The high-spin and low-spin states of Co(III) ion in Co$_3$O$_4$ studied by X-ray absorption spectroscopy

Xiao Cheng, 1, 2, 3 Jinghua Guo, 3 Per-Anders Glans, 3 and Yi Luo* 1, 2

1 Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, China
2 Department of Theoretical Chemistry, School of Biotechnology, Royal Institute of Technology, SE-10691 Stockholm, Sweden
3 Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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The Co 2p L$_{2,3}$-edge X-ray absorption spectrum of Co$_3$O$_4$ is studied using multiplet calculation method in two reciprocal corroborative approaches. The Co 2p L$_{2,3}$-edge XAS of Co$_3$O$_4$ originates from the intertwined spectra of Co$^{2+}$ and Co$^{3+}$ ions, which interfere the interpretation of its spectral features. The multiplet calculations of Co(III) in O$_h$ symmetry and Co(II) in T$_d$ symmetry compose a good Co$_3$O$_4$ absorption spectrum as compared with experiment. The results suggest that the spin state of Co$^{3+}$ ions is a hybrid state with both low spin LS($t^6_2e^0_6$) state and high spin HS($t^4_2e^2_6$) state at room temperature, which implies a reasonable dispute over the orthodox point of view that Co$^{3+}$ ions in Co$_3$O$_4$ are only in low spin states.

INTRODUCTION

In the dynamic development of material science, the tricobalt tetroxide Co$_3$O$_4$ becomes an attractive subject with various novel applications. The mesoporous nanostructures of Co$_3$O$_4$ are efficient catalysts for low temperature oxidation of CoO in air cleaning studies[1], artificial photosynthetic and other photocatalytic reactions[2–4]. In lithium-ion battery researches[5–8], the Co$_3$O$_4$ materials are vastly studied as potential electrode candidates. In the form of nanotube Co$_3$O$_4$ has potential application as gas sensor due to its characteristic mesoporous structure[9, 10]. As a good pseudocapacitive metal oxide, the Co$_3$O$_4$ is used to construct the novel hybrid metal oxide core/shell nanowire arrays for the electrochemical capacitor[11]. A lot of synthesis approaches also have been performed[12–17] on various Co$_3$O$_4$ nanoparticles.

These applications of Co$_3$O$_4$ require a clear understanding of its electronic structure especially for Co cations. The X-ray absorption spectroscopy is an important tool in probing the local electronic structure of the targeted metal site due to the exceptional element-selective property and short-range effect. Since the valence state and local symmetry are germane to Co 3d orbitals, the Co 2p L$_{2,3}$-edge XAS is used to investigate the electronic structure of Co cations in Co$_3$O$_4$. However, the bulk phase tricobalt tetraoxide Co$_3$O$_4$ contains two kinds of cobalt cation, tetrahedral interstice for Co$^{2+}$ ion around by four oxide ligands and octahedral interstice for Co$^{3+}$ ion around by six oxide ligands. The Co$^{2+}$ and Co$^{3+}$ cations both contribute to the Co 2p L$_{2,3}$-edge XAS of Co$_3$O$_4$, which makes it’s difficult to interpret the whole spectral features. In order to distinguish the specific contribution from Co$^{2+}$ and Co$^{3+}$ XAS features, theoretical calculation of Co$_3$O$_4$ becomes necessary. In this work, the Co$^{2+}$ and Co$^{3+}$ 2p L$_{2,3}$-edge XAS are studied by the
multiplet theory via two different approaches, the charge transfer multiplet (CTM) method and point charge cluster (MultiX) method, which have reciprocative assistance to each other.

The crystal structure of Co$_3$O$_4$ is shown in Fig.1(a) derived from previous experiment\cite{18}. The Co(II) ion is in a tetrahedral symmetric interstice and Co(III) ion is in octahedral symmetric interstice. The Co(II) ion with electronic configuration 2p$^6$3d$^7$ in T$_d$ symmetric interstice has three unpaired electrons in three degenerated T$_2$ orbitals, four paired electrons in two degenerated E orbitals. The energy levels of T$_2$ and E orbitals are split by the T$_d$ symmetric crystal field with a value 10Dq. Despite how the value 10Dq varies, Co(II) only have one possible spin state S=3/2, which is also confirmed by previous magnetic moment measurement\cite{19}. As for Co(III) ion with electronic configuration 2p$^6$3d$^6$ in O$_h$ symmetric interstice, its 3d orbitals are also split into two degenerated energy levels T$_{2g}$ and E$_g$ with the value 10Dq. The Co(III) may have two possible spin states, an high spin state S=2 and another low spin state S=0, which is determined by the magnitude of the crystal field. The low spin state (T$_{2g}^6$ E$_g^0$) has six paired electrons in T$_{2g}$ orbitals and the high spin state (T$_{2g}^4$ T$_{2g}^2$ E$_g^2$) has one paired electron at T$_{2g}$ orbital, four unpaired electrons at T$_{2g}$ and E$_g$ orbitals, as shown in Fig.1(b).

