Optical properties and correlation effects in Na_xCoO_2

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We have calculated the optical spectra of Na_xCoO_2 for $x=0.3$, 0.5, and 0.7 within the local density approximation (LDA). A comparison of our results to available experimental data shows good agreement of the important features and trends, but reveals a nearly uniform shift of peak positions and poor quantitative reproduction of intensities. We show, through application of a simple model, that these differences can be attributed to overhybridization between Co and O orbitals and spin fluctuations that renormalize the bandwidth. Application of the LDA+U procedure shifts the optical peaks farther from their experimental locations, indicating that this method of incorporating correlation effects is ill-suited for the case of Na_xCoO_2.

I. INTRODUCTION

The layered cobaltate Na_xCoO_2 is the subject of considerable interest not only because of a possibly unconventional superconducting state,[1] but also due to its unusual magnetotransport and thermoelectric behavior,[2–4] and an intriguing magnetic phase diagram.[5] As the Na content is varied from low to high, the system moves from a paramagnetic metal with Pauli-like susceptibility through a narrow, charge-ordered, insulating region around $x=0.5$ to a second metallic, but now Curie-Weiss-like, paramagnetic region. Near $x=0.75$, a magnetic transition, possibly signalling the onset of a spin density wave, appears.[6,7] It has been recently reported[8] that, at low temperatures, a second insulating state may set in at $x=0.25$.

Local density approximation (LDA) calculations[9] show a band structure that evolves smoothly with x, in contrast to the sharply different regions described above. The experimental magnetic phase diagram is not well reproduced, and a weakly magnetic metallic ground state is found incorrectly for all Na concentrations. Neglect of strong correlation effects by the LDA is the most obvious culprit, but their precise role in Na_xCoO_2 is so far not well understood. Circumstantial evidence indicates that it should be substantial, with most estimates of the Hubbard U quite large in comparison with the t_{2g} bandwidth. However, the system does not behave characteristically as a doped Mott-Hubbard insulator, particularly around the superconducting composition where a lack of local magnetic moments on Co d ions is indicated by susceptibility measurements.[10,11] Additionally, it has been observed that LDA calculations in systems with strong Hubbard correlations routinely underestimate the tendency to magnetism (the larger the difference, $U-I$, between the Hubbard repulsion and Hund's rule coupling, the greater the underestimation),[12] while overestimating the antiferromagnetic superexchange J. In the LDA, Na_xCoO_2 is magnetic,[13] but with in-plane antiferromagnetic instabilities that are smaller than ferromagnetic. Effects beyond LDA are required to suppress magnetism, but frustration is doubtful as a mechanism for this suppression. Because of this, and despite the large U/W ratio, spin fluctuations may offer a more plausible reason for deviations between calculated and observed magnetic ground states.

In this context, it is important to verify to what extent the LDA bands correctly describe the one-electron excitations and fermiology of Na_xCoO_2. Quantum oscillation probes would be ideal to investigate the Fermi surface (FS), particularly the predicted small pockets,[13,14] but so far no such studies have been reported. Several photoemission reports are available,[15,16] but because the electronic structure is expected to be sensitive to both surface states and surface quality, generalization of these results to the details of bulk electronic properties is questionable. Infrared optics has a penetration depth of $\sim c/\omega_p$ (where ω_{pl} is the plasma frequency), much longer than that of photoemission (~ 10 Å), and may therefore provide the most reliable probe of the electronic structure available to date. Several of these experiments have been reported.[8,17–20] Since optical absorption is an integrated property, involving a variety of interband transitions, it is usually difficult, if possible at all, to interpret the results in terms of the electronic structure without full first principles calculations.

