I. INTRODUCTION

An understanding of the electronic structure and phase diagrams of transition-metal (TM) oxides still poses a major challenge. The realistic modeling of strong electronic correlations in this family of compounds has been tremendously improved since establishing the combination of density functional theory (DFT) with dynamical mean-field theory (DMFT). The accentuated role of the oxygen valence orbitals in these compounds asks for an enhanced description of ligand-based correlations. Utilizing the rocksalt-like NiO as an example, we present an advancement of charge self-consistent DFT+DMFT by including self-interaction correction (SIC) applied to oxygen. This introduces explicit onsite O correlations as well as an improved treatment of intersite $p-d$ correlations. Due to the efficient SIC incorporation in a pseudopotential form, the DFT+sicDMFT framework is an advanced but still versatile method to address the interplay of charge-transfer and Mott-Hubbard physics. We revisit the spectral features of stoichiometric NiO and reveal the qualitative sufficiency of local DMFT self-energies in describing spectral peak structures usually associated with explicit nonlocal processes. The semiconducting nature of Li$_x$Ni$_{1-x}$O, along with prominent in-gap states, is verified by the present theoretical study.

While e.g. Cu oxides are typical charge-transfer compounds, the rocksalt-like NiO, a material of paramount importance for the development of quantum solid-state theory, is located in the intermediate regime of the ZSA diagram. This renders NiO particularly interesting, and more generally, marks nickelate compounds as exceedingly affected by various competing instabilities (see e.g. Ref. [1] for a review). Stoichiometric nickel oxide is insulating with a sizeable charge gap of $\sim$4.3 eV and becomes antiferromagnetic below $T_N = 523$ K. Substitutional doping of Li$^+$ for Ni$^{2+}$ is effective in providing holes to cause conductivity.

Numerous theoretical studies examined the interacting electronic structure of NiO. Advanced descriptions need to rely on a sophisticated treatment of $\Delta$, $U$ and further key quantum characteristics of the compound. In addition to cluster calculations, DFT+DMFT[12,16–19] and variational-cluster-approximation[20] studies provided already a good account of the electronic spectrum, but challenges remain[21]. For instance, to a certain degree, the correct determination and understanding of the specific nature/positioning of peaks within the valence-band spectrum is still a matter of debate. Furthermore, the increased importance of the role of ligand orbitals and their hybridization with TM orbitals in materials that lack a pure Mott-Hubbard character, renders an investigation of defect properties very demanding.

Therefore, the intention of this work is twofold. Using NiO as a test case, we first show that an improved description of the intriguing interplay between Mott-Hubbard and charge-transfer physics at stoichiometry is achieved by treating electronic correlations on the TM as well as on the ligand sites. This is realized by an efficient combination of the self-interaction correction (SIC) with the charge self-consistent DFT+DMFT framework. Thereby, SIC is applied on O and Ni marks the DMFT impurity problem. This theory advancement enables us to shed novel light on the intriguing features of the paramagnetic NiO spectrum. Second, the usefulness of this DFT+sicDMFT scheme for advanced correlated materials science is demonstrated by the application to the even more provoking case of Li-doped NiO. We verify the semiconducting nature of Li$_x$Ni$_{1-x}$O and straightforwardly reproduce the long-standing experimental finding of in-gap states at $\sim$ 1-2 eV above the valence-band maximum.

Late transition-metal oxides with small charge-transfer energy $\Delta$ raise issues for state-of-the-art correlated electronic structure schemes such as the combination of density functional theory (DFT) with dynamical mean-field theory (DMFT). The accentuated role of the oxygen valence orbitals in these compounds asks for an enhanced description of ligand-based correlations. Utilizing the rocksalt-like NiO as an example, we present an advancement of charge self-consistent DFT+DMFT by including self-interaction correction (SIC) applied to oxygen. This introduces explicit onsite O correlations as well as an improved treatment of intersite $p-d$ correlations. Due to the efficient SIC incorporation in a pseudopotential form, the DFT+sicDMFT framework is an advanced but still versatile method to address the interplay of charge-transfer and Mott-Hubbard physics. We revisit the spectral features of stoichiometric NiO and reveal the qualitative sufficiency of local DMFT self-energies in describing spectral peak structures usually associated with explicit nonlocal processes. The semiconducting nature of Li$_x$Ni$_{1-x}$O, along with prominent in-gap states, is verified by the present theoretical study.