The spin exchange interaction caused by the Pauli exclusion principle has an exchange splitting interaction E$_{ex}$ for 3d orbitals with different spin. If the spin exchange interaction is taken into consideration, the 3d orbitals of Co(II) and Co(III) have different splitting for spin-up and spin-down orbitals as shown in the spin polarized energy splitting diagram Fig.1(c). Both the Co(III) LS and HS states are shown in the figure. The relative energy levels are derived from previous theoretical studies on the band structure of Co$_3$O$_4$\cite{20–22}. If the Hartree repulsion between the electrons at E$^a$ and E$^b$ which share large spatial overlap is considered, the occupied E$^a$ orbitals would have higher energy siting between T$_{2g}^4$ and E$^b$ orbitals\cite{23}.

The Co(III) would be in high spin state (HS) when restricted frame, the energy splitting diagram is shown in Fig.1(b) for Co(II) and Co(III). The Co(II) ion with electronic configuration 2p$^6$3d$^7$ in T$_d$ symmetric interstice has three unpaired electrons in three degenerated T$_2$ orbitals, four paired electrons in two degenerated E orbitals. The energy levels of T$_2$ and E orbitals are split by the T$_d$ symmetric crystal field with a value 10Dq. Despite how the value 10Dq varies, Co(II) only have one possible spin state S=3/2, which is also confirmed by previous magnetic moment measurement\cite{19}. As for Co(III) ion with electronic configuration 2p$^6$3d$^6$ in O$_h$ symmetric interstice, its 3d orbitals are also split into two degenerated energy levels T$_{2g}$ and E$_g$ with the value 10Dq. The Co(III) may have two possible spin states, an high spin state S=2 and another low spin state S=0, which is determined by the magnitude of the crystal field. The low spin state (T$_{2g}^6$ E$_g^0$) has six paired electrons in T$_{2g}$ orbitals and the high spin state (T$_{2g}^4$ T$_{2g}^2$ E$_g^2$) has one paired electron at T$_{2g}$ orbital, four unpaired electrons at T$_{2g}$ and E$_g$ orbitals, as shown in Fig.1(b).

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For Co(III) ion in this O₈ symmetrical intersce, both interactions appear to be in the same order of magnitude[24]. The Co(III) in O₈ intersce of Co₂O₄ is commonly considered to be in the (LS) state based on the previous measurement[19] at low temperature (4.2 K). The interpretation becomes very influential for the following researches[25–30] related to the Co(III) spin s-state of Co₂O₄. However, this assumption brought too high magnetic moment value 3.88μΒ for the Co(II) ion compared with the spin-only contribution 3.0μΒ. Even in following researches[19, 31], the Co(II) magnetic moment was measured at 3.25μΒ or 3.26μΒ still slightly larger than the spin-only value. The recent DFT study[23, 32] of Co₂O₄ provides calculated values 2.46~2.90μΒ for Co(II) magnetic moment, which are still less than the previous experimental values. The discrepancy between the Co(II) theoretical value and Co₂O₄ experimental value in magnetic moment is attributed to several different mechanisms such as spin-orbital coupling in Co(II) cation[19], non-stoichiometric due to slight oxygen deficiency and small energy gap between the diamagnetic and paramagnetic states of Co(III) in octahedra site[19]. Meanwhile, the Co(III) high-spin configuration is also found in many Co₂O₄ systems due to the structural distortion caused by the defect of Co(III) vacancies in some non-stochiometric Co₂O₄ films[20, 33].

