Zhang-Rice Localization, Quasiparticle Dispersions, and the Photoemission of NiO

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It is shown that strong-coupling theory explains semiquantitatively the angular-resolved photoemission data of NiO. A linear spin-wave treatment of a generalized spin-fermion model, derived for a slab of NiO, shows that a well developed sector of Zhang-Rice bound states coexists with reasonably damped oxygenlike quasiparticle states at large energies.

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The nature of the electronic structure of Mott-Hubbard insulators (MHI) has been the subject of a long debate. One school of thought takes the viewpoint that effective single particle potential theory (especially so its modern implementation, the local spin density approximation, LSDA) is still appropriate [1], while opponents argue that the electron-electron interactions dominate to such an extent in these materials that independent electron theory is virtually worthless.

This issue seemed decided some time ago when the magnitude of the gaps in the $3d$ oxides could be determined unambiguously by (inverse) photoemission. It turned out that at best LSDA underestimated the size of the gaps by an order of magnitude, while in other cases large gaps were found where LSDA predicted metals [2]. Furthermore, the momentum averaged, overall structure of the photoemission spectra could be well interpreted in terms of various local (cluster [3], impurity [4]) approximations to multiband Hubbard models, characterized by on-site Coulomb interactions (U) much larger than any kinetic scale in the problem. However, recent angular-resolved photoemission (ARUPS) experiments on the archetypical MHI NiO show some strongly k-dependent features at relatively large ($\sim$ 7 eV) binding energies, which seem to compare reasonably well with LSDA band structure [5], while it might appear difficult to reconcile these high-energy quasiparticle (QP) peaks with strong correlations.

Substantial progress has been achieved recently in the understanding of the motion of carriers in doped MHI. If the Coulomb interactions are strong enough, it is in general possible to integrate out perturbatively the $3d$ charge degrees of freedom. The problem which remains is the strong coupling between the carrier and the spin background. Schmitt-Rink *et al.* [6] proposed that this problem can be treated with the powerful formalism of polaron theory. The idea is that only the linearized collective excitations (magnons) of the spin system matter. Comparison with exact results on t-J [7] and three-band spin-fermion [8] models show that this strongly coupled hole-magnon problem is accurately solved already in linear-spin-wave–self-consistent Born order (LSW-SCB), also with regard to the overall structure of the single hole spectral function. Up to now, this general approach has not been seriously confronted with experiment. In this Letter we derive a generalized spin-fermion model, describing all relevant electronic degrees of freedom (O2p: $2p_x$,$2p_y$; Ni3d: e_g,t_{2g}) for the valence band of NiO. We derive the spectral functions for this model within the LSW-SCB which turn out to describe the ARUPS spectra quite accurately. Most importantly, the coexistence of "localized" and "itinerant" behavior, as discussed above, finds a natural explanation. Because of the strong coupling between the O2p hole and the magnons, polaron-like QP states of the Zhang-Rice (ZR) [9] variety are formed at low energies, and coexist with strong momentum dependences found at higher energies.

NiO is best characterized as a charge-transfer insulator [10], where the O2p band lies in between the Ni3d upper (UH) and lower (LH) Hubbard bands. If the splittings between these bands is large enough, one finds that an oxygen hole interacts with the $S = 1$ ("$^3A_2$") spins on the neighboring Ni ions by Kondo-like exchange interactions, originating from the virtual hopping of the p hole into the Hubbard bands [11]. Although the UH band is of merely e_g character, the LH band is split up by exchange interactions, and a high-spin $^4T_{1g}$ and two low-spin ($^2T_{1g}$ and ^2E_g) subbands can be reached by hopping. We define e_g and t_{2g} symmetries for the oxygen orbitals locally by their coupling to the respective Ni3d states, i.e., pointing along and perpendicular to Ni-O bonds, respectively, and we restrict ourselves to a single two-dimensional (2D) slab, mimicking the (001) surface of NiO. The e_g oxygen orbitals hybridize with the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals (both occupied in the $^3A_2$ state) by t_x and t_z, respectively, while the t_{2g} orbitals hybridize only with (unoccupied) d_{xy} orbitals by t_t. In second order [11] we find for the Kondo interactions of the holes with the Ni spins $\mathbf{S}_i$ [12],

$$H_{h-s} = \sum_{imn} (J_{K,e}\mathbf{S}_i \cdot \mathbf{s}_{mn,e} - J_{K,t}\mathbf{S}_i \cdot \mathbf{s}_{mn,t}), \qquad (1)$$