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Late-TM oxides display a more intriguing interplay of hybridization and correlation effects and remain demanding. Reason is that in the latter systems with usually $d$ states are lower in energy, hence $\Delta$ shrinks, but $U$ on the other hand increases due the reduced orbital extension with larger nuclear charge. According to the famous Zaanen–Sawatzky–Allen (ZSA) scheme, correlation-induced insulators with $\Delta < U$ are of charge-transfer kind.

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II. THEORETICAL APPROACH

A. Problem and general framework

In simplest approximation\(^2\), the charge-transfer energy is given by the difference between the TM\((d)\) and O\((2p)\) single-particle levels, i.e. \(\Delta = \varepsilon_d - \varepsilon_p\). In early TM oxides, such as e.g. certain titanates or vanadates, the respective level separation is rather large with TM\((d)\) well above O\((2p)\). Then usually, electronic correlations matter most within the partially filled 2p subshell of TM\((d)\), since O\((2p)\) states are much deeper in energy than the scale of the lower-Hubbard-band formation. The local Hubbard \(U_{dd} := U\) within TM\((d)\) is the smaller energy and thus governs the correlation effects. On the contrary for late TM oxides, \(\Delta\) becomes the smaller energy and O\((2p)\) are often located between the lower- and upper-Hubbard-band formation scales.

In the latter case, the correlation physics is more subtle. Of course, \(U\) remains a vital player, since it triggers strong correlation. However, the charge-transfer energy and more generally also the Coulomb interactions of local O\((2p)\) kind and of intersite TM\((d)\)-O\((2p)\) kind gain significant impact. Extended model Hamiltonians, besides \(U_{dd}\) terms furthermore including additional onsite \(U_{pp}\) terms on oxygen and intersite \(U_{pd}\) terms, are believed to become relevant for a generic description of the correlated electronic structure. But especially in a realistic context, as e.g. DFT+DMFT, such extensions will raise issues: at least two new Coulomb parameters have to be quantified and questions concerning the quality of the many-body treatment adequate for the new terms arise. Moreover, the technical/numerical effort increases significantly, particularly for low-symmetry structures, heterostructure problems, defect properties, etc..

Therefore, we here introduce an efficient extension to the state-of-the-art charge self-consistent DFT+DMFT framework, geared to treat charge-transfer physics with a minimum of additional Coulomb parametrization and essentially without any further increase in technical/numerical effort. First, our DFT and DMFT parts remain structurally unmodified, i.e. a mixed-basis pseudopotential framework\(^{29,30}\) is utilized for the former and a continuous-time quantum Monte Carlo technique\(^{43,44}\) for the latter (see Ref. \(^{37}\) for further details). Besides these established building blocks, a third one is integrated. A self-interaction-correction (SIC) formalism\(^{35,36}\) is applied to cope with the correlations explicitly originating from the nickel site are here described within DMFT.

Projected local orbitals\(^{14,45}\) are employed to define the correlated subspace for the DMFT part. The five Ni\((3d)\) atomic-like orbitals are projected onto the Kohn-Sham valence states of NiO (i.e. eight bands for the stoichiometric compound). The complete Slater-Condon Hamiltonian

\[
\mathcal{H} = \frac{1}{2} \sum_{m_1m_2m_3m_4} \sum_{\sigma\sigma'} \sum_{l=0}^{4} U_{m_1m_2m_3m_4} c_{m_1\sigma}^\dagger c_{m_2\sigma'}^\dagger c_{m_3\sigma'} c_{m_4\sigma} , \tag{1}
\]

with \(m_i = 1 \ldots 5\) and \(\sigma, \sigma' = \uparrow, \downarrow\), is used for the electron-electron interaction in the correlated subspace. Coulomb matrix elements for \(l = 2\) are expressed in spherical symmetry via standard Slater integrals \(F^k\) through

\[
U_{m_1m_2m_3m_4} = \sum_{k=0}^{2l} a_k(m_1, m_2, m_3, m_4) F^k , \tag{2}
\]

with expansion coefficients \(a_k\) given by

\[
a_k(m_1, m_2, m_3, m_4) = \sum_{q=-\infty}^{\infty} (2l+1)^2 (-1)^{m_1+q+m_2} \times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} l & k & l \\ -m_1 & q & m_3 \end{pmatrix} \begin{pmatrix} l & k & l \\ -m_2 & -q & m_4 \end{pmatrix} . \tag{3}
\]
and parametrized using the Hubbard $U$ and Hund’s exchange $J_H$ via

$$F^0 = U, \quad F^2 = \frac{14}{1+r} J_H, \quad F^4 = r F^2.$$  \quad (4)