Since the exchange interaction is an intra-atomic property, the spin state of Co(III) is determined by the O₈ symmetrical crystal field strength. As a result, HS state Co(III) is expecting to have longer Co³⁺–O²⁻ bond length than that of LS state[36]. In Table.I, the spin state of Co(III) and the Co³⁺–O²⁻ bond length of various compounds are presented for comparison. The bond length Co³⁺–O²⁻ of Co₂O₄ was measured with different values from 1.89~2.02 Å in many previous experiments. The crystal-field in such bond lengths region is comparable with the spin exchange interaction considering other materials listed in the table. The transition energy between HS and LS states of Co(III) is found to be small in many researches[27, 38, 39]. The Co³⁺ ions in ZnCo₂O₄, MnCo₂O₄ and LaCoO₃ also lie in an O₈ symmetric coordination surrounding by six oxygen ligands. The structure of ZnCo₂O₄ and MnCo₂O₄ is the same as Co₂O₄, only with Co²⁺ ion substituted by Zn²⁺ or Mn²⁺ ion. The ZnCo₂O₄ is formed by Co₃O₄ doped with Zinc, and the Co(III) spin-unpairing transition (LS→HS) was observed with the increase of Zinc content[40]. As shown in Table.I, the Co³⁺ ions in ZnCo₂O₄ and MnCo₂O₄ have both HS and LS states with the Co³⁺–O²⁻ bond length from 1.87~2.10 Å corresponding to the same values measured in Co₂O₄. And the LaCoO₃ is a perovskite-like structure with La³⁺ in the cuboctahedron coordination and Co³⁺ in the octahedron coordination. The Co³⁺ ions in LaCoO₃ is always thought to be in ground state with low-spin[41] but the Co³⁺–O²⁻ bond length is 1.91 Å making the 10Dq comparable with Eex[42] and the transition energy between HS and LS states is only 0.05 eV[39] which is also supported by LDA+U calculation study[41]. There are several means to realize the spin transition in LaCoO₃ via Strontium doping[27] or thermal excitation under 500 K via Co–O stretching modes[43]. The transition from LS to HS of Co(III) in Co₂O₄ is observed in the high temperature X-ray diffraction study[18]. The endotherm in Co₂O₄ studied by various calorimetry and thermoelectric measurements[40, 44–46] also supports the LS to HS transition of Co(III) at certain high temperature.

As discussed above in magnetic and structure perspectives, it is reasonable to expect high spin state Co(III)
TABLE I: The spin state and Co^{3+}–O^{2−} bond length in various cobalt compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>High spin %</th>
<th>Low spin %</th>
<th>Co^{3+}–O^{2−} bond (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co_{3}O_{4}</td>
<td>0</td>
<td>100</td>
<td>2.02</td>
<td>[34, 35]</td>
</tr>
<tr>
<td>Co_{2}O_{4}</td>
<td>0</td>
<td>100</td>
<td>1.92</td>
<td>[18, 34]</td>
</tr>
<tr>
<td>Co_{3}O_{4}</td>
<td>0</td>
<td>100</td>
<td>1.89</td>
<td>[26, 34]</td>
</tr>
<tr>
<td>ZnCo_{2}O_{4}</td>
<td>15.5</td>
<td>84.5</td>
<td>2.10</td>
<td>[27, 35]</td>
</tr>
<tr>
<td>ZnCo_{2}O_{4}</td>
<td>15.5</td>
<td>84.5</td>
<td>1.87</td>
<td>[35, 36]</td>
</tr>
<tr>
<td>MnCo_{2}O_{4}</td>
<td>5.5</td>
<td>94.5</td>
<td>2.08</td>
<td>[27, 35]</td>
</tr>
<tr>
<td>LaCoO_{3}</td>
<td>0</td>
<td>100</td>
<td>1.91</td>
<td>[26, 37]</td>
</tr>
</tbody>
</table>

in the Co_{3}O_{4} at room temperature. Meanwhile the existence of Co(III) high-spin state is important to improve the catalytic property by inserting excess unoccupied 3d orbital closer to the Fermi level as shown in Fig.1(b)(c). It is necessary for us to elucidate that is there prospective existence of high spin state Co(III) in Co_{3}O_{4} at room temperature? The present work uses multiplet calculation study for Co 2p L-edge X-ray absorption spectrum of Co_{3}O_{4} to elucidate this dispute which is unsolved for a long time in XAS aspect. The multiplet calculation is carried out in two reciprocal corroborative approaches. The first one is charge transfer multiplet (CTM) approach based on atomic multiplet model with inclusion of both crystal field and charge transfer effects. The second is point charge cluster (MultiX) approach creating the crystal field from the surrounding atoms especially facilitating metal ion in low symmetric center. The new calculation XAS spectrum combined the Co(III) HS and LS state with Co(II) contribution gives much better fitting to the experimental data compared with the previous theoretical study. The spectral features which was not well resolved in the previous study are fixed by the inclusion of Co(III) HS state in Co_{3}O_{4}. The present work also set up an example of using CTM method and MultiX method in a collaborative way to improve each other’s calculation procedure.

