any value of U. The interactions between configurations with the same number of electron-hole pairs are represented by a set of two-body scattering t matrices, which can be calculated exactly. The Fadeev three-body scattering theory [14,15] is used to determine the total scattering matrix and the resolvent giving the energy of the many-body system. All the details for a single-band Hamiltonian are reported in Ref. [13], the generalization to the multiband case requiring only minor changes and an explicit use of the so-called local approximation [16,17].

The method allows us to obtain the energy of the interacting system with one removed or one added electron, the reference energy being the ground state of the interacting system. Since in the present approach the configuration expansion is truncated to included just one electron-hole pair, the energy of the interacting N particle system coincides with the noninteracting one [13]: The band eigenvalues and eigenvectors must be calculated once and for all, and no self-consistent loop is required.

The quasiparticle spectrum for electron and hole states is obtained starting from the single particle density of states and for a given value of the intrasite correlation. The hole state self-energy for a multiband system is given by

$$\Sigma^-_{n\underline{k}} = \sum_\beta |c^n_\beta(\underline{k})|^2 \left[\sum_\alpha U_{\alpha\beta} N^h_\alpha - \Sigma^-_\beta(\omega) \right], \tag{1}$$

where

$$\Sigma^-_\beta(\omega) = \sum_\alpha \int_{e_f}^{\infty} d\epsilon \, n_\alpha(\epsilon) T_{33}^{\alpha\beta}(\omega - \epsilon) \times [1 + U_{\alpha\beta} A^{\alpha\beta}(\omega - \epsilon)]. \tag{2}$$

$T_{33}^{\alpha\beta}$ is the t matrix describing the hole-hole multiple scattering

$$T_{33}^{\alpha\beta}(\omega) = \frac{U_{\alpha\beta}}{1 + U_{\alpha\beta} g_3^{\alpha\beta}(\omega)}, \tag{3}$$

with

$$g_3^{\alpha\beta}(\omega) = \int_{-\infty}^{E_f} d\epsilon' \int_{-\infty}^{E_f} d\epsilon \, \frac{n_\alpha(\epsilon) n_\beta(\epsilon')}{\omega - \epsilon' - \epsilon - i\delta}. \tag{4}$$

$A^{\alpha\beta}$ includes the hole-electron scattering and is determined by solving an integral equation which is identical to the one described in Ref. [13], except for the orbital dependence of the quantities involved.

The self-energy electron states are obtained similarly as

$$\Sigma^+_{n\underline{k}} = \sum_\beta |c^n_\beta(\underline{k})|^2 \left[-\sum_\alpha U_{\alpha\beta} N^e_\alpha + \Sigma^+_\beta(\omega) \right], \tag{5}$$

where now the scattering matrices and the related quantities are calculated by transforming the integration over empty states into integration over filled ones and vice versa.

In these expressions α and β label the different atomic orbitals, $c^n_\beta(\underline{k})$ are the orbital coefficients of the single particle eigenstates of band index n, $n_\alpha(\epsilon)$ is the orbital density of states, $U_{\alpha\beta}$ is the Coulomb repulsion between electrons on orbitals α and β on the same site; N^h_α (N^e_α) is the percentage of empty (filled) states of orbital character α over the total.

The k-vector and band index resolved spectral functions for hole and electron states are calculated as

$$D^\pm_{\underline{k}n}(\omega) = -\frac{1}{\pi} \operatorname{Im} \frac{1}{\omega - \epsilon_{\underline{k}n} - \Sigma^\pm_{\underline{k}n}(\omega)}; \tag{6}$$

which define the total density of quasiparticle states

$$D^\pm(\omega) = \sum_{\underline{k}n} D^\pm_{\underline{k}n}(\omega) \tag{7}$$

and the its projection onto the individual orbitals

$$D^\pm_\alpha(\omega) = \sum_{\underline{k}n} |c^n_\alpha(\underline{k})|^2 D^\pm_{\underline{k}n}(\omega). \tag{8}$$

We have applied this formalism to NiO. A LDA calculation has been performed in the LMTO-ASA (linear muffin tin orbital–atomic sphere approximation) scheme to get single particle eigenfunctions and eigenvalues of paramagnetic NiO [18]; we have intentionally not included any magnetic order since our point is to show that the inclusion of Hubbard correlation alone is sufficient to get the correct picture of the NiO excitation spectrum. Among the different single particle methods we have chosen the density functional approach for its success in the description of the N-particle ground state of most systems.

Figures 1 and 2 show the calculated single particle band structure and density of states: According to the single particle picture NiO turns out to be metallic, the Ni d band being partially occupied (5.99 and 2.56 d electrons for t_{2g} and e_g symmetries, respectively). Ni d states are strongly hybridized with oxygen states, as it appears from the mixed contribution of both Ni and O orbitals to the total density of states in the energy region around –5 eV. This hybridization is the result of the chemical bond between the two atomic species and must be included for a correct description of this system as well as of other transition metal compounds [17] and high T_c superconducting cuprates [19].