The $F^4/F^2$ Slater-integral ratio is chosen as $r = 0.625$, which is adequate for transition-metal atoms. For the present NiO study, $U = 10 \, \text{eV}$ and $J_H = 1.0 \, \text{eV}$ are employed. While the latter value is standard for this compound, the Hubbard interaction is somewhat larger than the usual value of $\sim 8 \, \text{eV}$.\textsuperscript{20,21} But charge self-consistent DFT+DMFT often enforces an enhanced local Coulomb interaction compared to one-shot calculation\textsuperscript{22} because of the increased number of screening channels. A recent computation\textsuperscript{23} of NiO Coulomb parameters for a $dp$ Hamiltonian within the constrained random-phase approximation yields also a Hubbard $U \sim 10 \, \text{eV}$. The DMFT problem is solved by hybridization-expansion continuous-time quantum Monte Carlo\textsuperscript{28} as implemented in the TRIQS package\textsuperscript{30,31} A double-counting correction of fully-localized-limit (FLL) type\textsuperscript{29} is applied. All calculations are performed in the paramagnetic regime at a system temperature of $T = 580 \, \text{K}$. In order to obtain the spectral function $A(\omega) = -1/\pi \text{Im} \, G(\omega)$, analytical continuation of the Green’s function $G$ from the Matsubara axis to the real-frequency axis is performed by the maximum-entropy method.

The NiO lattice constant is set to the experimental value\textsuperscript{23} $a = 4.17 \, \text{Å}$. Doping with lithium is realized by means of a supercell approach. Each symmetry-in equivalent Ni site poses a different single-site DMFT problem; all are coupled within the general multi-site many-body scheme\textsuperscript{34}. As DFT convergence parameters we used $E_{\text{cut}} = 16(13) \, \text{Ry}$ and a $k$-point mesh of $13(5) \times 13(5) \times 13(5)$ for the pristine (Li-doped) case.

III. RESULTS

A. Self-interaction corrected oxygen in NiO

Before delving into the results of the new DFT+SICDMFT scheme, it is illustrative to inspect the impact of the self-interaction correction to oxygen in nonmagnetic NiO from the effective single-particle LDA+SIC viewpoint.

Figure 1 displays the site- and orbital-projected density of states (DOS) within DFT and for two different SIC parameters $w_p = 0.7, 0.8$. The Ni-$t_{2g}$ states are completely filled and the strongly hybridized $\{\text{Ni}-e_g, \text{O}(2p)\}$ states are partially filled. Hence holes are located on the TM as well as on the ligand sites. Not surprisingly, each scheme renders the system metallic. It is well known that for gap opening on the static DFT($+U$) level, symmetry breaking in the form of magnetic ordering is indispensable and the same applies here. Note that we could apply SIC also on the TM sites\textsuperscript{35} and additionally allow for antiferromagnetic order to investigate the insulating state in that effective-single-particle approximation. The result would be qualitatively similar to the one obtained from a DFT+$U$ treatment\textsuperscript{34}, but we do not want to follow this route in the present work.

Instead, let us concentrate on the principal effects of SIC applied on the oxygen site. There are in essence two main effects. First, the $pd$ splitting and hence the charge-transfer energy is increased by SIC. Using $\Delta = \epsilon_d - \epsilon_p$, the value reads, respectively, $\Delta_{\text{LDA}} = 3.13 \, \text{eV}, \Delta_{\text{LDA+SIC70}} = 3.98 \, \text{eV}$ and $\Delta_{\text{LDA+SIC80}} = 4.50 \, \text{eV}$. Fits to experimental data yield $\Delta$ values in the range $\sim [−5, −4] \, \text{eV}$\textsuperscript{19,21,56}. Thus LDA severely underestimates $\Delta$ and the effect of SIC on oxygen brings the charge-transfer energy in line with experimental estimates. Second, band narrowing takes place with SIC, roughly on the order of $Z \sim 0.8$ for $w_p = 0.8$, as also visible from Fig. 1. Importantly, the band-narrowing effects are not only encountered for the O$(2p)$ contribution, but also for the dominant Ni$(3d)$ bands. Hence a nonlocal ligand-TM correlation effect occurs as a result of self-interaction correction applied to the oxygen pseudopotential. Those two key effects originate from the effective inclusion of $U_{pp}$ and $U_{pd}$ terms within the present LDA+SIC treatment.

