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Intrinsic charge transfer gap in NiO from Ni *K*-edge x-ray absorption spectroscopy

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Pre-edge features in x-ray absorption spectroscopy contain key information about the lowest excited states and thus on the most interesting physical properties of the system. In transition-metal oxides they are particularly structured but extracting physical parameters by comparison with a calculation is not easy due to several computational challenges. By combining core-hole attraction and correlation effects in a first-principles approach, we calculate Ni *K*-edge x-ray absorption spectra in NiO. We obtain a striking parameter-free agreement with experimental data and show that dipolar pre-edge features above the correlation gap are due to nonlocal excitations largely unaffected by the core hole. We show that in charge transfer insulators, this property can be used to measure the correlation gap and probe the intrinsic position of the upper Hubbard band.

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I. INTRODUCTION

The description of electronic excitations in correlated materials is a challenge since many relevant phenomena, such as magnetism in transition-metal (TM) compounds or high-T_c superconductivity in doped Mott insulators, are a consequence of strong electron-electron interaction. Core hole spectroscopies such as x-ray absorption (XAS) and resonant inelastic x-ray scattering (RIXS) have been particularly useful for measuring electronic excitations in correlated antiferromagnetic insulators[1–3] as well as in high-T_c superconductors.[4,5] Interpretation of these measurements is difficult and a theoretical interpretation is needed. For example, in La_2CuO_4, $K\alpha$ combined RIXS measurements and theoretical calculations[6] demonstrated that dipolar pre-edge features just above the correlation gap are due to intersite Cu 4*p*-3*d* hybridization. The basic requisite for a theoretical interpretation of core-hole spectroscopic data is a good description of the absorption process.

In *K*-edge XAS a 1*s* core electron is excited to the conduction band by an incident x-ray beam, leaving a hole in the core state. The presence of the core hole substantially complicates the interpretation of experimental data. Since core-hole attraction shifts the empty *d* states much more than the empty *p* states, typically by several eV, it is unclear to what extent the energy of the pre-edge features can provide useful information on the position of the corresponding excitations in the absence of a core hole. In correlated insulators core-hole attraction and Hubbard repulsion partially compensate each other so that using free parameters to describe these interactions is questionable. A treatment of both effects from first principles is needed.

In the case of *K*-edge XAS, theoretical calculations are difficult since excitations in a large energy window above the Fermi level need to be described. Thus methods dealing successfully with correlation effects in NiO in an energy window close to the Fermi level [such as dynamical mean field theory (DMFT) (Ref. 7) or cluster calculations[8,9]] cannot be used to describe pre-edge and near-edge structures in *K*-edge XAS spectra. On the other hand such a description is sorely needed because (i) low-energy pre-edge features provide relevant information on the local environment of the absorbing atom[3,6,10,11] and (ii) it has been suggested that in correlated oxides "shakedown" excitations occur as near-edge structures.[12]

In the prototype charge transfer insulator NiO, the elementary excitation is a charge transfer from O valence states to mainly Ni conduction states. This situation is not reproduced by standard density-functional theory (DFT) calculation, while DFT+U schemes correct this failure. In this work we present a first-principles approach to describe the *K*-edge XAS measurements in correlated insulators and apply it to NiO. The approach is based on a recently developed DFT+U method and includes core-hole attraction.[13] In contrast to other DFT+U schemes,[14] the U parameter is obtained by linear response.[15,16] Consequently, *U is not a fitting parameter* but an intrinsic linear-response property since it measures the spurious curvature of the energy functional as a function of occupation.[15] We demonstrate first that a pre-edge dipolar feature in the Ni *K*-edge XAS is due to nonlocal excitations to second-nearest-neighboring Ni atoms. We further find that due to its nonlocal nature, the dipolar pre-edge feature is unshifted by core-hole attraction, and it is a simple and reliable measure of the upper Hubbard band in the *absence* of a core hole in the final state. Finally exploiting this insensitivity of the pre-edge dipolar feature to core-hole attraction we show how to *directly* measure the charge transfer gap using *K*-edge XAS.