The self-energy and spectral functions are calculated according to Eqs. (1)–(8). We have chosen to include correlation between Ni d electrons only with a value of $U_{dd} = 10$ eV, which is in the range of the generally accepted estimates [12]. In the Hubbard picture the Coulomb repulsion can split the occupied and unoccupied states giving rise to the Mott-Hubbard transition. This is what happens here as shown in Fig. 3 where the calculated spectral function for hole and electron states is shown together with the orbital contributions $D^\pm_\alpha(\omega)$ for Ni and O states [20]. The energy separation between the top of the occupied band and the most prominent structure in the empty part of the spectrum is about 4.5 eV; assuming negligible matrix elements effects, the calculated quasiparticle excitation spectrum can be directly compared with direct and inverse photoemission results showing a remarkable agreement for the gap value [12], the energy position of the valence band top, and of all the

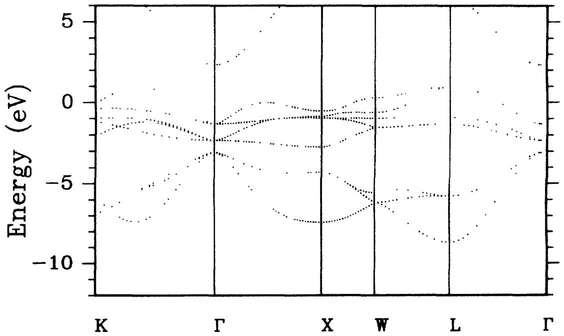

FIG. 1. Single particle band structure of NiO calculated in the LMTO-ASA scheme along high symmetry directions. Energies are referred to the Fermi level.

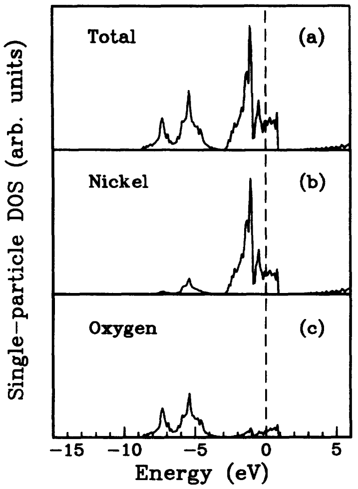

FIG. 2. Total single particle density of states of NiO (a) and contributions to it from Ni (b) and O states (c). Dashed line indicates the Fermi level.

other relevant structures [10,21]. By looking at the orbital composition of the density of quasiparticle states it is quite important to notice that the strongest contribution to the top of the valence band comes from oxygen related states as it is observed experimentally.

A more detailed analysis can be performed by considering the k and band index resolved spectral function (6). Figure 4 shows this quantity calculated for a k point at the center of the Γ-X direction and for two band indices, together with the corresponding k and band index dependent self-energy as a function of energy ω. The quasiparticle energies as maxima of the spectral function can be graphically identified by looking at the interception of the straight line $\omega - \epsilon_{kn}$ and the real part of $\Sigma_{kn}(\omega)$. Each of these lines intercepts more than once the curve describing the real part of Σ_{kn}: Interceptions can occur either in a region where the imaginary part of the self-energy is very small or where the imaginary part of the self-energy is large, giving rise to states of different lifetime and, therefore, to structures in the spectral function of different intrinsic linewidth. In Fig. 4 the structures at higher binding energies can be defined mainly as satellites, while those closer to E_f are more bound-state-like.

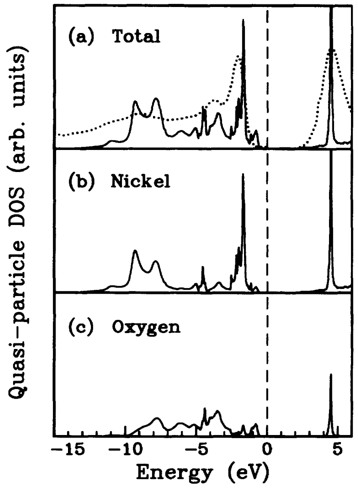

FIG. 3. (a) Quasiparticle density of states of NiO (continuous line) compared with experimental results (dotted line) from angle integrated photoemission obtained from the (001) surface of a NiO single crystal with a monochromatic Al $K\alpha$ source [21] and inverse photoemission [8]; the orbital contributions from Ni (b) and O (c) states are also reported. Dashed line indicates the Fermi level.