Here we report such calculations. By comparing our calculated LDA spectra with optical experiments reported for various Na contents, we are able to assign the three main peaks to specific interband transitions and thereby examine in detail the dependence of these peak positions and strengths on bandwidths and energies. The peak shifts one expects to see in Mott-Hubbard-type compounds are not realized in this system, even for the insulating compounds. Furthermore, application of the LDA+U methodology exaggerates rather than rectifies the systematic discrepancies between the LDA and measured spectra. We employ a simple model to illustrate that overestimation of Co—O hybridization due to overly extended d orbitals would produce precisely the kind of peak shifts we see in our LDA spectra. Spin fluctuations predicted early on[21] and later observed[22] at some values of x, could also affect the spectra by renormalizing the bandwidth of the t_{2g} complex. This is also consistent with the differences we observe in our transitions compared with experiment.

II. CALCULATED OPTICAL CONDUCTIVITY

Using the *Wien2k*[23] full-potential augmented plane wave +local orbital code (APW+lo), we calculated the optical
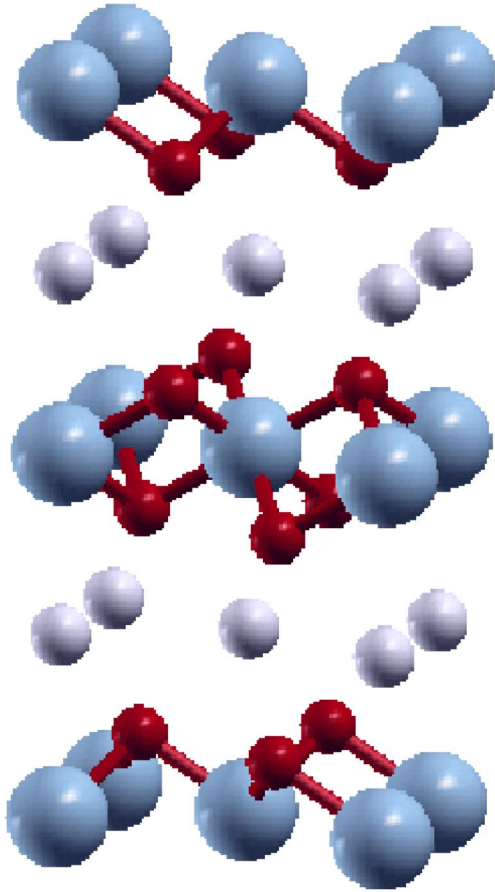
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FIG. 1. (Color online) The layered structure of Na_xCoO_2, CoO_2 octahedra make up the top, middle, and bottom planes, and light atoms are intercalated Na in the virtual crystal approximation (all sites occupied).
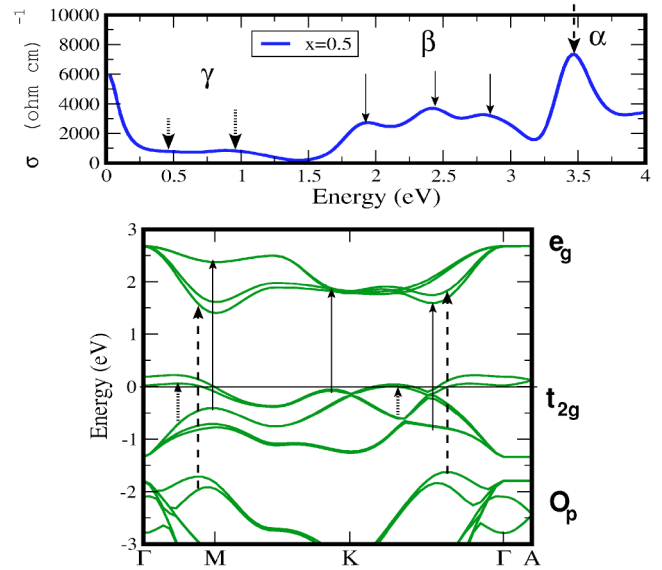

FIG. 2. (Top panel) The LDA optical conductivity for $Na_{0.5}CoO_2$ with arrows delineating the three main peaks, γ (lined arrows), β (solid arrows), and α (dotted arrows). A Gaussian broadening of 0.06 eV was used. (Bottom panel) Interband transitions corresponding to peaks in the optical conductivity.

