Band Theory for Ground-State Properties and Excitation Spectra of Perovskite $LaMO_3$ (M = Mn, Fe, Co, Ni)

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It is shown that the local spin-density approximation describes well electronic structures of perovskite $LaMO_3$ (M = Mn, Fe, Co, Ni) for the ground-state and single-electron excited-state properties. Inclusion of details of crystal structures distorted from the cubic structure is crucial to reproduce different magnetic structures and insulating states. Calculated x-ray photoemission spectra are in very good agreement with experimental ones, and its angular momentum characters are in conformity with ultraviolet photoemission spectra.

Electronic structures of correlated systems containing $3d$, $4f$, or $5f$ electrons are difficult to describe due to the simultaneous presence of strong electron-electron interaction strength (U) and sizable hopping interaction strength (t). While large U leads to the formation of local magnetic moments, sizable t tends to form delocalized bands. Thus the simultaneous presence of these two opposing tendencies gives rise to the wide and often exotic spectrum of physical and chemical properties; however, it also makes theoretical treatments of such systems very difficult, necessitating various approximate schemes. On one end, very often a single impurity Hamiltonian (such as Anderson impurity Hamiltonian) is employed, entirely neglecting the lattice periodicity of the correlated site [1,2]. This approximation is justified if U/t in the system is very large. On the other end, band structure theories, mainly within the local spin-density approximation (LSDA), have been employed [3,4]; within this approach, U is treated in an approximate average way. Such approaches are expected to be successful for systems with smaller U/t. To avoid divergence in arguments, hereafter we shall concentrate our attention on $3d$ transition metal oxides. Early works on electronic structures of $3d$ transition metal oxides with the rocksalt structure MO with M = Mn-Ni using LSDA [3], and subsequently taking account of the generalized gradient approximation (GGA) [5] provided reasonable descriptions of ground-state magnetic structures, but these *ab initio* approaches fail to reproduce excitation spectra of MnO-NiO properly. Only very recently a few attempts [6,7] have been made to perform an *ab initio* procedure to calculate the quasiparticle spectrum starting from LSDA calculations. On the contrary, qualitatively correct descriptions for the excitation spectra have been obtained by the configuration interaction approach based on *parametrized* cluster [8] and impurity Anderson [2] models for more than a decade. These models have further emphasized the need to include multiplet interaction

terms besides U and J, since these often represent one of the largest energy scales in the problem, but neglected in band theories.

With such a background, however, we shall now show that both magnetic and electronic structures of $3d$ transition-metal perovskite oxides $LaMO_3$ (M = Mn-Ni) are well described by band theories based on the LSDA. This class of compounds is structurally related to high temperature superconducting cuprates and has attracted a lot of attention in recent times [9]. The only quantity the present approach fails to predict quantitatively is energy band gaps, though in almost all cases it predicts the correct ground state in terms of insulating or metallic behavior. The underestimation of band gaps is well known even for band insulators and can be rectified by an extension of the theory [7,10]. On the other hand, the present approach describes the very complicated ground-state magnetic properties as well as the excitation spectra very accurately, establishing that LSDA provides a very reasonable starting point for a class of transition-metal oxides that have been considered describable only in the opposite limit of impurity model including full multiplet interactions.

We have performed these calculations with linear augmented plane wave (LAPW) and linear muffin-tin orbital–atomic sphere approximations (LMTO-ASA). The results with both methods are almost identical, and we present total energy calculations performed with LAPW for all possible magnetic structures and excitation spectra calculated with LMTO-ASA for the ground-state magnetic structure. In each case the experimentally observed crystal structure was used with 20 atoms per orthorhombic unit cell of $LaMnO_3$ and $LaFeO_3$, and with 10 atoms per rhombohedral unit cell of $LaCoO_3$ and $LaNiO_3$. To avoid any adjustable parameter, we have even calculated photoemission matrix elements within the single-scatterer final-state approximation [11]. Experimentally determined resolu-

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tion function and lifetime broadenings were fixed to what have been obtained by an earlier detailed analysis of excitation spectra of Ga and In [12].