THEORY AND COMPUTATION DETAILS

In the present work, the calculation for Co 2p L-edge XAS is carried out in CTM and MultiX method. The CTM method[47] uses semiempirical parameters to simulate the crystal field and charge transfer effects induced by the local structure around the center metal site and calculate the corresponding absorption spectrum. The MultiX method[48] uses cluster model constructed by the point charges in the real crystalline locations to simulate the crystal field and then calculate the corresponding absorption spectrum. Each method has its merits and disadvantages, but they can work collaboratively to achieve better result. The MultiX calculation provides heuristic approach to reach reasonable initial guess values for the CTM calculation’s crystal field effect parameters. While the CTM method can include the charge transfer effect in the calculation, and has large freedom in using some adjustable physics parameters to handle both the crystal field and charge transfer effects, so to reveal each physical parameter’s specific effect on XAS features. The crystal-field multiplet calculation for the XAS of Co(II) and Co(III) HS/LS are carried both in CTM method and MultiX method. The charge-transfer multiplet calcula-
tion for the XAS of Co(II) and Co(III) HS/LS are carried in CTM method using the charge transfer parameters considering the previous charge-transfer multiplet calculation[25].

The symmetry of the local structure for Co$^{3+}$ or Co$^{2+}$ ion is used in CTM calculation method to determine the $3d$ orbital crystal field splitting as shown in Fig.1. The symmetry of the Co(III) local structure is a D$_{3d}$ with only slight distortion from O$_h$. Therefore, in the following CTM calculation it is treated in an O$_h$ symmetry, which is also proved by the crystal field calculation from MultiX method. The whole crystalline structure is used to perform the MultiX calculation from small cluster to increased large cluster until a stable result is reached. The corresponding crystal field data derived from the MultiX calculation can be treated as preliminary guess for the Co(II) and Co(III) CTM calculation crystal field parameters.

<table>
<thead>
<tr>
<th>Ion</th>
<th>10Dq</th>
<th>∆</th>
<th>$U_{pt}$</th>
<th>$U_{dd}$</th>
<th>T($e_g$)</th>
<th>T($t_{2g}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co$^{2+}$</td>
<td>-0.357</td>
<td>7.0</td>
<td>9.0</td>
<td>7.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Co$^{3+}$ (HS)</td>
<td>1.374</td>
<td>4.5</td>
<td>9.0</td>
<td>7.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Co$^{3+}$ (LS)</td>
<td>1.900</td>
<td>4.5</td>
<td>9.0</td>
<td>7.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The crystal-field multiplet calculation XAS features of Co(II) and Co(III) changes with crystal field strength 10Dq as shown in Fig.2. From the spectral features change trend in Co(II) XAS, it is found that the high spin ground state for the Co(II) is very stable with the increased energy gaps in the T$_d$ symmetry. This is easy to understand since the lowest three T$_2$ orbitals are all occupied with paired electrons even in the relative small energy gap, no matter how the energy gap increases there will be no spin unpaired transition to E$_g$ orbitals. However the Co(III) XAS changes suddenly when 10Dq decrease over 2.20 eV, where spin unpaired transition happens between the E$_g$ and T$_{2g}$ orbitals. Considering the parameters used in previous multiplet calculation study[25] and the unscaled crystal field splitting values calculated by MultiX in the following part, we have 10Dq=0.714 eV for Co(II) and 10Dq=1.674 eV for Co(III) HS, 10Dq=2.200 eV for Co(III) LS in crystal-field multiplet calculation. When charge transfer effect is included, the parameters for charge-transfer multiplet calculation are listed in Table.II.