conductivity for Na_xCoO_2 within the $P63/mmc$ symmetry (SG No. 194) at three Na contents, $x=0.3, 0.5$, and 0.7. To vary the Na content, we used the virtual crystal procedure of occupying every $2b$ site with an ion of fractional charge (see Fig. 1). For both c and a lattice constants, we used experimental data[5] but relaxed the O height separately for each x. The APW sphere radii were the same for all calculations, 2.0 for Na, 1.85 for Co and 1.55 for O. RK_{max} (essentially a measure of the plane-wave cutoff) was set to 7.0, giving a basis set of 833 APW's and 60 local orbitals. Our density was well converged using 480 k points in the irreducible Brillouin zone (BZ).

We first calculated the imaginary part of the dielectric constant, $\epsilon''(\omega)$, in the random phase approximation (RPA)[24,42] using the standard code of the *Wien2k* package. The real part of the optical conductivity, $\sigma'(\omega)$, can then be obtained by $\sigma'(\omega)=(\omega/4\pi)\epsilon''(\omega)$. The resulting spectra exhibit three main peaks, which we label γ, β, and α, according to the notation of Wang *et al.*[18] We can identify the specific interband transitions giving rise to these peaks using a band-by-band decomposition of $\epsilon''(\omega)$. Each of γ, β, and α have distinct origins. The γ peak corresponds to transitions between different bands of the metallic t_{2g} complex, the β

peak to t_{2g}-e_g transitions, and the α-peak to transitions from fully occupied O-p states to unoccupied e_g states. Our calculated peaks and the identification of their origins agrees well with tight-binding results[25] obtained for $Na_{0.5}CoO_2$. The t_{2g} and the e_g complex, although formally labeled according to $l=2$ (i.e., d) symmetry representations, are in reality substantially hybridized with O. Therefore, as opposed to real d-d transitions in a free atom, such "d-d" dipole transitions are allowed because of the O admixture and physically are of charge transfer nature. The t_{2g} bands are split into an a_{1g} and two e_g' bands by the trigonal crystal field,[13] and all γ transitions are from a lower e_g'-like state to an upper e_g'-like or a_{1g}-like state. The e_g'-e_g' transitions are wholly due to small hole FS's near the K points of the BZ and contribute to a just visible shoulder beneath the lowest energy peak in the calculated spectrum (an arrow designates this shoulder near 0.4 eV in Fig. 1). However, there are allowed e_g'-a_{1g} transitions in the same energy range that contribute roughly equally to the peak intensity and therefore, the existence of these hole pockets cannot be inferred from the existence of the shoulder. The calculated β peak has several distinguishable subpeaks corresponding to transitions from different parts of the BZ. In Fig. 2, the peaks of the spectrum for $Na_{0.5}CoO_2$ are shown and representative transitions are indicated along high symmetry points of the corresponding band structure. The ratio of $\epsilon''(\omega)$ to the joint density of states (JDOS), provides a gauge of the magnitude of the matrix elements for these transitions. In contrast to the JDOS itself, which is largest for the t_{2g}-e_g transitions (β peak), the matrix elements are, predictably, larger for the α peak and, surprisingly, for the γ peak (t_{2g}-t_{2g}) even larger. The largest γ elements are roughly a factor of 3 greater than the largest α elements which are nearly twice the size of the largest β elements.
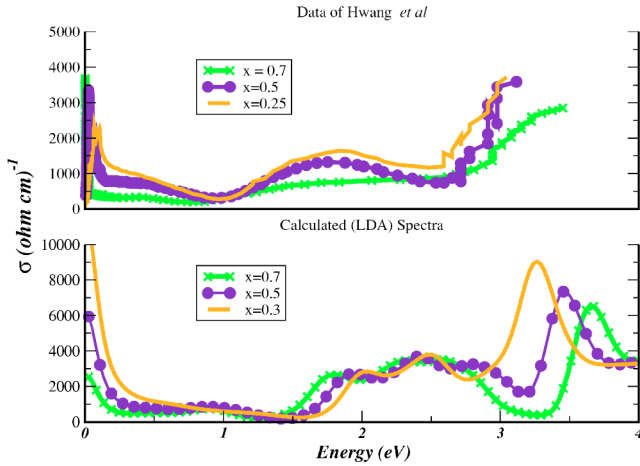
FIG. 3. (Color online) A comparison of experimental (top panel) and calculated (lower panel) optical spectra. Note that the lowest calculated Na concentration is 0.3, slightly different from the experimental value of 0.25.