II. TECHNICAL DETAILS

We use the NiO experimental crystal structure. The paramagnetic-cell group space is then $Fm\bar{3}m$; Ni occupies the 4*a* position and O the 4*b*. The cubic lattice parameter is $a=4.1788$ Å for NiO.[17] DFT calculations are performed using the QUANTUM-ESPRESSO code.[18] We use Troullier-Martins[19] pseudopotentials, the spin-polarized generalized gradient approximation (GGA) (Ref. 20), and the DFT+U method of Refs. 15 and 16. The wave functions are expanded using a 140 Ry energy cutoff. The calculated value of U is $U=7.6$ eV. XAS spectra are computed using the XSPECTRA package[18] in a supercell approach including core-hole effects in the pseudopotential of the absorbing atom. The continued fraction[13] and the projected augmented wave

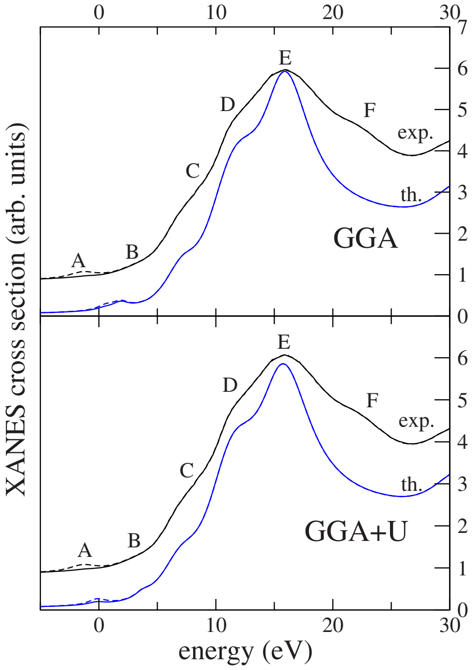

FIG. 1. (Color online) Calculated and measured (Ref. 23) Ni *K*-edge XAS of NiO. The dashed (solid) curves correspond to e_g (t_{2g}) orientation.

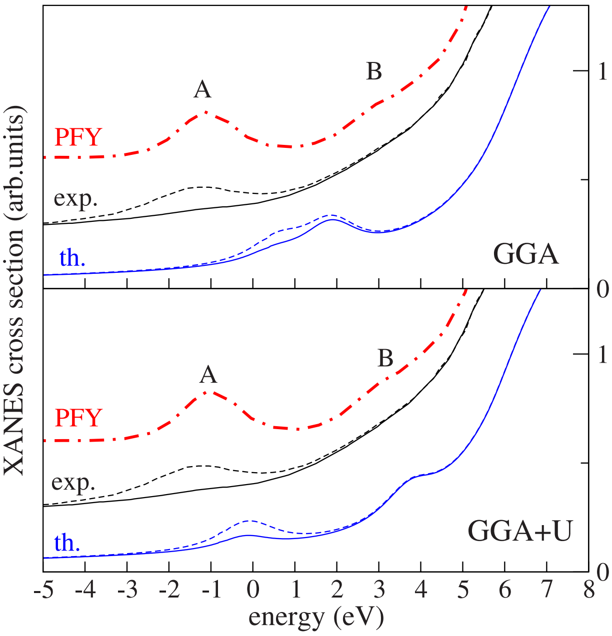

FIG. 2. (Color online) Calculated and measured (Ref. 23) Ni *K*-edge XAS of NiO including partial fluorescence yield (PFY) (this work), in the pre-edge region. The dashed (solid) curves correspond to e_g (t_{2g}) orientation.

(PAW) method of Ref. 21 are used. We considered $2\times2\times2$ supercells of the magnetic cell (32 atoms). We used a $4\times4\times4$ *k*-point grid both for the charge density and the continued fraction calculation. The NiO partial fluorescence yield (PFY) absorption data were obtained at the ESRF on a single-crystal sample using a crystal spectrometer with a total resolution of about 1 eV (Ref. 22) and the analyzer energy set at the peak of the Ni *K* beta line.