In Table I, we show the total energies of $LaMnO_3$ and $LaFeO_3$ for various magnetic configurations, namely, ferromagnetic, A-type antiferromagnetic (AF), C-type AF, and G-type AF. While A-type AF appears as the lowest energy solution in $LaMnO_3$, G-type AF is the ground state in the case of $LaFeO_3$ in perfect agreement with experimentally observed magnetic structures [13]. We find that the Jahn-Teller distortion around the Mn atom is important to stabilize the A-type AF structure in $LaMnO_3$; the ferromagnetic state becomes slightly stabler for the undistorted structure. $LaCoO_3$ and $LaNiO_3$ are predicted to be nonmagnetic in agreement with experiments [14]. Geometry optimization with respect to the lattice parameter for $LaCoO_3$ gave a value only slightly smaller (about 1%) than experiment. Interestingly, the energy difference between the ferromagnetic and the nonmagnetic solutions at this point was about 9 meV (100 K) per unit formula in very good agreement with the observed low-spin to high-spin transition at about 100 K in this compound [15]. Furthermore, the ferromagnetic state has the lowest energy for lattice constants observed at room temperature. LSDA describes this very subtle energy balance well, in the controversial issue of spin-state transition. Calculated magnetic moments on the transition-metal ion within a muffin-tin sphere of 1.16 Å are $3.4\mu_B$ and $3.7\mu_B$ compared to experimental values of $3.7\mu_B$ and $4.6\mu_B$ for $LaMnO_3$ and $LaFeO_3$, respectively [13]. The agreement is remarkably good for $LaMnO_3$, with somewhat larger disagreement for $LaFeO_3$. While this difference may arise from an overestimation of the mixing of O $2p$ and Fe $3d$ states in LSDA, the analysis of the neutron diffraction may also overestimate the local magnetic moment, since the magnetic form factor is distorted by this mixing. The calculated fundamental gaps for $LaMnO_3$, $LaFeO_3$, and $LaCoO_3$ are 0.2, 0.3, and -0.2 eV, respectively. Thus the present calculations, while underestimating the resistivity gaps, obtain the correct insulating ground state for $LaMnO_3$ and $LaFeO_3$. For $LaCoO_3$ it shows a semimetallic nature with a direct gap (0.04 eV) in comparison to resistivity data, indicating a small band gap (about 0.1 eV [15]). The calculation correctly predicts $LaNiO_3$ to be a metal. Thus it is clear that both magnetic and electronic

ground-state properties and the subtle interplay of these with the lattice structure are very well described by the present results.

Before moving to arguments about spectroscopic properties, we give here the amount of the d component in the states at the valence-band top (VBT) and the conduction-band bottom (CBB) in order to elucidate the nature of the band gap obtained by the present calculation: At VBT (CBB), they are 58% (73%), 44% (76%), and 70% (76%) for $M =$ Mn, Fe, and Co, respectively. In the case of $LaMnO_3$, the band gap opens in the $d\gamma$ band due to the Jahn-Teller distortion. For $LaFeO_3$, VBT is a $d\gamma$ state of majority spin with strong p-d hybridization and CBB is a less-bonding $d\varepsilon$ state of minority spin leading to a stronger p-d character of the band gap. On the other hand, in the case of $LaCoO_3$, the band gap comes from the ligand-field splitting between $d\varepsilon$ and $d\gamma$ states. It is to be noted that there is always significant admixture in VBT in each of these compounds, suggesting strongly mixed valent characters of the ground states.

In Fig. 1, we show the experimental and calculated x-ray photoemission valence band spectra of $SrTiO_3$ (d^0 system), which is structurally related to $LaMO_3$ and a well-accepted example of a band insulator, to establish limits of our *ab initio* approach with least influence from electron correlation in d bands. In order to align the first peaks in the two, a *rigid* shift of 1.3 eV was needed for the calculated spectrum due to the previously mentioned underestimation of band gaps in LDA formalism even for band insulators. Figure 1 shows a very good agreement between the calculated and the experimental spectra in terms of both energy positions and widths of various spectral features. The only difference

TABLE I.   Total energies (meV/unit formula) of various magnetic configurations measured from the most stable configuration in $LaMnO_3$ and $LaFeO_3$.