III. COMPARISON WITH EXPERIMENT

The three (γ, β, α) conductivity peaks are clearly recognizable in all available optical data. The reported positions and strengths of these peaks, however, vary somewhat between experiments, even for identical dopings.[8,18,20] For consistency of comparison, we use mainly the report of Hwang *et al.*,[8] where spectra for several compounds of different Na content are available. Overall, the LDA spectra are seen to be in good qualitative, but poor quantitative agreement with experiment (see Fig. 3), a situation we will attribute to LDA overhybridization, and/or spin fluctuations in the next section. But first, we discuss the doping dependencies and general shape of the spectra. These are quite well reproduced by calculation. At both $x=0.25$ and $x=0.5$, optical measurements at very low frequency detect a small semiconducting gap. At all energies above the calculated Drude peak, this gap has no effect on the optical spectra.[8] There are two clear trends followed by both the LDA and measured $\sigma_1(\omega)$ as electron count is increased (Na added). First, the α and β peaks shift away from each other and become broader. Second, the γ peak sharpens and moves slightly lower in energy. Both effects have their origin in an upward shift of Co-derived bands as the Co d-band filling is increased. The greater energy difference between the O-p states and the shifted e_g band determines the α-peak position, and a reduction in hybridization between Co and O orbitals, now further separated in energy, weakens the t_{2g}-e_g crystal field splitting, causing the downward β-peak shift. Since the γ peak is due to transitions within the t_{2g} band complex, its sharpening and shift down are both attributable to a slightly narrowed t_{2g} bandwidth caused by decreased O mixing. Our calculated in-plane plasma frequency at $x=0.7$, $\omega_p=1.39$ eV, agrees well with values extracted from experiment,[18,20] $\omega_p=1.48$ eV and $\omega_p=1.17$ eV. The c-axis plasma frequency is calculated to be 1.48 eV, nearly the same as the in-plane value, reflecting the lack of anisotropy at higher Na levels. Here we note that the effect of the virtual crystal approxima-

tion (VCA) for disordered ions is to underestimate the anisotropy for all values of x. A detailed comparison with supercell calculations[26] shows that it is only interlayer hopping that is affected by the VCA and that the features relevant to optics are well reproduced such that the trends reported here are not affected by this approximation. We do expect that a calculation employing real, disordered Na ions would result in a broadening of the peaks (as compared to the VCA) due to leaking of the indirect transitions. As Na is removed, the in-plane plasma frequency and the electronic anisotropy increase until, at $x=0.3$, the in-plane ω_p is 2.86 eV and the c-axis ω_p is 0.337 eV, approximately an order of magnitude apart. The increase in Drude weight and concurrent enhancement of anisotropy with electron removal compare favorably with experimental observations.[8,19]