III. INTERPRETATION OF XAS IN NiO

In Fig. 1 we show calculated NiO XAS spectra and their decomposition into dipolar and quadrupolar parts using GGA and GGA+U, as compared to experimental data[23] on single crystals. The Fermi level in the presence of a core hole is considered as the zero energy in the plot. We consider the following two sets of polarization $\boldsymbol{\epsilon}$ and wave vector $\mathbf{k}$: (i) $\boldsymbol{\epsilon}\|[110]$ and $\mathbf{k}\|[-110]$, denoted by e_g orientation (dashed lines), and (ii) $\boldsymbol{\epsilon}\|[100]$ and $\mathbf{k}\|[010]$, denoted by t_{2g} orientation (solid lines) with components in terms of the paramagnetic cubic crystal cell. We note that U has no effect on high-energy near-edge and far-edge features (labeled C, D, and E). On the contrary the energy and angular dependence of pre-edge structures (Fig. 2) are incorrect in the framework of GGA. Peak B is at too low an energy and a too large mixing occurs between structures A and B. In the GGA+U calculation the dipolar peak B is shifted to ≈2 eV higher energies and the angular dependence is in agreement with experimental data. The GGA+U calculation also shows that a very small dipolar component is present in peak A, commonly interpreted as purely quadrupolar.[23] Detailed analysis of the angular dependence of the experimental NiO XAS spectra[23] shows that even for the t_{2g} orientation, where no quadrupolar transition occurs because the t_{2g} states are occupied, a small peak is present,[24] in agreement with our findings. Thus, in correlated insulators, the use of the DFT+U approximation is mandatory to obtain a correct description of the pre-edge features.

To complete the understanding of the pre-edge features in NiO we resolve the XAS spectrum in its spin dependence and calculate the density of states projected over atomic orbitals using Löwdin projections. In order to simplify the discussion we consider the absorbing Ni to be spin-up polarized. As can be seen in Fig. 3, the quadrupolar part of peak A is mostly due to intrasite excitations to *d* states lowered by core-hole attraction. However, since the hybridization between Ni and O is very strong, core-hole attraction lowers a small portion of the O $2p$ states generating a small dipolar component in peak A. In an atomic-orbital picture, peak A is due to direct dipole transitions from Ni $1s$ states to O $2p$ states. In our calculation the intensity of this excitation is of the order of 1% of the edge jump. In experiments it is somewhat smaller because of the larger linewidth. This estimate is crucial for the quantitative description of this off-site excitation in multiplet calculations.

The spin-resolved dipolar spectrum shows that peak B is mostly due to transition to up-spin-polarized states. Since the absorbing atom has five up electrons in *d* states, the B excitation *must* have an off-site component. Our calculation demonstrates that it is due to transitions to on-site Ni empty $4p$ states hybridized to empty $3d$ states of next-to-nearest-neighbor Ni atoms (Fig. 4). The B peak is thus determined by intersite Ni $4p$-$3d$ mixing via strong Ni $3d$-O $2p$ hybridization and is a direct probe of the upper Hubbard band in NiO.