Let us remark again that the parameter setting $\alpha = 0.8$ is not specifically adjusted to NiO, but this $\alpha$ value turns out to be a proper choice for many TM oxides\textsuperscript{14,15}. In other words, a present SIC parametrization with $w_p = \alpha$ is much less case sensitive as the usual choice/calculation of the Hubbard interaction(s).
B. NiO many-body spectrum

1. DFT+sicDMFT examination

We now discuss the spectral results from the complete DFT+sicDMFT approach, employing \( w_p = 0.8 \). Figure 2 shows the main outcome for stoichiometric NiO together with the combined experimental data\(^8\) from photoemission and inverse-photoemission.

Let us first briefly recall the state-of-the-art interpretation\(^8\) of the experimental spectrum. NiO is a correlation-induced insulator subject to the interplay of Mott-Hubbard and charge-transfer physics. The Ni ground state in the 3d-shell amounts to \( d^8 \), and \( L \) describes a hole in the ligand O(2\( p \)) states. The crucial charge-transfer process, associated with the energy \( \Delta \), is described by the transition \( d^8 \rightarrow d^9L \), i.e. electron transfer from O(2\( p \)) to Ni(3\( d \)). This energy scale sets the NiO charge gap of \( \sim 4.3 \) eV. An added electron conclusively enters the \( d^9 \) state associated with peak E. On the other hand, adding a hole to the system either results in the high-energy \( d^7 \) state (i.e. lower Hubbard band) associated with peak C, or gives rise to \( d^8L \) at a much lower energy of peak A. The shoulder D is usually interpreted as originating from the nonbonding part of O(2\( p \)). The most-controversially discussed peak B is build from a substructure of the \( d^8L \) state and often associated with nonlocal excitations\(^8\) (see Ref.\(^{19} \) for a detailed discussion). Let us note that Taguchi et al.\(^{13} \) suggested an alternative scenario for the lower-energy peaks A and B. Namely, peak A should originate from a \( d^8Z \) state and only peak B builds up from \( d^8L \) without the need of invoking explicit nonlocal processes. 

Here, \( d^8Z \) refers to a Zhang-Rice (ZR) bound state, a strongly correlated TM-O-hybridized low-energy entity, presumably most relevant for low-energy cuprate physics.\(^{52} \) In NiO, the ZR (doublet) bound state is based on the interaction of the O(2\( p \)) hole with both Ni(3\( d \)) holes. Loosely speaking, \( d^8Z \) is the tightly-bound ‘collective’ counterpart of the weakly-bound \( d^8L \) excitation.

The upper part of Fig. 2 displays the total spectral function \( A_{\text{tot}}(\omega) = \sum_{\nu} A_{\nu}(\omega) \), with \( \nu \) as the Bloch (band) index, from DFT+sicDMFT compared to the experimental data. Additionally, the projection of \( A_{\text{tot}}(\omega) \) onto Ni(3\( d \)) and O(2\( p \)) is depicted. Note that this site- and orbital-resolved spectrum is strictly not identical to the true local spectral function in a many-body sense. Since the projection is performed from the Bloch-resolved \( A_{\nu}(\omega) \) it carries the complete hybridization on the lattice and moreover results from an analytical continuation of the Bloch Green’s function \( G_{\nu} \). Overall, the agreement with experiment is quite remarkable: the theoretical charge gap of \( \sim 4 \) eV matches perfectly, and also the further features A–D are well reproduced. The principal charge-transfer character is obvious from the fact that the dominant part of O(2\( p \)) is located between the lower Hubbard band at \( \sim -9 \) eV and the upper Hubbard band at \( \sim 4 \) eV. As already expected from the previous discussion, the lower-energy region \( \Lambda = [-3.5, 0] \) eV indeed asks for a deeper analysis.