Despite these instances of good agreement, some dramatic differences between the spectra are obvious. The experimental peak intensities are almost a factor of 2 smaller and approximately 0.5 eV lower in energy than our calculated ones when using a Gaussian broadening of 0.06 eV. This value was chosen to match peak widths to experiment, but because the broadening should in reality be energy dependent, the lower peaks of our spectrum are somewhat over-broadened. Experimentally, the strong dip just below the α peak deepens from $x=0.25$ to $x=0.5$, but then becomes shallow again at $x=0.7$, whereas the LDA gap deepens and widens monotonically with increasing Na content. It has been previously suggested that both β and α peaks could be identified with transitions across the t_{2g}-e_g energy gap and that spin splitting of the t_{2g} states could account for differences between observed peak positions and calculated paramagnetic band positions.[18] Though no observation of static magnetism has been made for any $x<0.75$, the LDA is known to predict an FM ground state for all x, suggesting that magnetic fluctuations may be present in the system.[13,21] Direct observations of FM spin fluctuations,[22] a spin density wave[7] at $x=0.75$, and c-axis AFM ordering[27] at $x=0.85$ further support the idea that magnetism may play a role in optics. However, since regular optics does not allow for spin-flip transition, spin splitting may shift optical transitions only if one of the two electronic states involved in a transition is split while the other is not. This is not the case for either γ or β peaks. There is some effect on the position of the α peak because of oxygen admixture, but it is merely 0.15 eV even at $x=0.3$. Thus, the observed shifts of the absorption peaks with respect to the LDA, especially the two high-energy peaks, α and β, cannot be due to magnetic effects.

IV. CORRELATIONS EFFECTS AND BAND RENORMALIZATIONS

The small t_{2g} and e_g bandwidths of Na$_x$CoO$_2$ suggest that correlation effects in Co-d may be important. Our renormalized atom calculations for Hubbard U on Co yield $U \gtrsim 3.7$ eV, while the t_{2g} bandwidth W is 1.5 eV, so that the Hubbard ratio (accounting for degeneracy) is $U/W\sqrt{3} \gtrsim 1.5$. Spin-unrestricted band structure calculations yield a half-metallic ferromagnetic ground state, contrary to experiment. All this suggests that we adopt a circumspect attitude toward

conventional LDA calculations for this compound as it is quite likely that the actual experimental electronic structure is considerably renormalized compared to the LDA results.[28] Indeed, angle-resolved photoemission spectroscopy (ARPES) measurements[15,16] have detected a heavy quasiparticle band near the Fermi energy with a total width of ~70 meV, much smaller than the LDA bandwidth. This is an interesting finding, but surface sensitivity should be kept in mind. Indeed, differences between surface electronic structure, as measured accurately by ARPES, and bulk electronic structure have been established in other oxides, including cuprate,[29] ruthenate,[30] and manganite[31,32] compounds. Optical experiments, with their longer penetration depth, have the potential to tell us more about the specific shortcomings of LDA calculations in Na_xCoO_2. The optical spectra of good metals are reproduced remarkably well for a very large energy range,[33] and even in strongly correlated systems, good agreement is often achieved.[34] Deviation of the LDA spectra from experiment, if properly analyzed, is an indispensable probe of the nature of the relevant many-body effects.

Let us first recall the typical inadequacies of LDA calculations in systems with localized electrons. The best known case is exemplified by Mott-Hubbard insulators. Here the missing physics is mainly the Coulomb repulsion between electrons localized at the same site. Typical examples are f-electron compounds, high-T_c cuprates, or $3d$ oxides. This group is characterized by (1) underestimation of propensity toward magnetism (up to the level of total loss of a magnetic ground state, as in cuprates), (2) underestimation of band gaps between occupied and empty bands, and (3) overestimation of the superexchange antiferromagnetic interaction (this increases with hopping and decreases with the band gap; the former is overestimated and the latter underestimated in LDA). As a leading correction to the LDA, the LDA+U method has been very successful in the prototypical systems listed above. For these, the LDA+U method reproduces the missing Mott-Hubbard effects, such as a downward shift of the occupied bands relative to the unoccupied bands (with corresponding shifts of interband transitions to higher energies). In metallic systems, it must be kept in mind that the main correlation effects are dynamic, and best accounted for by methods such as dynamical mean field theory (DMFT), to which LDA+U is only a static approximation. Nonetheless, the LDA+U methodology has been used for metals and, particularly because Na_xCoO_2 has insulating phases for at least one value of x, the optical effects of Mott-Hubbard-type correlations in the system, if they exist, should be reproduced by this scheme.