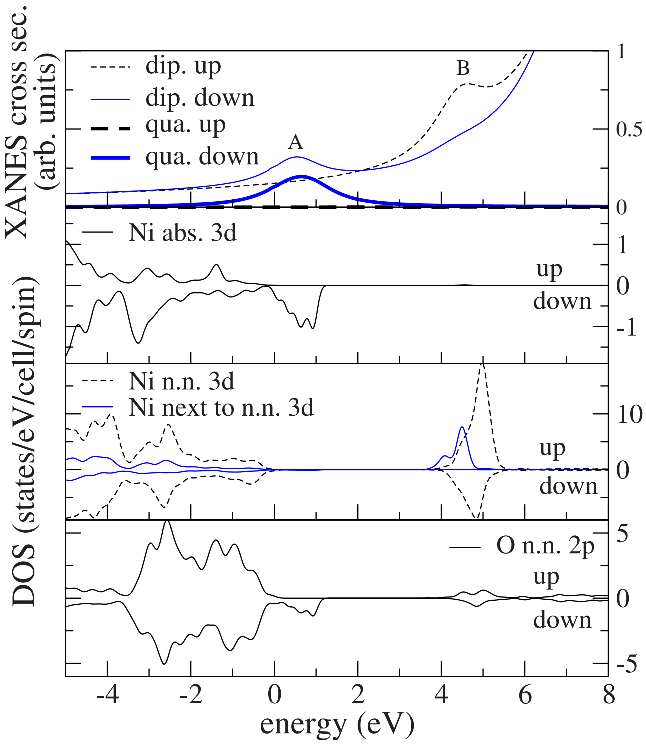

FIG. 3. (Color online) Comparison between GGA+U calculated K-edge Ni XAS and Löwdin projected density of states.

The occurrence of dipolar pre-edge features due to off-site transitions is not obvious. XAS spectra measure mostly the on-site p-projected empty density of states (DOS) in the presence of a core hole. Features occurring in the pre-edge structures of the XAS spectrum are due to transition to states localized in energy. Such a localization in energy implies that these states are not part of the continuum and thus are localized in real space. Intuitively one should expect that the main contribution to this feature is due to transition to on-site localized states of the absorbing atom. However, we have shown that this is not the case since hybridization with on-site p states of the absorbing atom can promote transitions to off-site localized states that are fourth-nearest neighbors of the absorbing atom.

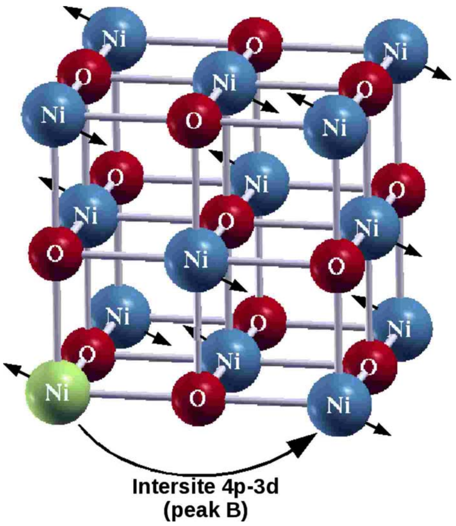

FIG. 4. (Color online) NiO crystal structure. Ni atoms are in blue and O atoms are in red. The absorbing atom is green. The charge transfer process responsible for peak B in XAS spectra is schematically represented.

The interpretation of the experimental spectroscopic features (A and B peaks) through our calculation in turn allows us to physically interpret the role of the Hubbard term. This term reduces the hybridization of the Ni 3d and O 2p states via larger occupation of the Ni 3d states and their consequent energy downshift. As a result of the loss of hybridization, the energy of empty Ni 3d states is raised and the separation between the peaks A and B is increased.

The current calculation differs from previous calculations[23,25] since (i) it is parameter free and (ii) in other works the attribution of the A peak is incorrect. To understand core-hole effects on the A and B features we have performed calculations with and without a core hole in the final state. We found that peak A is shifted by 4 eV with respect to the edge by core-hole attraction. On the contrary peak B is essentially unshifted since the electronic states forming the B peak are mostly localized on atoms which are fourth-nearest neighbors from the absorbing atom where the core hole resides. The difference in the behavior of the two peaks is due to the nonlocal nature of peak B.