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where $J_{K,e} = 2[J_K(\Delta) + J_K(^2E)]$, $J_{K,t} = \frac{4}{3}[J_K(^4T) - J_K(^2T)]$, and the (nonlocal) hole spin operators are

$$s^+_{mn,s} = a^\dagger_{m,s\uparrow}a_{n,s\downarrow},$$
$$s^z_{mn,s} = \frac{1}{2}(a^\dagger_{m,s\uparrow}a_{n,s\uparrow} - a^\dagger_{m,s\downarrow}a_{n,s\downarrow}). \quad (2)$$

$a^\dagger_{m,s\sigma}$ are hole creation operators in a $s = e, t$ (e_g and t_{2g}) orbital at site m. Compared with the usual spin-fermion model derived from a spin-degenerate Hubbard model [11], the present model is more complicated. Besides, of the two flavors of fermions (e, t), the multiplet structure of the LH band manifests itself in the form of one ferromagnetic (FM), $J_K(^4T) = t_t^2/[U(^4T) - \Delta]$, and two antiferromagnetic (AF), $J_K(^2E) = (t_x^2 + t_z^2)/[U(^2E) - \Delta]$ and $J_K(^2T) = t_t^2/[U(^2T) - \Delta]$, exchange interactions, in addition to the UH-band derived interaction $J_K(\Delta) = (t_x^2 + t_z^2)/\Delta$. Further, a hopping of oxygen holes via the Ni sites is found,

$$H_h^J = \sum_{imn\sigma}(T_{ee}a^\dagger_{m,e\sigma}a_{n,e\sigma} + T_{tt}a^\dagger_{m,t\sigma}a_{n,t\sigma}), \quad (3)$$

with the effective hoppings $T_{ee} = \frac{1}{2}[J_K(\Delta) - J_K(^2E)]$ and $T_{tt} = -\frac{1}{3}[2J_K(^4T) + J_K(^2T)]$.

The model Eqs. (1) and (3) has to be augmented with the direct oxygen-oxygen hopping between O2$p_{x(y)}$ orbitals,

$$H_h^0 = \sum_{mn\sigma}[t_{xx}(a^\dagger_{m,x\sigma}a_{n,x\sigma} + a^\dagger_{m,y\sigma}a_{n,y\sigma}) + t_{xy}(a^\dagger_{m,x\sigma}a_{n,y\sigma} + a^\dagger_{m,y\sigma}a_{n,x\sigma})], \quad (4)$$

and the mutual interactions between the Ni spins,

$$H_s = J_1 \sum_{(ij)\in(A,B),(C,D)} \mathbf{S}_i \cdot \mathbf{S}_j - J_2 \sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (5)$$

where the AF interaction J_1 couples the pairs of Ni ions being separated by one oxygen ion in x and y directions. These ions form two interpenetrating pairs of magnetic sublattices, (A, B) and (C, D), with AFII ground state. The weak FM interaction, $J_2 = \alpha J_1$, couples the nearest-neighbor Ni ions and is frustrated in the AFII.

The LSW-SCB approach turned out to be surprisingly accurate for $S = \frac{1}{2}$ models. It amounts to the leading contribution of an $S \to \infty$ expansion, and thus it is expected to work even better in the present context ($S = 1$ instead of $S = \frac{1}{2}$). In LSW order we find in $\mathbf{k}$ space,

$$H_{\rm LSW} = \sum_{\mathbf{k},\mu\sigma}\varepsilon_\mu(\mathbf{k})a^\dagger_{\mathbf{k},\mu\sigma}a_{\mathbf{k},\mu\sigma} + \sum_{\mathbf{q}}\omega_{\mathbf{q}}\beta^\dagger_{\mathbf{q}}\beta_{\mathbf{q}} + \frac{1}{\sqrt{N}}\sum_{\mathbf{kq},\mu\nu\sigma} M_{\mu\nu}(\mathbf{k},\mathbf{q})(\beta^\dagger_{\mathbf{q}} + \beta_{-\mathbf{q}}) \times a^\dagger_{\mathbf{k}-\mathbf{q},\mu\sigma}a_{\mathbf{k}\nu,-\sigma}, \quad (6)$$