Inspection of the LDA band structure of Na_xCoO_2 in conjunction with experimental data indicates the Mott-Hubbard effects discussed above are not applicable here. The tendency toward magnetism is overestimated, and so is the band gap between the t_{2g} and e_g bands. The LDA ground state is ferromagnetic, and not antiferromagnetic. Not surprisingly then, LDA+U calculations[35,36] only worsen the situation. The t_{2g}-e_g distance, already 0.5 eV too large, increases further, and the tendency towards magnetism becomes even stronger. Additionally, for more subtle reasons, the two e_g' subbands of the t_{2g} manifold are shifted down with respect to the a_{1g} band. This in turn shifts the γ peak, already too high in
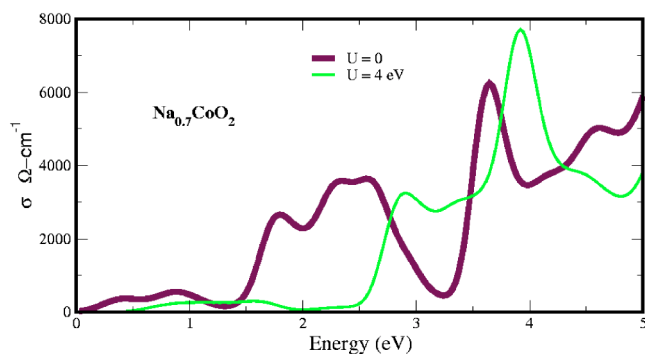

FIG. 4. A comparison of LDA+U and LDA optical spectra at $x=0.7$ (spin-up and spin-down spectra are added together). All three peaks shift upward with the application of U, further deviating from experimental results.

energy, up even further. In Fig. 4, the upward shift of the β peak, with an applied U of 4 eV, is enough to merge it with the α peak. In comparison with the LDA spectra (also shown) the agreement with experiment is significantly worse. We conclude that the *LDA+U approach is not appropriate for Na_xCoO_2*.

Another possible manifestation of electron-electron correlations is found in ^{3}He and in CrO_2.[37] Here collective excitations (magnons or paramagnons) play the same role as phonons in the sense of "dressing" quasiparticles and increasing their mass.[38] As a result, the optical spectra more or less proportionally squeeze toward the low frequency. Softening of magnetic excitations near a quantum critical point leads to large spin fluctuations and suppression (full or partial) of magnetic ordering.[39,40] A comparison of the experimental and calculated properties of Na_xCoO_2 indicates the presence of such effects. Thus, *quantum criticality is likely to be an important reason for deviation from the LDA in Na_xCoO_2*.

Finally, one should not forget about a very prosaic shortcoming of the LDA, it includes a spurious self-interaction that leads to overextended $3d$ orbitals, and thus overestimated hybridization with ligand orbitals. This effect becomes stronger for more localized d orbitals.

We shall now try to assess qualitatively the ramification of these two effects. The first, "dressing" of one-electron excitations is qualitatively similar to the electron-phonon coupling induced renormalization, except it occurs in a larger energy range. It is reasonable to expect it to affect the whole t_{2g} band or a large part of it, leading to overall narrowing of all three t_{2g} bands. This, in turn should shift both components of the γ transition, the e_g'-e_g' one and the e_g'-a_{1g} one to lower energies, without much change in their intensity (the extra spectral weight is transferred to high energies, as in the electron-phonon coupling). It is unlikely that, as sometimes assumed, the top of the e_g' band will be shifted down with respect to the a_{1g} band. First, dressing of the quasiparticles makes them heavier, but normally does not shift different states near the Fermi energy with respect to each other. Second, this would not only eliminate the e_g'-e_g' transitions, but would also shift the e_g'-a_{1g} to higher energy, worsening the agreement with experiment. It is also unlikely that such

"dressing" would affect the unoccupied e_g band, which is too far away from the Fermi level.