Therefore, the lower part of Fig. 2 shows the Ni(3\( d \)) local spectral function \( A_{\text{loc}}(\omega) \) as obtained from analytical continuation of the local Green’s function \( G_{\nu} \). Locally, the \( t_{2g} \) manifold is completely filled and the upper Hubbard band is exclusively of \( e_g \) character. Within \( \Lambda \) the \( e_g \) part displays a three-peak structure, whereas the \( t_{2g} \) part a two-peak structure. The first sharp resonance closest to the valence-band maximum (VBM) at \( \sim -0.1 \) eV is of exclusive \( e_g \) kind, in line with previous studies\(^{12} \). A second sharp peak resonates in both cubic 3\( d \) sectors roughly at the same energy \( \sim -0.85 \) eV, while a slightly broader peak occurs at \( \sim -1.8 \) eV for \( t_{2g} \)(\( e_g \)). We interpret this intriguing structure as follows: the first sharp substructure at \( \geq -1.2 \) eV belongs to \( d^8Z \), whereas the higher-energy substructure in \( \Lambda \) belongs to \( d^8L \).

Then the experimental peak A is a \( \{d^8Z, d^8L\} \) superposition (with larger \( d^8Z \) content) and peak B results from a superposition of \( d^8L \) with part of the nonbonding O(2\( p \)) spectrum. Explicit nonlocal correlations, e.g. through an inter-site Ni-Ni self-energy, appear not necessary to qualitatively account for a sizeable Ni spectral weight within peak B. As our many-body method is (charge) self-consistent on the lattice, implicit features of
nonlocality are included. It may still be that explicit nonlocal self-energies beyond DMFT enhance the Ni weight in peak B. Thus in essence, the present study highlights the intricate entanglement between the more basic aspects of charge-transfer physics and its highly-correlated ZR ramifications.

2. Comparing with standard DFT+DMFT

Finally, we want to comment on the methodological aspect of our approach. In order to compare the present scheme with the traditional DFT+DMFT method for NiO, Fig. 3 shows the total spectral function as well as the Ni-$e_g$, $t_{2g}$ local spectral function with and without SIC for oxygen. The most obvious striking difference concerns the gap size: without SIC, the charge gap turns out only of order $\sim 0.7 \text{ eV}$. A similar observation has been made by Panda et al.\(^{22}\), who noted that they reached only a small NiO charge gap with the FLL double counting in charge self-consistent DFT+DMFT. On the occupied high-energy side, the lower Hubbard band is shifted to more negative energies without SIC. On the other hand, the structure in the $\Lambda$ region is not dramatically altered, albeit the fine structure appears less detailed without SIC. For instance, the local Ni-$t_{2g}$ spectrum exhibits only a single peak in standard DFT+DMFT. Altogether, even if focusing only on the occupied spectrum, the agreement with experiment concerning peak signature and position is less satisfactorily than with SIC. We also performed DFT+DMFT calculations for smaller $U = 8 \text{ eV}$, but the gap size did not change.

The very fact that charge self-consistent DFT+DMFT with standard double counting fails in reproducing the correct paramagnetic gap size for a charge-transfer(-like) compound, is not that surprising. As observed, the main Mott-Hubbard physics, i.e. the formation of Hubbard bands and their splitting in energy, is rather similar with and without SIC. However without SIC, the O(2$p$) level is too strongly shifted in the direction of the upper Hubbard band, rendering the final charge gap small. Because energy-beneficial charge fluctuations are suppressed on the Ni site, the formalism tries to shift O(2$p$) towards the upper Hubbard band to enable as much as possible the (virtual) charge fluctuations between O(2$p$) and Ni-$e_g$. Since there is no Coulomb penalty from SIC, the charge-transfer energy shrinks. In this regard, note that one-shot DFT+DMFT calculations\(^{20,21}\) obtain a charge gap somewhat smaller than in experiment, but still of reasonable size. This is understandable, as the O(2$p$) level remains essentially fixed in those calculations, and the DFT charge-transfer energy of $\sim 3.2 \text{ eV}$ is nearly unaltered. Hence when promoting the method to charge self-consistency, it is essential to include also the ligand-based Coulomb interactions. Of course, it may be that some other double-counting protocol “fixes” the problem. But the present approach is more physical, it is applicable to general charge-transfer problems and allows one the use of the identical standard double-counting form for Mott-Hubbard and charge-transfer systems without any further adjustments. Last but not least, we are confident that the correct interplay of Mott-Hubbard, charge-transfer and charge self-consistent processes is very well provided by our DFT+sicDMFT framework.

C. Li-doped NiO

Lithium doping of NiO has first been studied in detail in the 1960s\(^{10,11}\) and remained of research significance ever since\(^{11,12,15}\). Recently, it furthermore gained interest in the context of hybrid organic-inorganic perovskite solar cells\(^{58,59}\).