where ω_q is the magnon dispersion in the unfolded zone,

$$\omega_{\mathbf{q}} = 4J_1[(1 - \alpha\zeta_{\mathbf{q},+})^2 - (\gamma_{\mathbf{q}} - \alpha\zeta_{\mathbf{q},-})^2]^{1/2}, \quad (7)$$

with $\gamma_{\mathbf{q}} = \frac{1}{2}(\cos 2q_x + \cos 2q_y)$, $\zeta_{\mathbf{q},\pm} = \frac{1}{2}\cos(q_x \pm q_y)$, and $\varepsilon_\mu(\mathbf{k})$, $\mu = e, t$, are derived from Eq. (4) (inset Fig. 1)

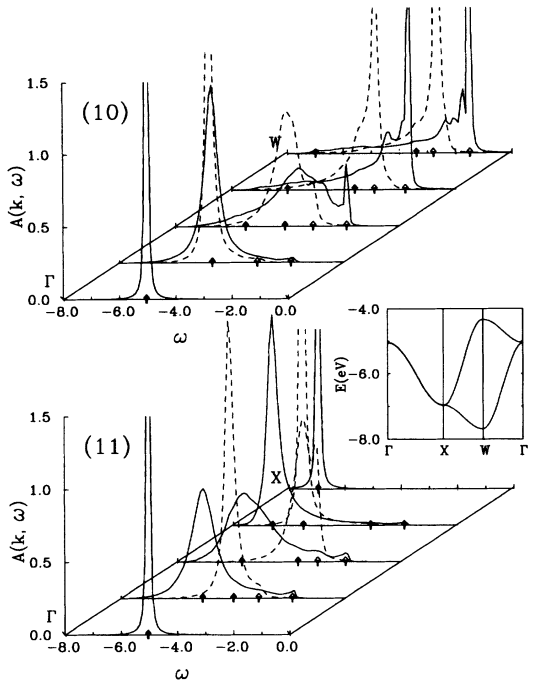

FIG. 1. Spectral functions, $A_{\mu\mu}(\mathbf{k},\omega)$, for $\mathbf{k} = (\frac{n\pi}{8}, \frac{n\pi}{8})$ in the (10) direction and for $\mathbf{k} = (\frac{n\pi}{4}, 0)$ in the (11) direction ($n = 0, 1, 2, 3, 4$). The inset shows the oxygen hole dispersions as obtained from the free-hole terms in Eq. (4).

including the T_{ee} and T_{tt} hoppings (3). The hole-magnon bare vertex, $M_{\mu\nu}(\mathbf{k},\mathbf{q})$, depends on the geometrical factors which follow from the Bogoliubov transformations for fermions ($V^\xi_{\mu,\mathbf{k}}$) and bosons ($u_{\mathbf{q}}$, $v_{\mathbf{q}}$),

$$M_{\mu\nu}(\mathbf{k},\mathbf{q}) = \frac{1}{\sqrt{2N}}(u_{\mathbf{q}} + v_{\mathbf{q}})\sum_{\xi\eta} V^\xi_{\mu,\mathbf{k}}V^\eta_{\nu,\mathbf{k}-\mathbf{q}}F_{\xi\eta}(\mathbf{k},\mathbf{q}), \quad (8)$$

$$F_{11}(\mathbf{k},\mathbf{q}) = J_{K,e}[\cos q_x - \cos(2k_x - q_x)] - J_{K,t}[\cos q_y - \cos(2k_y - q_y)],$$
$$F_{12}(\mathbf{k},\mathbf{q}) = 2J^-_{K,e}\sin k_x \sin(k_y - q_y) - 2J_{K,t}\sin k_y \sin(k_x - q_x), \quad (9)$$

where $J^-_{K,e} = (t_x^2 - t_z^2)\{1/[U(^2E) - \Delta] + 1/\Delta\}$. $F_{22}(\mathbf{k},\mathbf{q})$ and $F_{21}(\mathbf{k},\mathbf{q})$ are obtained from $F_{11}(\mathbf{k},\mathbf{q})$ and $F_{12}(\mathbf{k},\mathbf{q})$ by the transformation $(k_x, q_x) \leftrightarrow (k_y, q_y)$.