The Lorentzian broadening half-width half-maximum (HWHM) for Co(II) is set to 0.2 eV for the L$_3$-edge region and 0.4 eV for the L$_2$-edge region. The Lorentzian broadening HWHM for Co(III) is set to be 0.4 eV for the L$_3$-edge region and 0.7 eV for the L$_2$-edge region. The Gaussian broadening for all calculation is set to 0.2 eV HWHM for resolution of the measurement. Considering the energy gaps between the L$_3$ and L$_2$ edges, the spin-orbital coupling interaction for core-hole from the atomic calculation has been scaled to perform the spec-

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**FIG. 2:** The XAS features of Co(II) and Co(III) change with increased energy gaps in T$_d$ and O$_h$ symmetries.
trum simulation. This scale factor for Co(II) is 1.02 and for Co(III) is 0.97. The Slater-Condon integrals from the atomic HF calculation are also scaled with commonly used factor 0.80 to have better fitting to the experimental spectrum.

![Graph showing energy splitting of Co²⁺ and Co³⁺ with cluster size increase](image)

**FIG. 3:** The 3d orbitals energy splitting of Co²⁺ and Co³⁺ changes with the cluster size increase as calculated from MultiX code.

The only semi-empirical parameters needed for MultiX calculation are the scale factors used to scale calculated Coulomb interaction, crystal field splitting strength, spin-orbital (SO) coupling interaction for core-hole and valence orbitals. When the scale factor for crystal field splitting is set to be 1.0 in MultiX calculation with spin-orbital coupling turning off for valence orbital, the 3d orbital energy level splitting diagram is calculated as shown in Fig.3. The 3d orbital energy level splitting diagram changes as the size of the calculation cluster increases. The Co(III) tends to have a O₅₇-like symmetric crystal field splitting with unscaled energy gap 0.837 eV in larger cluster model, while Co(II) keeps the T₅₇ symmetric crystal field splitting with unscaled energy gap 0.714 eV. This is consistent with previous studies assumption that despite Co(III) in a local D₅₇d symmetry we can still use O₅₇ symmetry in the multiplet calculation to simulate its X-ray absorption spectrum. The neighboring ions beyond the local structure around the center Co(III) ion abates the distortion of D₃d compared to O₅₇ symmetry.

These scale factors for the MultiX spectrum calculation are listed in Table III for Co(II) and Co(III) HS/LS with the consideration of previous multiplet calculation study [25] and the crystal-field multiplet calculation mentioned above. The core-hole Gaussian broadening starts with 0.20 eV with linear increase 0.20 eV from L₃ to L₂ region for Co(II). While for Co(III) the broadening starts with 0.40 eV with linear increase 0.30 eV from L₃ to L₂ region.

In order to combine the XAS of Co(II) and Co(III) for the final Co₃O₄ spectrum, the pre-edge peak of L₃-edge in Co₃O₄ XAS is assumed to have major contribution from Co(II) and the main peak of L₃-edge is assumed to be from Co(III). As a result, when the spectra of Co(II) and Co(III) are combined, the spectrum of Co(II) is shifted so that its main peak matches with the pre-edge peak of L₃-edge, and the spectrum of Co(III) is shifted to match the main peak of L₃-edge. The calculation spectrum is scaled to have the same main peak intensity with experiment data.

**TABLE III:** The MultiX calculation scale factors for Co(II) and Co(III) HS/LS.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Coulomb</th>
<th>Crystal</th>
<th>SOcore</th>
<th>SOvalence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co²⁺</td>
<td>0.750</td>
<td>2.000</td>
<td>1.000</td>
<td>0.700</td>
</tr>
<tr>
<td>Co³⁺ (HS)</td>
<td>0.750</td>
<td>2.000</td>
<td>0.920</td>
<td>0.750</td>
</tr>
<tr>
<td>Co³⁺ (LS)</td>
<td>0.750</td>
<td>2.600</td>
<td>0.976</td>
<td>1.000</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

The crystal-field multiplet calculation results are shown in Fig.4. Since the content ratio of Co²⁺ and Co³⁺ is 1:2 in Co₃O₄, the final XAS intensity is combined from Co(II) and Co(III) spectrum with 1:2 ratio for (a) and
FIG. 4: The crystal-field multiplet calculation for Co 2p L-edge X-ray absorption spectrum of Co$_3$O$_4$. (a) Co(III) in LS state. (b) Co(III) in HS state. (c) Co(III) in both HS and LS states with 1:1 ratio. (b) spectrum, where Co(III) ions are only in pure LS or HS state. For (c) spectrum, Co(III) ions are assumed to be both in HS and LS states with 1:1 ratio so that the contribution from Co(III) HS and LS states to the final XAS features is distinguishable.