IV. MEASURE OF THE CHARGE TRANSFER GAP IN NiO USING Ni *K*-EDGE XAS

We now demonstrate that the nonlocal nature of the B excitation and its insensitivity to core-hole effects can be used to measure the correlation gap. We consider hole-doped NiO. In practice this can be achieved through Li doping,[26] as in the case of $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$. A large range of doping can be experimentally obtained with $0<x<0.7$. It has been shown[27,28] that when NiO is doped with holes, the holes mainly reside on O atoms due to the charge transfer character of NiO. Thus the top of the NiO valence band has mainly p character. This suggests that in Ni K-edge XAS of $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$, in the low doping regime, an additional dipolar peak should occur in the pre-edge, resulting from the holes entering the top of the valence band. This is confirmed by oxygen K-edge absorption where the top of the valence band is seen even at dopings as low as $x=0.05$.[27] At somewhat larger doping, a similar peak due to oxygen p holes should also occur in the dipolar part of Ni K-edge XAS. Since no experimental data are available in the literature, we directly simulate Ni K-edge XAS in $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$.

We calculate hole doping of NiO in two different ways, namely, (i) by rigid-band doping of NiO and (ii) adding a compensating-charge background and recalculating self-consistently the charge density and the XAS spectra. The results of the Ni K-edge XAS in $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$ in the pre-edge region with and without a core hole in the final state are shown in Fig. 5. We find that the top of the valence band should be visible in Ni K-edge XAS at dopings of $x \approx 15-20\%$. In the calculated spectra, with or without a core hole in the final state, the energy positions of the top of the valence band and of peak B are independent on doping. The

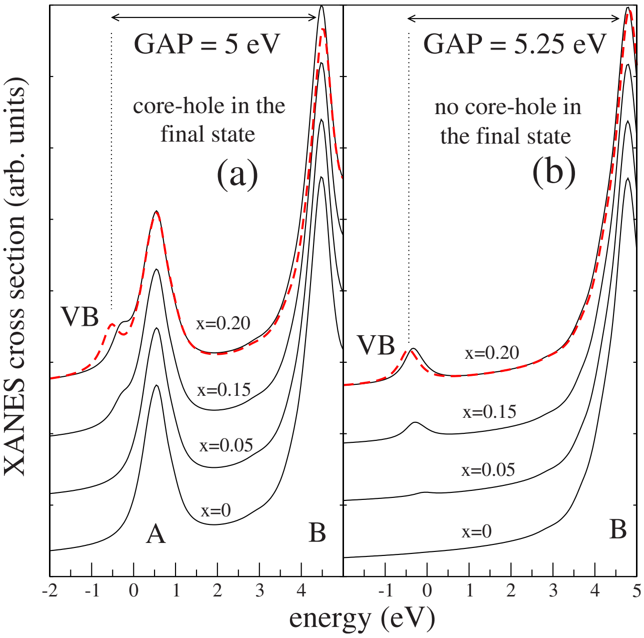

FIG. 5. (Color online) Calculated pre-edge features of Ni K-edge XAS spectra of $\mathrm{Li}_x\mathrm{Ni}_{1-x}\mathrm{O}$ with (a) and without (b) core-hole effects using a rigid doping (solid line) approach or adding a compensating-charge background (red dashed lines). Peak labeling is the same as in Fig. 1; VB stands for valence band.

agreement between the rigid-band picture and the compensating-charge background calculation validates the rigid-band picture for $0<x<0.2$

In NiO the experimentally measurable gap is due to the excitation between the top of the valence band and the empty d states. In DFT+U (Ref. 29) and GW (Ref. 30) calculations the lowest single-particle excitation is between the valence band and an s band occurring at energies lower than the empty d states (see Fig. 6). This band is invisible in experiments since its optical matrix elements are extremely weak.[29] Moreover it is also invisible in K-edge XAS since it is highly dispersive and has mostly Ni s and O s components. Thus in the absence of core-hole effects, the energy between the top of the valence band and peak B is a measure of the correlation gap, the dependence of the energy position on doping being very weak (see Fig. 5, right panel). When core-hole attraction is considered (see Fig. 5, left panel), we find that the distance between the top of the valence band and peak B is largely unaffected (≈5%). Consequently in lightly hole-doped NiO the distance between the top of the valence band and peak B is a measure of the correlation gap even in the presence of a core hole in the final state.