The single hole spectral function ($\mu = e, t$),

$$A_{\mu\mu}(\mathbf{k},\omega) = \pi^{-1}{\rm Im}G_{\mu\mu}(\mathbf{k},\omega), \quad (10)$$

and the Green function,

$$G^{-1}_{\mu\nu}(\mathbf{k},\omega) = \omega - \varepsilon_\mu(\mathbf{k})\delta_{\mu\nu} - \Sigma_{\mu\nu}(\mathbf{k},\omega), \quad (11)$$

are determined in the SCB by the hole self-energy obtained from the bare vertex and the self-consistently dressed Green function,

$$\Sigma_{\mu\nu}(\mathbf{k},\omega) = \sum_{\alpha\beta,\mathbf{q}} M_{\mu\alpha}(\mathbf{k},\mathbf{q}) M_{\beta\nu}(\mathbf{k},\mathbf{q}) \times G_{\alpha\beta}(\mathbf{k}-\mathbf{q},\omega-\omega_{\mathbf{q}}). \quad (12)$$

Equations (10)–(12) have been solved numerically on a 16×16 lattice with torroidal boundary conditions.

The noninteracting ($U, J_H = 0$, etc.) version of the above model, together with the parameters [13] obtained by van Elp *et al.* [14] from cluster model fits to the angular integrated spectra, yields a satisfying fit to the (unpolarized) LDA band structure [5]. This is not entirely unproblematic since the band structure of a thin 2D slab is compared with that of the fully 3D system. It turns out, however, that the bands derived from the planar $2p$ orbitals map quite well on the LDA bands of the same character, at least as long as $k_z = 0$ and the only major difference is in our neglect of the out-of-plane p_z orbitals. Along the (01) direction this band is degenerate with one of the planar bands, but the most dispersive feature in the (11) direction (Fig. 16 of Ref. [5]) turns out to be of this character. We are of the opinion that this band can be better neglected because it is most strongly affected by the loss of k_z as a good quantum number. More generally, we expect that in fact no further complications occur because of our neglect of the third direction insofar as the hole-magnon scattering is involved. The reason is that it mainly involves magnons capable of creating a spin backflow opposite to the momentum of the hole [15].

In order to have a meaningful comparison with experimental photoemission data one should keep in mind that ARUPS does not measure directly $A_{\mu\mu}(\mathbf{k},\omega)$, but instead a related quantity modulated by dipole matrix elements, etc. For instance, it is impossible to measure the calculated O2p spectral density. Further, our strong-coupling approximation introduces inaccuracies in the overall distribution of spectral weight because of its rapid transfer to low energies for decreasing U [16]. There is even a more severe problem with the perturbation theory. Taking van Elp's parameters [14], we find that the $d_{x^2-y^2}$ related features are basically formed but the d_{xy} related exchange turns out to be too weak to form ZR bound states. This is not unexpected since the ${}^4T$ d^7 states are nearly degenerate with the $2p$ band, while the ZR states in this sector are rather weakly bound anyhow. We repair this by taking a larger t_π by a factor of 1.8, although this tends to smear the scattering states at larger energies. Finally, the interoxygen hopping has been increased by a factor of 1.2 [13] in order to come closer to the observed dispersion between the Γ and X points.

Keeping this in mind, our results compare quite well with the experimental data. In Fig. 1 we show the spectral functions A_{ee} (full line) and A_{tt} (dashed line), as functions of frequency for different $\mathbf{k}$ values along high symmetry directions in the 2D Brillouin zone (X and W points at the zone boundary correspond with nearest-neighbor Ni-O and Ni-Ni bond directions). Instead of the sharp QP peaks expected for the bare $2p$ holes with dispersions as shown in the inset, complicated line shapes are found. First, at the Γ and X points simple poles are found. The reason is that these $2p$ states are p-like with respect to the Ni sites, and therefore these do not couple to the magnons at all. On the contrary, at the W point the magnon-hole coupling is at maximum, both for the x^2-y^2-like state at the top of the valence band, as well as for the lower-lying xy state. The e spectral function is characterized by a peak at threshold, lying ~ 2 eV above the top of the $2p$ band, accompanied by a "shoulder" extending to the top of the bare $2p$ band. As we will discuss in more detail elsewhere [17], these findings confirm the hierarchy expected from the ZR mapping procedure [9,16,18,19]. The oxygen hole binds locally to a spin flip into a ZR bound state with approximate local spin coherence, and this process is responsible for the large (1–2 eV) binding energies. The motion of this composite object through the spin background is described approximately by a t-J model with the characteristic pattern of states [20] between threshold and the top of the bare oxygen bands: a polaronlike peak [21] dispersing on a scale $\sim J_1$ accompanied by incoherent spectral weight at higher energies. In NiO the situation is further complicated by the fact that more than one ZR sector is realized. The bound state in the e channel is of the ${}^2E(e_g^3)$ variety. Also in the t sector a bound state is realized, presumably of the ${}^4T$ variety, although much more weakly bound because of the combined effect of the smaller Kondo exchange and the larger energy of the bare $2p$ band.