The alkali element enters as a substitutional Li\(^{+}\) defect replacing Ni$^{2+}$ and thus providing holes to the compound. The Li$_x$Ni$_{1-x}$O system is stable for a wide $x$ range up to LiNiO\(^{26}\). Importantly, Li doping does not render NiO metallic, but semiconducting with ingap states appearing at $\sim 1.2 \text{ eV}$ above the valence-band maximum\(^{20,21}\). In the following, Li$_x$Ni$_{1-x}$O is studied for $x = 0.125$ by our DFT+sicDMFT method within a supercell approach. We kept the stoichiometric lattice constant for the 16-atom cell and relaxed the atomic positions in LDA (see Fig. 4). Upon structural relaxation the O sites surrounding the Li ion are pushed away from the defect. There are two symmetry-in inequivalent Ni classes in the supercell. Identical local Coulomb parameters as chosen for stoichiometric NiO are used for the defect problem. The number of Kohn-Sham projection states of is properly scaled from 8 at $x = 0$ to 59 ($= 7 \text{ Ni} \times 5 \text{ d-orbitals } + 8 \text{ O} \times 3 \text{ p-orbitals}$) at $x = 0.125$. 

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![Graph showing spectral information from DFT+sicDMFT and DFT+DMFT](image)

FIG. 3. (color online) Comparison of NiO spectral information from DFT+sicDMFT and DFT+DMFT. Top: total spectrum, middle: local Ni-$e_g$ and bottom: local Ni-$t_{2g}$. 

The energy location of the IGS is in excellent agreement with inverse-photoemission data\textsuperscript{12,13,15} in the local Ni spectrum, as already seen for the upper Hubbard band, there is no $t_{2g}$ contribution to the IGS. The question arises at the expense of which spectral weight do the IGS appear? Inspection of the weight transfers among the Bloch-resolved spectral function $A_\nu(\omega)$ may help to answer this question. Figure 5b displays the whole 59 $A_\nu$ functions and highlight the four ones with a maximum contribution to the IGS. From this one observes that the ‘spectral growth’ of the IGS corresponds with a ‘spectral shrinkage’ of weight that is especially located in the transition region of peak A,B in the occupied spectrum. It is  

1. Many-body spectrum with in-gap states

Figure 5 depicts the collected spectral results together with inverse-photoemission data from van Elp et al.\textsuperscript{12} The total spectrum in the upper part of Fig. 5a shows minor shifts and changes of intensity for the occupied states compared to the stoichiometric case. A shift of the spectrum to smaller binding energies with Li doping is also observed in experimental data\textsuperscript{12,13,15}. Peak E in the conduction states is shifted to higher energies, which qualitatively coincides with available experimental data from Reinert et al.\textsuperscript{13} Note in addition that the inverse-photoemission data in Ref. 12 were aligned at 5 eV. The resonant feature at and slightly above the valence-band maximum, rendering the doped system seemingly metallic(-like), is an artifact of the present supercell model and will be discussed in the next section.

Concerning the joint appearance of the $d^8Z$ and $d^8L$ states, the inspection of the local spectral function again turns out to be useful (see lower part of Fig. 5a). In the energy window $\Lambda = [-3.5,0]$ eV the $t_{2g}$ spectral weight is increased with smearing out its two-peak substructure, i.e. only a shoulder of the first subpeak remains below the VBM. The changes in the $e_g$ spectrum within this region have an even larger bearing: the stoichiometric peak at $\sim 2.6$ eV is lost for $x = 0.125$. This means that the vital Ni(3d) peak contribution to peak B in the total spectrum is missing. Thus the subtle balance between $d^8Z$ and $d^8L$ as observed in the stoichiometric case becomes qualitatively disturbed with Li doping. The spectral weight of $d^8Z$ states close to the valence-band maximum remains robust.

Finally, let us focus on the in-gap states (IGS) easily visible in the range $[1.1,2.1]$ eV of the total spectrum. FIG. 4. (color online) Supercell of Li$_x$Ni$_{1-z}$O for $x = 0.125$, consisting of 16 lattice sites in the primitive fcc cell. Ni: large blue, O: small red and Li: large grey.
therefore tempting to directly associate the IGS with the disappearance of the original \(d^8L\) subpeak in the local Ni-\(e_g\) spectrum as noted above.