Let us now estimate the possible effects of contraction of the Co-d orbitals. To this end we use the simplest possible tight binding model, namely one where only nearest neighbor Co—O $pd\sigma$ and $pd\pi$ hoppings (we will call these t_σ^2 and t_π^2, respectively) are included, and the energy of the O-p level is taken to be sufficiently far removed from the Co-d level that it can be integrated out. Both assumptions are extremely crude, as direct Co—Co and especially O—O overlaps are not small, nor is the p-d energy separation small. The model nonetheless provides a useful qualitative framework. The resulting 5×5 Hamiltonian has a 2×2 e_g subblock with diagonal elements proportional to t_σ^2. Because there is no path connecting an e_g orbital on one site to any neighboring e_g orbital via oxygen, there is no dispersion in this subblock. The 3×3 t_{2g} subblock has noticeable dispersion controlled by t_π^2, with the overall upward shift of the same order. Finally there is a dispersive off-diagonal subblock, corresponding to O-assisted hopping between neighboring t_{2g} and e_g orbitals. The scale of this block is set by the product $t_\sigma t_\pi$. Note that in a cubic structure, such t_{2g}-e_g hopping through an intermediary O is impossible.

We now make the further simplifying assumption that $t_\sigma \gg t_\pi$. We can then neglect the ligand field on the t_{2g} orbitals (proportional to t_π^2,), leaving only the ligand field on the e_g orbitals (proportional to t_σ^2). Since the β peak is due to t_{2g}-e_g transitions, its position reflects a crystal field splitting of the Co-d states which results from a combination of electrostatic and ligand field effects. Using a linearized muffin-tin orbital (LMTO) calculation with all Co—O hybridization suppressed, we found that the crystal field splitting reduces from ≈ 3.4 eV to ≈ 1 eV, i.e., the electrostatic crystal field is 1 eV, and the ligand field is 2.4 eV. The latter is probably overestimated because the LDA overhybridizes the Co-d orbitals. Specifically, if t_σ were 12% smaller than it's LDA value ($\sqrt{2.4/1.9}=1.12$), the β peak would shift down by 0.5 eV, in agreement with the experiment. Furthermore, the intensity of this peak would also be reduced, because the optical matrix elements in a two-band tight binding model scale with the off-diagonal elements of the Hamiltonian (this follows from the tight binding definition of dipole matrix elements as $\langle A_1 | \partial H / \partial \mathbf{k} | A_2 \rangle$, where A are the eigenvectors), and these scale as $t_\sigma t_\pi$. This is in accord with overestimation of the β-peak intensity and lends further support to our assumption that the LDA overestimates the $pd\sigma$ hopping amplitudes in Na$_x$CoO$_2$ by approximately 10%. This is a static effect. On the other hand, the dressing of the quasiparticles is dynamic in nature and requires a methodology that explicitly includes fluctuations. Some notable work along this line, based on simplified models, has been recently reported in the framework of DMFT.[41]

V. CONCLUSIONS

We have calculated the LDA optical conductivity spectra of Na$_x$CoO$_2$ and compared it with experimental data for several different Na contents. There is good qualitative agreement in terms of the number of peaks and their behavior with changing x, but exact peak heights and positions are not well reproduced. Though the underlying reasons for this are likely correlation effects neglected by the LDA, we argue that using LDA+U as a remedy is inappropriate for this compound. Spin fluctuation driven renormalization of the t_{2g} band complex and overextension of Co-d orbitals are shown to affect the optical spectrum in a manner consistent with the discrepancies between calculation and experiment. These cause narrowing of the t_{2g} band and reduction of crystal field splitting, respectively, bringing LDA optical peaks into good agreement with experimental reports.

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