Moving out in $\mathbf{k}$ space the threshold peaks disperse slightly, suggesting a renormalized bandwidth < 0.5 eV (empty circles in Fig. 2), while they rapidly lose spectral weight without losing their identity. This is even more nicely illustrated along the (11) direction, where the coupling vanishes at both end points and is relatively weak in between. As soon as the d-p coupling switches on, we see directly a long tail extending all the way to the threshold seen at the W point. Undoubtedly, if d weight were allowed the threshold region would be dominated by two peaks, as in experiment, regardless of the momentum. However, our prediction of strong dependence of the $2p$ character in the threshold peaks as a function of $\mathbf{k}$ is alien to single particle theory and offers an opportunity to test our theory directly by experiment.

The ZR binding energies are of order of the p bandwidths and at first sight this seems hard to reconcile with sharp $2p$ QP states. In fact, both in the (10) and (11) directions only a single truly dispersive feature has to be explained (full circles in Fig. 2). Since we omit the p_z states, we find the nonbonding p states at the end points of the (11) direction, and the rather underdamped QP states in between, reflecting the bare dispersions, because the hole-magnon couplings are here relatively weak. We note that this assignment overestimates the binding energy especially at the Γ point. On the contrary, at the "strongly coupled" W point we identified a scattering state at the bottom of the bare oxygen band, being

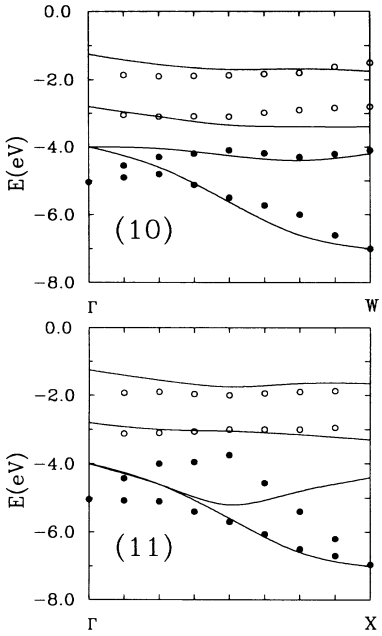

FIG. 2. The maxima of the calculated spectral densities $A_{\mu\mu}(\mathbf{k},\omega)$ (full and empty circles) for the Γ-W (11) and Γ-X (10) directions in the AF Brillouin zone. The lines show the electronic structure of NiO as measured in ARUPS experiments by Shen *et al.* (see Figs. 6 and 16 of Ref. [5]).

the mirror image of the e_g-ZR state at the top of the band. Moving away from this point, this scattering state becomes more bare $2p$-like, merging finally into the nonbonding p state at Γ, at net producing a dispersive feature. In the t_{2g} sector we find at W at most a low-energy shoulder which also gradually changes into a band, much like the fourth feature seen as well in experiment [5] along this direction.

In summary, the good agreement we find between the calculated spectral functions and the measured spectra of NiO shows that the strong-coupling theory of doped Mott-Hubbard insulators (spin-fermion models, spin-wave analysis) does apply to nature. The above results make previous interpretations obsolete. The similarities with the outcomes of naive band calculations turn out to be accidental to a large extent. This is best illustrated by the fact that we find at most four identifiable features instead of the twelve or so LDA bands. At the same time, the present work shows once again that both "localized" and "itinerant" features are central to the electronic structure of Mott-Hubbard systems and, although less wrong than naive band structure, the cluster and impurity model approaches do miss this essential aspect.

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