In our calculation the charge transfer gap is 5 eV (peak-to-peak). In NiO optical absorption starts at 3.1 eV and reaches its maximum at 4.0 eV.[31,32] This value is reduced with respect to ours because of excitonic effects. In combined photoemission-inverse photoemission[33] the gap (peak-to-peak) is roughly 5.5 eV, in fairly good agreement with our value. Our proposal thus allows for an independent estimate of the gap in NiO.

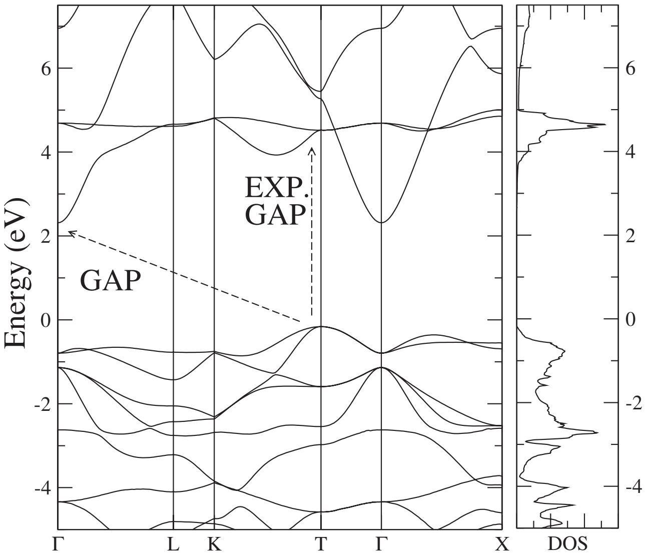

FIG. 6. NiO band structure and density of states (in units of states/cell/spin/eV) calculated in the DFT+U approximation. The smallest lowest single-particle excitation is shown by the dashed arrow labeled "GAP." This excitation is between the valence band and an s band occurring at energies lower than the empty d states. This band is invisible in experiments since its optical matrix elements are extremely weak (Ref. 29). Furthermore it cannot be seen in K-edge XAS since it is highly dispersive and has mostly Ni s and O s components. The measured charge transfer gap is shown by the dashed arrow labeled "EXP. GAP."

The procedure outlined for NiO can be used to measure the charge transfer gap and the upper Hubbard band in other charge transfer insulators. In these systems the top of the valence band is due to oxygen p states and it is thus visible in dipolar TM K-edge XAS upon doping. If the doping necessary to detect this feature is low enough not to affect substantially the electronic structure, then a rigid-band doping picture applies and the top of the valence band is at the same energy as in the undoped system. Since hole states are dipolar, the effects of core-hole attraction are weak. The top of the valence band of the doped system can then be used as a reference energy to measure the excitations seen in TM K-edge XAS. The second necessary condition is the occurrence of nonlocal dipolar features[3,6] (peak B) in the pre-edge region due to transitions to d states of neighboring TM atoms promoted by hybridization with the TM absorbing atom p states. If these excitations are visible, we have shown that they represent the upper Hubbard band of the material. The energy difference between this excitation and the top of the valence band in the hole-doped system is a measure of the charge transfer gap. Thus, TM K-edge XAS in hole-doped charge transfer insulators is an unbiased experimental tool to measure the correlation gap.

V. CONCLUSION

In this work we have developed a first-principles parameter-free method to calculate K-edge XAS spectra including core-hole effects in the final state and electronic correlation at the DFT+U level.[18] We have shown that the method provides spectra in good agreement with experimental data for NiO, the prototype correlated insulator. We have interpreted all the pre-edge and near-edge features in the experimental data. In particular, we have identified a dipolar pre-edge feature as due to nonlocal excitations to *d* states of the second-nearest-neighboring Ni atoms, namely, the upper Hubbard band. We have shown that due to its nonlocal nature, this excitation is unaffected by the presence of a core hole in the final state. Starting from this result we have proposed a way to measure the intrinsic correlation gap in charge transfer insulators based on TM *K*-edge XAS. This method is complementary to optical measurements and more straightforward than a combined photoemission-inverse photoemission experiment.

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