2. Where are the holes?

The rigorous real-space location of the holes introduced by Li doping of NiO is a tenacious matter of debate.\(^{211,215}\) Originally, data have been interpreted via the formation of Ni\(^{3+}\), yet more recent studies favor the picture of the holes being located in the O(2p) shell. From a theoretical point of view it is indeed notoriously difficult to uniquely associate valence charges in a condensed matter system with a certain lattice site. Depending on the choice of local orbitals and the kind of charge analysis, often rather different results are obtained.

From a general point of view, underlined by the previous discussions of spectra, the relevant charge-transfer physics in NiO render the tight entanglement of Ni(3d) and O(2p) in the immediate neighborhood of the VBM obvious. The Zhang-Rice doublet state is a direct consequence thereof. Quantitatively, doping of \(x\) Li ions introduces a hole doping of \(\delta = x/(1-x)\) on the remaining Ni sites. Thus in the present case of \(x = 0.125\), this amounts to \(\delta = 0.143\). The Ni(3d) occupation from the local Green’s function reads \(n_d = 8.175\) at stoichiometry and \(n_d = 8.07\) with Li doping. Hence a number \(\delta_d = 0.105\) of effective nickel holes and \(\delta_p = \delta - \delta_d = 0.038\) of effective oxygen holes results here. The mixed character of hole formation is in line with doping into the entangled Ni(3d)-O(2p) VBM states.

Note that the real-space hole distribution is of course also subject to the actual choice of the supercell. In our present 16-atom supercell model (cf. Fig. 1) there are two symmetry-inequivalent Ni sites, namely Ni1 with multiplicity six and Ni2 with multiplicity one. The Ni2 site is located in a symmetry-unique position, perfectly surrounded by O sites pushed away from the Li defect. Therefore, charge fluctuations are most prone to this Ni site, giving rise to some artifact response. In fact, the quasiparticle-like resonance right and above the VBM in Fig. 3 may solely be traced back to a Ni2 origin. An advanced supercell design is eventually necessary to avoid such artifacts. For instance, a larger supercell with more than one Li defect in most-random positioning may be conceived. However, this will then ask for a numerical treatment of many more symmetry-inequivalent Ni sites. Current limitations in computational and memory performance render such challenging DFT+(sic)DMFT studies, especially for local five-orbital manifolds, very demanding. Work along these lines will thus postponed to future studies.

IV. SUMMARY

A methodological advancement of the combination of density functional theory and dynamical mean-field theory, geared to especially address materials problems with substantial charge-transfer character, has been presented. The combination of self-interaction correction on the ligand sites within the state-of-the-art charge self-consistent DFT+DMFT framework proves to be a powerful tool. Not only to approach long-standing ‘basic’ problems of late TM oxides, but due to its efficient and easily scalable structure also for application to novel problems e.g. occurring from nanoscale structuring.

We exemplified this DFT+(sic)DMFT method for the case of stoichiometric and Li-doped NiO, two persistently problematic correlated materials. A faithful description of the NiO spectrum at stoichiometry with very good accordance to experimental findings was given. The interplay of different forms of Ni(3d) and O(2p)-hole states, in the form of \(d^8Z\) and \(d^8L\), reemerged\(^{18}\) from this analysis. Importantly, the present scheme based on still-local DMFT self-energies is sufficient to account for the experimentally-derived demands of Ni(3d) contributions to the double-peak structure (i.e. peak A and B) below the valence-band maximum. The introduction of explicit nonlocal Ni-Ni self-energies (e.g. via cluster-DMFT) is not needed for a qualitative appearance of such contributions. In the case of Li\(_x\)Ni\(_{1-x}\)O, the semiconducting nature of the doped material is verified from theory, along with the long-standing experimental observation of ingap states \(\sim 1-2\) eV above the VBM. Our examination suggests that spectral-weight transfer from \(d^8Z\leftrightarrow d^8L\) into the gap region causes the IGS.

The successful state-of-the-art DFT+DMFT approach for early/middle-row transition-metal oxides is thus complemented with the DFT+sicDMFT framework for late-row TM oxides. Various realistic interacting problems, such as e.g. rare-earth nickelates or high-\(T_c\) cuprates, await (renewed) investigation.

ACKNOWLEDGMENTS

We gratefully acknowledge financial upport from the German Science Foundation (DFG) via the project LE-2446/4-1. F.L. thanks L. F. J. Piper for helpful discussions. Computations were performed at the University of Hamburg and the JUWELS Cluster of the Jülich Supercomputing Centre (JSC) under project number hhh08.

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