The (a) calculation spectrum with Co(III) all in low-spin state has good fitting with experiment in the pre-edge peak of L$_3$-edge at 776 eV. The peak at 780 eV in the calculation spectrum (a) deviates from the high energy side of experiment L$_3$-edge. The calculation L$_2$-edge has the same features as compared with experiment with one main peak at 792 eV and another high energy side peak at 794 eV, but the L$_2$-edge calculation intensity is less than the experiment.

(b) calculation spectrum with Co(III) all in high-spin state has better fitting with experiment in the high energy side of L$_3$-edge, but a bit of over estimate at the 776 eV pre-edge peak. The calculation spectrum in L$_2$-edge has not so obvious side peak at 794 eV and the whole intensity is even less than in (a).

When Co(III) is considered to have HS and LS states with 1:1 ratio in content, the combined calculation spectrum in (c) set has almost perfect match to the experiment in L$_3$-edge both at 776 eV pre-edge peak and 780 eV high energy side. Look into the detailed features of Co(II) and Co(III) around 780 eV, it’s so clear that only the contribution both from Co(III) HS and LS states could result in a perfect match to the high energy side of L$_3$-edge. The calculation spectrum in (c) at L$_2$-edge also have very good fitting with two obvious peaks at 792 eV and 794 eV. The intensity is less than experiment but at least not worse than in (a).

When the charge transfer effect is introduced, the charge-transfer multiplet calculation results is shown in Fig.5. The calculation spectrum in (a) set with Co(III) all in low-spin state has very good fitting to experiment in L$_3$-edge, which is also used as the only calculation spectrum of Co$_3$O$_4$ in previous multiplet calculation study[25]. However, there are still some obvious discrepancies between calculation and experiment in the high energy side of L$_3$-edge around 780 eV. In the previous research[25], such discrepancies are attributed to the imperfect simulation of the low spin Co(III) sites[25]. In present work when the high-spin Co(III) is included as in (c) set, the calculation spectrum is improved both at 776 eV pre-edge peak and high-energy side around 780 eV in L$_3$ region. Similar to the situation in crystal-field multiplet calculation, the improvement comes from the combination of detailed features of Co(III) HS and LS.
FIG. 5: The charge-transfer multiplet calculation for Co $2p$ L-edge X-ray absorption spectrum of Co$_3$O$_4$. (a) Co(III) in LS state. (b) Co(III) in HS state. (c) Co(III) in both HS and LS states with 1:1 ratio.

states especially in the pre-edge peak at 776 eV and high energy side around 780 eV of L$_3$-edge. The calculation is also fairly good in L$_2$-edge compared with experiment.

The same calculations are also done in MultiX method using different crystal field scale factor to simulate the Co(III) HS and LS XAS for combination. The calculation results are shown in Fig. 6. The similar analysis stands as discussed above in CTM method’s crystal-field and charge-transfer multiplet calculations, that either Co(III) HS or LS alone with Co(II) can not combine best calculation spectrum compared with experiment. Only when Co(III) HS and LS states are introduced with coexistence in Co$_3$O$_4$ at about 1:1 ratio, the calculation spectrum can be improved from old model with only octahedral Co(III) low spin ($^1A_1$) state and tetrahedral Co(II) ($^4A_2$) state[25].

CONCLUSION

The multiplet calculation study of Co $2p$ L$_2,3$-edge X-ray absorption spectrum compared with new experiment data reveals high possibility that there are both high-spin and low-spin state Co(III) sites in Co$_3$O$_4$ bulk phase, which was believed only Co(III) LS state could exist. The origin of the stabilization of Co(III) HS in Co$_3$O$_4$ bulk sample may caused by endotherm under X-ray illumination or slight changes in Co$^{3+}$–O$^{2−}$ bond length due to other element doping, Co(III) vacancy defect. The nature is still unrevealed requiring much more further work such as new magnetic susceptibility measurement to be
performed. The existence of Co(III) HS state in Co$_3$O$_4$ has an importance in the application of the material, since the Co(III) high-spin site increases its catalytic property due to the half filled T$_{2g}$ orbitals much more closer to Fermi level as compared with valence bands formed by other Cobalt 3d orbitals\[20\]. Further work on high resolution XAS of Co$_3$O$_4$ is needed to learn the spectral features especially at 780 eV region in order to identify whether the spin state of Co(III).

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