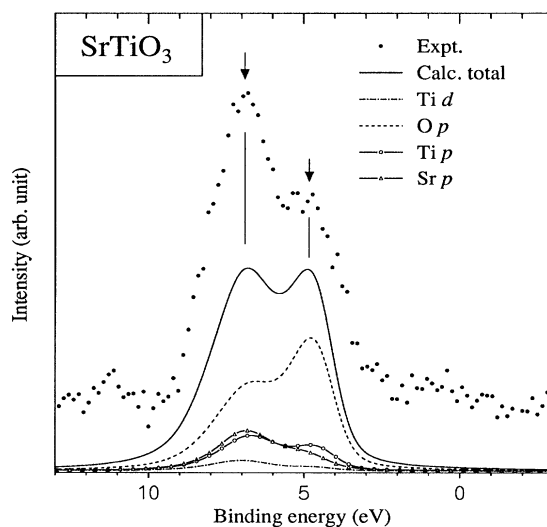|	$LaMnO_3$	$LaFeO_3$
Ferromagnetic	18 meV	147 meV
A-type AF	0	49 meV
C-type AF	52 meV	57 meV
G-type AF	42 meV	0

FIG. 1.   Calculated (solid line) and experimental (dots) x-ray photoemission spectra in $SrTiO_3$. Important site and angular momentum contributions are also shown. Characteristic peaks are indicated by arrows.

appears to be an underestimation of the intensity of the higher binding energy feature at about 7 eV arising from an underestimation of matrix elements for Sr p states. This is consistent with our earlier findings in the case of Ga and In [12] that cross sections of more delocalized states appear to be underestimated compared to more localized ones within the single-scatterer approximation.

Having established the limits of our approach to describe even a band insulator, we now compare experimental x-ray photoemission spectra of LaMO$_3$ compounds with calculated ones in Fig. 2, where the experimental spectrum of LaMnO$_3$ is taken from Saitoh *et al.* [16]. Once again we had to shift the calculated spectra by 1.3, 2.0, 0.4, and 0.0 eV for the cases of M = Mn, Fe, Co, and Ni, respectively. Beyond this, the agreement between the experimental spectra and the calculated ones appear to be surprisingly good with each and every feature at the right energy position and with the correct width. The agreement is remarkable considering that even weak features, for example, a rather flat feature with three peaks within 3–7 eV in LaMnO$_3$, the 3 eV binding energy shoulder in LaFeO$_3$, features at about 3 and 6.5 eV binding energies in the case of LaCoO$_3$, and asymmetry of the 1 eV main peak in LaNiO$_3$, are very accurately described by the calculation. Unfortunately, it is not possible to calculate the matrix elements involved in the ultraviolet photoemission (UP) process due to the limitations of the single-scatterer approximation. However, peaks in calculated O p components shown in Fig. 2 agree very well with prominent

FIG. 2. Calculated (solid line) and experimental (dots) x-ray photoemission spectra in LaMnO$_3$, LaFeO$_3$, LaCoO$_3$, and LaNiO$_3$. The metal d component (dot-dashed line) and the oxygen p component (dashed line) are also shown. Characteristic features are indicated by arrows.

peaks in UP spectra of compounds with Mn (5 eV), Fe (4.5 eV), Co (3 and 5 eV), and Ni (2.4 and 4.7 eV) [17], since oxygen p partial density of states is expected to become more intense in this case. This establishes that the calculation not only obtains an accurate description of the overall shape of the excitation spectrum, but also provides a correct description of the site and angular momentum projected character of the spectrum. Considering that *no adjustable parameter except the rigid energy shift* appears in preparing the calculated spectra, Fig. 2 represents a very strong case in favor of LSDA. It is easy to see that some mismatches in intensities in Fig. 2 arise evidently from an underestimation of the contribution of oxygen p-like states compared to that of transition-metal d-like states and are consistent with earlier discussions. Our results further show that bremsstrahlung isochromat and oxygen K-edge absorption spectra (not shown here for brevity) corresponding to the unoccupied states are also well described by the present band approach. Since most of these spectra are rather featureless with a single peak for the states related to p-d interactions, these do not provide as critical a test as by the rich variety of structures in the occupied spectra in Fig. 1.