By looking at the energy position of the maxima of $D^{\pm}_{kn}(\omega)$ one gets the quasiparticle eigenstates and satellite energy dispersion reported in Fig. 5. Self-energy corrections affect dramatically the band structure giving rise to many flat structures and shifting the bands of mixed O-Ni character with a strong dependence on the k vector. A more detailed analysis will be presented elsewhere; here we want to stress only that this very complex quasiparticle band structure is in fact what has been observed in angle resolved photoemission: Figure 6 summarizes this comparison along the Γ-X direction showing quite a good agreement as far as the energy position of quasiparticle states and satellites is concerned [22]. The empty states are much less affected, the only new feature being the flat structure around 4.5 eV which originates from the empty bands with a strong Ni d orbital character.

In conclusion, we have demonstrated that the Hubbard correlation among Ni d electrons is responsible for the

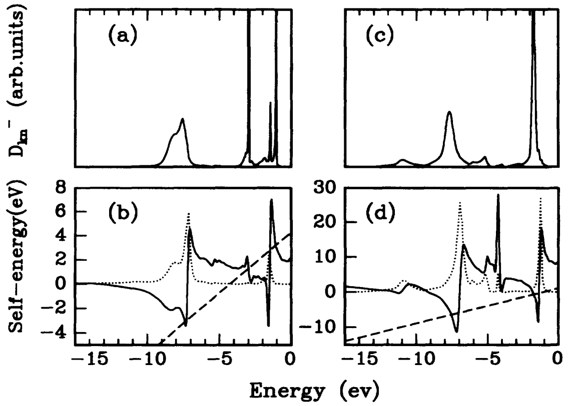

FIG. 4. Spectral function and self-energy corrections for two states at a k point in the middle of the Γ-X direction corresponding to the double degenerate band ($\epsilon_{kn} - E_f = -4.25$) with mixed $2p\,\mathrm{O}-3d\,\mathrm{Ni}$ character [(a) and (b)] and the upper ($\epsilon_{kn} - E_f = -1.08$) of $3d$ Ni character [(c) and (d)]. Panels (b) and (d) show the real part (continuous line) and imaginary part (dotted line) of self-energy; the dashed lines $\omega - \epsilon_{kn}$ are reported in (b) and (d) to indicate the poles of the single particle Green function. Panels (a) and (c) show the corresponding spectral functions. Energies are referred to the Fermi level.

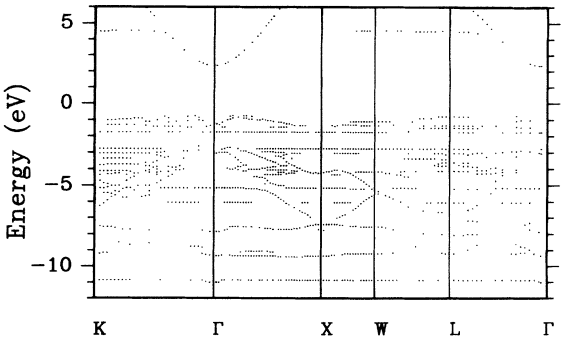

FIG. 5. Quasiparticle band structure of NiO along high symmetry directions of the Brillouin zone. Energies are referred to the Fermi level.

insulating behavior of NiO and that—via the inclusion of many-band effects—it is possible to reproduce both the gap value and the orbital character of the valence band edge, largely involving O $2p$ states. The explicit calculation of self-energy allows us to identify quasiparticle states and to discriminate among them according to their lifetime. The very rich quasiparticle and satellite structure is in excellent agreement with photoemission data. The present approach allows us to reconcile the controversial interpretations on the origin of the band gap in NiO, since both O $2p$−Ni $3d$ hybridization and d-d interaction are essential in order to reproduce the quasiparticle spectrum: The O-Ni interaction is fully described in the single particle band structure, while the d-d Coulomb interaction is the only many-body term which must be additionally included and treated beyond mean field theory.

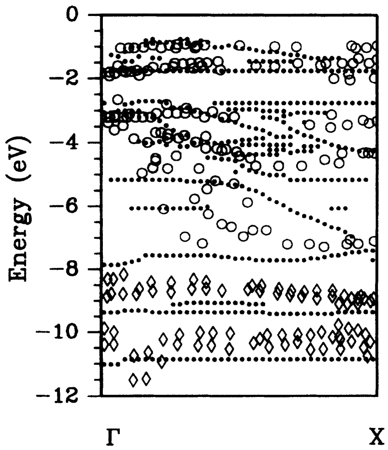

FIG. 6. Comparison between the calculated dispersion of hole quasiparticle states (dots) and photoemission results obtained for normal emission in the energy region between 0 and −7.5 eV (open circles) (Fig. 6 of Ref. [10]) and for off-normal emission and different incident angles between −8 and −12 eV (diamonds) (Fig. 25 of Ref. [10]). Notice that each of the lowest lying experimental structures has a reported error bar of about 1 eV.

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