We now discuss why LSDA calculations work better for LaMO$_3$ than for the rocksalt MO oxides, with particular reference to Ni oxides as an example; however, the discussion is valid also for other materials. There are three basic quantities characterizing properties of transition-metal oxides: the p-d electron hopping integral t, the p-d energy separation Δ, and the on-site Coulomb interactions U. The M-O distance in LaMO$_3$ is appreciably shorter than that in the rocksalt oxide MO, for example, the Ni-O distance being 1.928 and 2.084 Å for LaNiO$_3$ and NiO, respectively. Therefore the canonical band theory predicts $t(\text{LaNiO}_3)/t(\text{NiO}) = (2.084/1.928)^4 = 1.37$. There are two competing factors in Δ: the Madelung potential difference between the oxygen site and the transition-metal site, ΔV_M, and the ionization energy of the transition metal in the $+\nu$ charge state, I_ν, according to Torrance *et al.* [18]. $e\Delta V_M$ are 60.981 eV (perovskite) and 48.296 eV (rocksalt), and I_ν are 35.17 eV ($\nu = 3$, perovskite) and 18.17 eV ($\nu = 2$, rocksalt). Thus the large difference in the Madelung potential between the perovskite and rocksalt oxides is overcanceled by the difference in the ionization energies; as the result, Δ becomes much smaller in LaNiO$_3$ than in NiO. By using appropriate ionization energies, the estimated values of unscreened U are 19.73 eV for Ni^{3+} and 17.0 eV for Ni^{2+}. From the analysis of photoemission spectra in the single-impurity models, however, U of Ni is about 5–7 eV in LaNiO$_3$ [17,19] and about 7.5–10 eV in NiO [8,20]. Therefore the on-site U of Ni is screened more efficiently in LaNiO$_3$ than NiO. The stronger screening in LaNiO$_3$ may be due to stronger electrostatic screening by the surrounding oxygens with a smaller Ni-O distance and also stronger screening due to
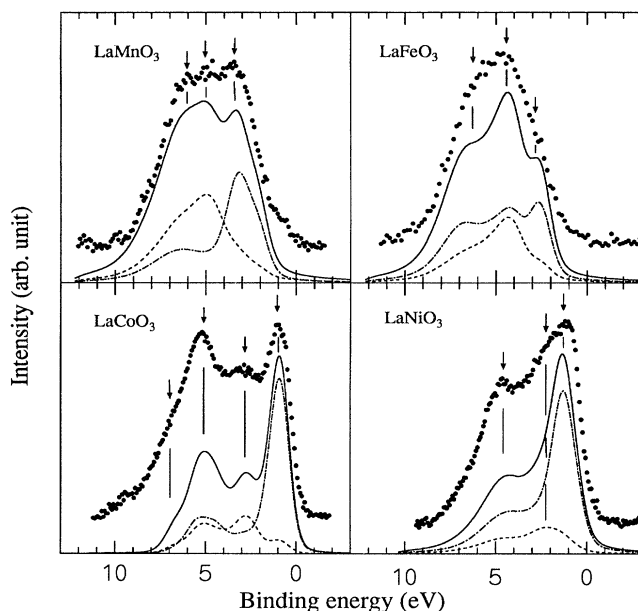
larger d-d hybridization, since U in the impurity models is renormalized to include the d band screening.

Summarizing the argument, we find that t is larger, Δ is smaller, and U is smaller in the perovskite oxides than in the rocksalt oxides. From the localized state limit, the effective d-d hopping is proportional to $t^2(1/U + 1/\Delta)$. Therefore, in $LaMO_3$ series, delocalization effects are considerably stronger than localizing effects of U and Δ when compared to the corresponding MO series. This is further supported by the experimental observation that photoemission valence-band spectra of these $LaMO_3$ compounds do not exhibit any appreciable intensity in a correlation induced satellite at higher binding energies in contrast to intense satellite features present in the MO series (e.g., NiO). These facts make this series more describable in terms of band theories. It is to be realized here that while the present *ab initio* calculations describe electronic excitation spectra very well, it also gives a very accurate description of magnetic properties; this, of course, is beyond the scope of any impurity model. Our results have further established the subtle interplay between fine structural details and magnetic properties and simultaneously undermine the importance of multiplet interaction that normally plays a vital role as parameters in single-impurity models. Thus we are led to the conclusion that the band theory rather than single-impurity models is a better starting point for this important class of materials, since the latter misses out the strong transition metal-transition metal interaction and the structural details that appear to dominate physical properties here.

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